PLASMON-ENHANCED PHOTOELECTROCHEMICAL CELLS FOR SOLAR-TO-FUEL ENERGY CONVERSION

By

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To my family
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PLASMON-ENHANCED PHOTOELECTROCHEMICAL CELLS FOR SOLAR-TO-FUEL ENERGY CONVERSION

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Solar-driven water splitting via a photoelectrochemical cell represents a promising approach to sustainably satisfy the escalating energy demands of an ever-expanding global population. Adequately harvesting this vast solar resource, however, presents unique technological challenges. Here, we present the use of plasmonic-metal nanocrystals as a means to augment the optical response of semiconductor-based photoelectrochemical cells to enhance the conversion of sunlight into chemical fuels. We use two separate plasmonic photoelectrochemical systems to systematically explore the mechanisms responsible for plasmon-enhanced photoelectrochemistry.

In one approach, we show that by placing gold (Au) nanoparticles proximal to a suitable n-type semiconductor (titanium dioxide, TiO$_2$) they can be used as visible-light-harvesting assemblies via a process known as plasmon-mediated electron transfer (PMET). Notably, we find that these hot electrons exhibit excited-state lifetimes that are orders of magnitude longer than that observed for charge carriers created directly within the semiconductor by UV excitation. Electron paramagnetic resonance (EPR) spectroscopy was further used to follow the fate of these hot electrons within the
semiconductor following PMET and identify the structural sites within the semiconductor where hot electrons reside.

In a completely separate strategy, we show that Au nanoparticles can be used as optical antennas within photoelectrochemical cells to enhance the collection of light by the semiconductor and increase overall device efficiency. Embedding Au@SiO$_2$ (core@shell) nanoparticles within cuprous oxide (Cu$_2$O)-based nanowire networks provides a means to exploit the large optical cross section of plasmonic nanostructures to enhance the light-harvesting capability of Cu$_2$O-based photocathodes. The introduction of Au@SiO$_2$ nanoparticles provides substantial enhancements in light absorption to the device, enabling a ~40% reduction in the semiconductor film thickness while maintaining photoelectrochemical performance.

These studies demonstrate the merits of incorporating plasmonic-metal nanostructures within photoelectrochemical cells to boost the efficiency of the composite device. We further highlight specific future directions of both fundamental and applied photoelectrochemical research that are anticipated to further inform the construction of advanced artificial photosynthetic constructs for solar-to-fuel energy conversion.
CHAPTER 1
SOLAR PHOTOCATALYSIS AND PHOTOELECTROCHEMISTRY

Motivations

The procurement of a sustainable supply of clean energy is arguably the greatest scientific challenge facing humanity in the 21st century.\textsuperscript{1,2} Increasing levels of carbon dioxide (CO\textsubscript{2}), methane (CH\textsubscript{4}) and other harmful atmospheric pollutants (e.g. HSO\textsubscript{4}\textsuperscript{-}, NO\textsubscript{x}, etc.) threaten the integrity of our global climate, with potentially disastrous consequences for the overall ecological health of the planet.\textsuperscript{1-3} The rapid pace of industrialization amongst less-developed nations and the simultaneous increase in per capita energy demands amongst the developed world places tremendous pressure on finite fossil fuel reserves.\textsuperscript{1,3} A worldwide surge in industrialization without the foresight to develop alternative energy technologies threatens global economic instability and national unrest as vital natural resources become increasingly scarce.\textsuperscript{2,3} Accordingly, we must transition from a fossil-fuel based economy to include a more diverse energy portfolio. We have fortunately been blessed with a nearly inexhaustible source of renewable energy in the form of the sun (Figure 1-1); in fact, more energy in the form of sunlight strikes the Earth's surface every hour than the entire global community uses in an entire year.\textsuperscript{1,3,4} Although promising, adequately harvesting this electromagnetic energy presents some unique technical challenges. Diurnal variations in solar insolation require an efficient means of capturing the radiative energy and storing it in a medium (e.g. battery or chemical fuel) for discharge on demand.\textsuperscript{1,4-6} Furthermore, to date, no single material meets all the requirements necessary for efficiently harvesting this solar energy source under sustained operating conditions at a scale commensurate with global demand.\textsuperscript{1,6} Significant scientific investments in solar energy conversion and
Solar Photocatalysis for Solar-to-Fuel Energy Conversion

Artificial photosynthesis, or solar water-splitting to produce chemical fuels (e.g. H₂) via a semiconductor-based photocatalyst, represents a promising approach to alleviate the demand on fossil fuel reserves and sustainably produce energy in an environmentally-friendly manner (Figure 1-2).¹⁻⁹ Inspired by the strategy invoked by photosynthetic organisms such as green algae and terrestrial plants, artificial photosynthesis attempts to capture sunlight with a photoresponsive semiconductor and convert this radiative energy into chemical energy stored in the form of chemical bonds. The initial discovery of solar-driven water photolysis by a titanium dioxide (TiO₂)-based photocatalyst in 1972 demonstrated the possibility of capturing sunlight with a semiconductor to generate H₂ and O₂ gas from water.¹⁰ Ever since, scientists have aspired to replicate the photocatalytic machinery of naturally-evolving photosynthetic organisms for the sustainable production of chemical fuels.¹¹⁻¹⁴

A solar-driven water-splitting system requires a light-absorber to capture sunlight, electrocatalysts to facilitate the fuel-forming reactions, an electrolyte to support the photoelectrochemistry, and a membrane to separate the reaction products (i.e. H₂ and O₂ in the case of water splitting). A photocatalytic system that mimics biological water splitting can take many forms with various degrees of cost and complexity.⁵ At one end of the continuum are colloidal semiconductor photocatalysts freely-dispersed in aqueous solution – such systems are cheap and easy to implement, but generally exhibit low efficiencies. On the opposite end of the spectrum are photovoltaic cells coupled to an electrolyzer for solar fuel production. Although efficient and comprised of storage are therefore required to sufficiently exploit the potential of this vast renewable resource.
mature technologies, these systems are currently too costly to enable implementation on a global scale. Integrated photoelectrochemical devices offer the potential to bridge the gap between these two extremes in a cost-effective manner.\textsuperscript{4-6}

The essential aspects of semiconductor photocatalysis for solar-driven water splitting are depicted in Figure 1-3A. The photochemical processes can be divided into three primary steps: (i) light absorption to generate charge carriers, (ii) carrier transport to the active site, and (iii) surface reaction to form products.\textsuperscript{11-14} Absorption of a photon with energy ($\hbar \omega$) equal to or greater than the band gap ($\hbar \omega > E_G$) promotes an electron from the valence band (VB) to the conduction band (CB) of the semiconductor (step i), leaving behind an unoccupied state in the VB referred to as a “hole.” The electrons in the CB migrate to the hydrogen evolution reaction (HER) catalyst while the holes diffuse to the oxygen evolution reaction (OER) catalyst (step ii). Excite-state charge carriers accumulate on the HER and OER cocatalysts where surface reactions occur to produce $\text{H}_2$ and $\text{O}_2$, respectively (step iii). The free energy change for the conversion of one molecule of $\text{H}_2\text{O}$ into $\text{H}_2$ and $\frac{1}{2} \text{O}_2$ under standard conditions is $\Delta G = 237.2 \text{ kJ mol}^{-1}$, which corresponds to $\Delta E^0 = 1.23 \text{ V}$ per electron transferred, according to the Nernst equation.\textsuperscript{7,9} To drive this chemical reaction using sunlight requires a semiconductor that can absorb photons of the appropriate energies: $\hbar \omega \geq 1.23 \text{ eV (} \lambda \leq 1000 \text{ nm)$.}^7$ Ideally, a single semiconductor photocatalyst with a band gap $E_G \geq 1.23 \text{ eV}$ that exhibits appropriate CB and VB energy levels relative to the electrochemical potentials $E^0(\text{H}^+/\text{H}_2)$ and $E^0(\text{O}_2/\text{H}_2\text{O})$ for water splitting can drive the HER and OER using charge carriers generated via photon absorption (Figure 1-3B). Although this simple photocatalytic picture is sufficient to understand the basic strategy behind solar-to-fuel energy
conversion; in practice, several thermodynamic and kinetic challenges complicate the requirements for furnishing an efficient semiconductor photocatalyst.\textsuperscript{5-7}

There are three primary constraints that exist on the choice and combination of material components to provide a viable water-splitting photocatalyst: efficiency, stability, and scalability.\textsuperscript{5} Engineering challenges arise due to competition between these requirements, such that it is not sufficient to separately optimize each component individually. Accordingly, multiple materials must be linked together to achieve the required operational efficiency. There are various light-absorbers, electrocatalysts, and membranes available that individually meet all these requirements; unfortunately, these components cannot be arbitrarily combined to yield a viable integrated device, as they do not yet operate optimally under mutually compatible conditions.\textsuperscript{5} Numerous competing processes must all be simultaneously optimized to provide a scalable photoelectrochemical system capable of efficiently performing solar-driven water splitting over prolonged operational periods. As such, the construction of a viable photoelectrochemical device requires a thorough understanding of the fundamental physics governing the optoelectronic properties of semiconductor photoelectrodes, the thermodynamics of semiconductor/liquid junctions, and the kinetics of photochemical reactions occurring at the semiconductor surface. These considerations will be elaborated upon in the following sections.

**Semiconductor Photoelectrochemistry**

The overall scheme of solar water splitting via a photoelectrochemical cell is depicted schematically in Figure 1-4. The most basic photoelectrochemical system consists of a single light-absorbing semiconductor photoelectrode electrically wired to another counter electrode. Each electrode separately performs a redox half-reaction
(reduction or oxidation) to effect a complete electrochemical reaction. A typical n-type photoanode and p-type photocathode is shown in Figure 1-4A and B, respectively. The device consists of two gas evolving components: a photoanode (photocathode), which harvests sunlight to oxidize (reduce) water and evolve $\text{O}_2$ ($\text{H}_2$), and the cathode (anode) where water is reduced (oxidized) to evolve $\text{H}_2$ ($\text{O}_2$). Upon absorption of a photon with energy ($\hbar \omega$) equal to or greater than the band gap ($\hbar \omega > E_G$), an electron is promoted from the valence band (VB) to the conduction band (CB) of the semiconductor, leaving behind an unoccupied state in the VB referred to as a “hole.” The majority carriers (electrons in n-type or holes in p-type) are extracted from the semiconductor through an Ohmic contact formed with the underlying conductive substrate and passed to the Pt wire cathode (anode) via the external circuit to reduce (oxidize) water and evolve $\text{H}_2$ ($\text{O}_2$). Meanwhile, the hole (electron) left behind in the VB (CB) diffuses to the semiconductor surface where it can participate in photochemistry with adsorbed surface species to oxidize (reduce) water and generate $\text{O}_2$ ($\text{H}_2$). The overall process yields the photolysis of water ($\text{H}_2\text{O}$) into its gaseous constituents ($\text{H}_2$/O$_2$). The following sections examine the energetics of semiconductor/liquid contacts in more detail.

**Interfacial Energetics in Semiconductor/Liquid Junctions in the Dark**

Upon immersion of a semiconductor into a solution containing a reversible redox couple ($A/A'$) of electrochemical potential, $-qE^0(A/A')$, where $E^0$ is the Nernst potential of the redox pair, charge transfer occurs between the solid and the solution until the Fermi level ($E_F$) of the two phases have equilibrated ($E_F = E_{F,\text{Redox}}$).\textsuperscript{7,15} This initial exchange of charge across the solid/liquid interface establishes an interfacial electric field that offsets the initial disparity in electrochemical potentials between the two phases (Figure 1-5A). Thus, the interfacial electric field strength depends on the initial difference in Fermi level
between the semiconductor photoelectrode \((E_f)\) and the acceptor species in solution \((E_{F,\text{Redox}})\), which is typically on the order of 1 eV.\(^7\) The pertinent redox couples to consider for a photoelectrochemical water-splitting device are the \(E^0(H^+/H_2)\) couple for a p-type photocathode or the \(E^0(O_2/H_2O)\) couple for an n-type photoanode.

It is important to note that the redox potentials for water reduction and oxidation are pH dependent, as both reactions involve protons (at low pH) or hydroxyl ions (at high pH).\(^7,15\) The change in reduction potentials with increasing pH is given through analysis of the Nernst equation for the case of water reduction and oxidation, as given by the following expressions:

\[
E^0(H^+/H_2) = 0.0 V - \left(0.059 \text{ V pH}^{-1} \times \text{pH}\right)
\]

\[
E^0(O_2/H_2O) = 1.23 V - \left(0.059 \text{ V pH}^{-1} \times \text{pH}\right)
\]

It must be noted that the surfaces of semiconductors in contact with water are heavily populated with hydroxyl ions (or protons at low pH). As the pH of the solution changes, these surface groups protonate/deprotonate, resulting in a pH-dependent surface dipole on the semiconductor electrode. This surface dipole induces a potential drop within the semiconductor that shifts the bands in unison with the shifting redox potentials of water reduction and oxidation. Such similar behavior effectively renders the relative interfacial energetics between the semiconductor band edge and the redox couple in solution pH independent, as both semiconductor bands and solution energetics change concertedly.\(^7,15\)

As a result of Fermi level equilibration between the solid and liquid phase, an excess of positive (negative) charge accumulates within the n-type (p-type) semiconductor that is distributed throughout the depletion width \((W)\) in the
semiconductor, and an excess of negative (positive) charge resides across the Helmholtz layer in solution, near the electrode surface (Figure 1-5B).\textsuperscript{7,13-16} The extent of the depletion width within the solid is dependent upon the dopant density ($N_D$) of the semiconductor according to the following equation:

$$W = \sqrt{\frac{2\varepsilon_s V_{B-I}}{qN_D}}$$

(1-3)

where $\varepsilon_s$ is the dielectric constant of the semiconductor, $N_D$ is the dopant density, $q$ is the (unsigned) charge of an electron, and $V_{B-I}$ is the built-in potential.\textsuperscript{7} The interfacial electric field established at the semiconductor/liquid junction induces band-bending across the depletion layer within the semiconductor, which helps to separate electron-hole (e-h) pairs within the solid and preferentially directs the photogenerated minority carriers toward the semiconductor/liquid junction where they can participate in water-splitting photochemistry (Figure 1-5B).\textsuperscript{7,15} Thus, n-type (p-type) semiconductors are used as photoanodes (photocathodes) as these internal fields selectively drive holes (electrons) to the solution and electrons (holes) to the back contact (Figure 1-4).

Figure 1-6 shows three types of space-charge layers that can form in an n-type semiconductor in contact with a liquid electrolyte.\textsuperscript{13-16} In an n-type semiconductor, the majority carriers are electrons, and so the density of free electron carriers ($n_e$) is higher than that of hole carriers ($n_h$); the opposite condition holds for p-type semiconductors. The semiconductor flat-band potential ($E_{fb}$) denotes the potential at which the energy bands of the semiconductor are flat, that is, there is no band bending within the solid (Figure 1-6A). It is a very useful quantity in photoelectrochemistry as it facilitates location of the energetic position of the VB and CB edge of a given semiconductor material.\textsuperscript{7,8} If a positive space-charge layer exists at the surface then downward band-
bending occurs as electrons accumulate in the semiconductor near the surface, causing an increase of $n_e$ and a decrease of $n_h$. The space-charge region in the semiconductor is called an accumulation layer to denote the accumulation of majority carriers (electrons) in the n-type semiconductor (Figure 1-6B). If negative charges exist at the semiconductor surface and positive charges accumulate in the semiconductor then a depletion layer is established within the semiconductor, causing a decrease in $n_e$ and an increase in $n_h$ (Figure 1-6C). Under extreme depletion conditions, such that the electron concentration is depleted below the intrinsic level ($n_i$), the semiconductor can effectively behave as a p-type semiconductor near the surface ($n_e < n_i < n_h$). Under such a condition the space charge region is referred to as an inversion layer to denote the change in electronic character from n-type to p-type near the semiconductor/liquid junction (Figure 1-6). $^{13-16}$

It should be noted that in general, the semiconductor must possess a certain critical size to support an internal field distribution and maintain the band bending near the semiconductor-liquid junction. $^{4,13,15}$ The potential drop within a colloidal semiconductor nanoparticle is usually very small and requires a large dopant level ($N_D \sim 10^{19}$ cm$^{-3}$) to sustain a potential difference between the surface of the nanoparticle and the interior. $^{13}$ As shown in Figure 1-7, a space-charge layer ($\varphi_{sc}$) cannot be sustained within the solid if the diameter ($d$) of the semiconductor is smaller than the width of the depletion region. $^{4,13,15}$

The application of external electrical bias provides an additional experimental parameter to modulate the reaction kinetics at the semiconductor surface. The kinetics of charge transfer across the semiconductor/liquid junction depends on both the number
of minority charge carriers (electrons for p-type or holes for n-type) at the semiconductor surface and the energetics of the semiconductor band edges.\textsuperscript{7,15} In the dark, the electron concentration at the surface of an n-type semiconductor ($n_s$) is given by the difference between the externally-applied potential ($E$) and the flat-band potential, $E_{fb}$, according to the following expression:

$$n_s = N_D \exp\left[q\left(E_{fb} - E\right)/k_B T\right]$$ \hspace{1cm}(1-4)

where $N_D$ is the concentration of donor atoms, $k_B$ is Boltzmann’s constant, and $T$ is the absolute temperature (in Kelvin) of the system. This Boltzmann-type relationship reveals that $n_s$ increases (decreases) exponentially with the application of a negative (positive) potential, inducing a net current across the semiconductor-liquid junction. The net flux of electrons from the semiconductor CB to the acceptors levels in solution determines the measured current density, and is given by the rate law:

$$J(E) = -q k_{ET} [A] n_s$$ \hspace{1cm}(1-5)

where $J$ is the current density, $k_{ET}$ is the rate of electron transfer, and $[A]$ gives the concentration of acceptor species A in solution.\textsuperscript{7} The application of an external potential induces a change in the observed current density by modulating the surface concentration of charge carriers, rather than the rate constant or the energetics of the interfacial charge-transfer process.\textsuperscript{7} As we will see in the next section, the incidence of optical energy similarly alters the free-carrier concentration within the semiconductor.

**Interfacial Energetics in Semiconductor/Liquid Junctions under Illumination**

Upon illumination of the semiconductor photoelectrode, the interfacial energetics are modified by the incident light energy, as the Fermi level of electrons ($E_{F,n}$) and holes ($E_{F,p}$) diverge into two separate “quasi-Fermi” levels (Figure 1-5C).\textsuperscript{7,15} The free energy
generated within the semiconductor that is available for photochemical reactions is given by the difference between the quasi-Fermi levels of electrons ($E_{F,n^*}$) and holes ($E_{F,p^*}$) under illumination. The prefix “quasi-” is used to indicate that these charge carriers are not technically in true thermodynamic equilibrium, in which a single Fermi level describes the statistical distribution of all charge carriers within the solid, as this condition only be realized in the dark. However, the thermalization of excited-state charge carriers occurs very quickly ($t \sim ps$) relative to the electron-hole pair lifetimes ($t \sim ns$), leaving the collection of charge carriers in quasi-thermal equilibrium under steady-state illumination conditions. The quasi-Fermi level therefore considers the free energy of each charge carrier separately under non-equilibrium conditions (i.e. illumination) using Fermi-Dirac statistics to describe the individual populations of both electrons and holes at steady-state, as given by the following expression:

$$n = N_{CB} \exp\left(\frac{E_{CB} - E_{F,n^*}}{k_BT}\right) \quad \text{for electrons} \quad (1-6)$$

$$p = N_{VB} \exp\left(\frac{E_{VB} - E_{F,p^*}}{k_BT}\right) \quad \text{for holes} \quad (1-7)$$

where $N_{CB}$, $E_{CB}$ and $N_{VB}$, $E_{VB}$ are the energy levels and density of states of the CB and VB, respectively. The pre-exponential factors are given by the following relations:

$$N_{CB} = \frac{2(2\pi m_e^* k_BT)^{3/2}}{h^3} \quad \text{for electrons} \quad (1-8)$$

$$N_{VB} = \frac{2(2\pi m_h^* k_BT)^{3/2}}{h^3} \quad \text{for holes} \quad (1-9)$$

where $h$ is Planck’s constant, $m_e^*$ is the effective mass of the electrons in the CB, and $m_h^*$ is the effective mass of the holes in the VB. Analysis of these expressions shows
that the surface minority-hole concentration for an n-type semiconductor is described by the energy difference between the quasi-Fermi level of the holes \( (E_{F,p}^*) \) and the VB edge (Equation 1-7).\(^{15}\) As such, the major influence of light irradiation is to amplify the concentration of minority carriers such that useful chemical reactions can be performed on the semiconductor surface. It is further noted that the driving force for charge transfer to solution is dictated by the energy difference between the VB edge and the redox levels of the species in solution (e.g. H\(_2\)O, OH\(^-\)) and is independent of the light intensity.\(^7\) Thus, the energy difference between the VB edge and the formal potential for the redox couple of interest provides a “built-in” overpotential for driving the electrochemical process.

The splitting of quasi-Fermi levels upon optical excitation of the semiconductor establishes a photovoltage \( (V_{ph}) \) across the semiconductor-liquid junction given by:

\[
V_{ph} = \frac{n_d k_B T}{q} \ln \left( \frac{J_{ph}}{J_0} \right) \tag{1-10}
\]

where \( n_d \) is diode quality factor, \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, \( q \) is the unsigned charge of an electron, \( J_{ph} \) is the photocurrent density, \( J_0 \) is the saturation current density, and \( \gamma \) is the roughness factor (the ratio of actual junction area to the geometrical surface area of the electrode).\(^7\) Examination of this equation reveals that \( V_{ph} \) is dependent on the illumination intensity, as a higher photon flux produces more minority carriers and therefore a larger splitting of the quasi-Fermi levels. It must be noted that the magnitude of the photovoltage determines the electrochemical reactions that can be driven by the photoelectrode. Regardless of the band edge positions of the semiconductor relative to the water oxidation/reduction half-reactions, water splitting is
not feasible unless a photovoltage of $V_{ph} = 1.23$ V is obtained by the semiconductor photoelectrode.$^7$

There are numerous kinetic processes occurring within semiconductor photoelectrodes that may limit the maximum achievable photovoltage predicted from a thermodynamic analysis of semiconductor band gaps and redox energy levels.$^7$ These kinetic processes govern the relative populations of electrons and holes (quasi-Fermi levels) within the semiconductor under steady-state illumination, and are illustrated schematically in Figure 1-8. These photogenerated charge carriers may (1) recombine radiatively or non-radiatively within the bulk of the semiconductor ($J_{br}$), (2) recombine within the depletion region ($J_{dr}$), (3) tunnel through the electric potential barrier near the surface ($J_t$), (4) thermally surmount the interfacial barrier ($J_{et}$), or (5) recombine at surface states (such as trap states and surface defects) at the semiconductor/liquid junction ($J_{ss}$).$^7$ The sum of these recombination processes is termed the saturation current density, $J_0$. In contrast to these deleterious charge carrier pathways, electron collection at the back contact (6) and hole collection at the semiconductor/liquid junction (7) originate from the desired photoelectrochemical reaction pathway, and contribute positively to the measured photocurrent density, $J_{ph}$. The overall $V_{ph}$ is limited when any of the recombination processes (2—5) significantly contribute to the overall device photocurrent, as these processes alter the relative populations of electrons and holes within the semiconductor, and subsequently limit the quasi-Fermi level splitting (i.e. $V_{ph}$) within the device.$^7$ Thus, kinetic processes actually influence what are perceived to be strictly thermodynamic quantities. This interconnected issue illustrates the significant challenges associated with the design of photoelectrochemical systems. The following
sections outline the design criteria that must be considered for the construction of a solar-driven photocatalytic system capable of effecting overall water splitting.

**Design Considerations for Solar-to-Fuel Energy Conversion**

Numerous thermodynamic and kinetic challenges place severe material restrictions on photocatalysts for solar water splitting and hinder the development of artificial photosynthetic constructs for solar fuel production. Here, we identify these restrictions and highlight approaches currently used to mitigate material limitations. Due to the often-opposing nature of these requirements, it is rare that a semiconductor simultaneously exhibits all the material properties necessary for efficiently harvesting solar insolation over prolonged periods. These stringent thermodynamic and kinetic requirements remain a major challenge within the solar-to-fuel paradigm.

**Thermodynamic Considerations for Solar-to-Fuel Energy Conversion**

There are numerous material properties that must be considered for the design of an appropriate photocatalyst. As the initial step in any photocatalytic process requires light absorption, the first consideration involves the semiconductor band gap, which must be appropriately matched to the solar emission spectrum to adequately capture solar insolation and generate electron-hole pairs within the photocatalyst. As shown in Figure 1-1, the solar spectrum primarily emits visible (~45%) and infrared (~50%) light, with only a tiny fraction (~5%) composed of UV light. Consequently, a solar photocatalyst must possess a band gap less than 3.0 eV to harvest visible light. The band gap of most semiconductors is typically in the range of $E_g \sim 1 - 3.5$ eV as a result, which covers the entire UV-visible-near IR range.

Not only must the semiconductor absorb visible-light to generate charge carriers capable of initiating catalytic reactions, the thermodynamic positions of the CB and VB
must be appropriately poised relative to the reduction potentials of the desired reaction of interest to effectively couple sunlight into chemical bonds. Figure 1-3B illustrates the band gap of several semiconductors commonly-used for photocatalysis along with the absolute energy levels of their band edge positions with respect to both the vacuum level and the standard hydrogen electrode (SHE), respectively. The HER and OER reduction potentials are also shown relative to the semiconductor band edge positions to facilitate comparison. For overall water splitting, the CB and VB levels must “straddle” the reduction potentials of both redox half-reactions to thermodynamically allow such a reaction to occur. That is, the CB level of the semiconductor must be more negative than the reduction potential of the HER to enable photoexcited electrons to perform the reduction and the VB level of the semiconductor must be more positive than the reduction potential of the OER to enable photoexcited holes to perform the oxidation reaction. Therefore, if the CB level (VB level) is below (above) the HER (OER) potential an additional energy input is required to raise (lower) the energy of the electrons (holes) to meet the thermodynamic requirements for reduction (oxidation). This thermodynamic condition places stringent requirements on photocatalytic materials; note that to effectively harvest sunlight and produce vast quantities of charge carriers requires a relatively modest band gap (such as Si), while to generate strongly reducing/oxidizing carriers in the semiconductor requires a large band gap (such as TiO$_2$). These opposing requirements present considerable engineering challenges for the design of solar photocatalysts. Such constraints indicate that the ideal semiconductor band gap would be ca. $E_g \approx 1.3–1.7$ eV so that the light-absorber harvests a significant fraction of incident sunlight while still exhibiting a substantial photovoltage to provide sufficient
power conversion efficiency. As mentioned previously, numerous factors affect the semiconductor’s ability to sustain a significant photovoltage under illumination. Thus, while it is true that the semiconductor band edges must straddle the HER and OER potentials, these conditions alone are not sufficient to ensure that the photoelectrochemical system can drive unassisted water photolysis.

Finally, from a practical perspective, the photocatalyst must exhibit robust chemical stability in aqueous solution to yield a device capable of continuous operation over prolonged timescales. Although numerous semiconductors are suitable for solar energy conversion within the confines of a conventional photovoltaic device, the harsh oxidizing/reducing conditions employed in water-splitting photocatalysts place stringent material requirements on which semiconductors are appropriate for photochemical applications. As such, only a limited number of semiconductors exhibit the chemical stability requisite for use as water-splitting photocatalysts.

**Kinetic Considerations for Solar-to-Fuel Energy Conversion**

In addition to the thermodynamic requirements for a solar photocatalyst, there are numerous kinetic challenges that must also be overcome to facilitate efficient photocatalysis. Analysis of the excited-state dynamics of semiconductor photocatalysts reveals the source of such challenges. The lifetimes of photogenerated electron-hole pairs (t ~ps—μs) are often incommensurate with the prolonged timescales required to facilitate photocatalytic reactions (t ~ms—s) at the semiconductor surface. As a consequence, most semiconductor photocatalysts exhibit limited solar-to-fuel conversion efficiencies. This temporal inconsistency is often referred to as a "kinetic bottleneck" in fuel-forming photochemical reactions. To circumvent this challenge, electrocatalysts are placed on the semiconductor surface. These catalysts serve two
functions: (1) to physically-separate photogenerated charges across the semiconductor/electrocatalyst interface and reduce geminate recombination probability within the semiconductor; and (2) to facilitate the concerted transfer of multiple redox equivalents to surface-adsorbed species, enabling the multi-electron reactions requisite for solar-driven water splitting.\textsuperscript{17-21} Although the introduction of electrocatalysts onto the semiconductor surface enhances the rate of fuel-forming reactions, it inadvertently impairs the absorption of incident light within the underlying semiconductor support, as the electrocatalyst itself interacts with visible light.\textsuperscript{5,22,23} Low catalyst loadings are therefore required to alleviate the optical obscuration that is accompanied by the addition of electrocatalysts. A seemingly innocuous solution, this approach actually necessitates the use of precious metals (Pt, Ir, Ru) to achieve the requisite activity at modest mass loadings, as the intrinsic activity of catalysts composed of Earth-abundant materials is currently too low to enable such sparse surface coverage.\textsuperscript{22,23} Combinatorial approaches have actively pursued new Earth-abundant electrocatalysts that exhibit higher intrinsic activity to enable lower loadings\textsuperscript{24} while novel device architectures attempt to limit optical obscuration effects by manipulating the physical arrangement of light-absorbing and fuel-forming components within the integrated system.\textsuperscript{25} While promising, further work is needed to achieve viable device efficiencies.

Another long-standing challenge in semiconductor photocatalysis involves the significant discrepancy between the optical absorption depth ($\alpha$) required for efficient photon absorption ($\alpha \sim \mu m$) and the relatively short diffusion length ($l_D$) of photoexcited minority carriers within the semiconductor ($l_D \sim nm$).\textsuperscript{7,19} Deleterious recombination processes occurring within the semiconductor bulk often dominate the excited-state
dynamics of charge carriers within the solid. Consequently, only a small fraction of all the charge carriers generated within the semiconductor are able to diffuse to the photocatalyst surface where they can participate in chemical reactions.

The extent to which a charge carrier can diffuse within the semiconductor prior to recombination is termed the diffusion length ($l_d$), which is defined according to the following expression:

$$l_d = \sqrt{D \tau}$$

(1-11)

where $\tau$ is the minority-carrier lifetime and $D$ is the minority-carrier diffusion coefficient. The diffusion coefficient itself is related to the mobility of the minority carriers, $\mu$, through the Einstein-Smoluchowski equation:

$$D = \frac{\mu k_B T}{q}$$

(1-12)

where $q$ is the (unsigned) charge of an electron, $k_B$ is the Boltzmann constant, and $T$ is the temperature. Typical values of $\mu$ for bulk semiconductors range from $\mu \sim 1$—200 cm$^2$ V$^{-1}$ s$^{-1}$, though it should be noted that these values vary significantly depending on the electronic quality of the semiconductor material used. The semiconductor must be “optically thick” enough to efficiently capture photons, but must also remain of sufficient electronic quality to enable photogenerated charge carriers to reach the semiconductor surface and participate in photochemistry. Such a constraint requires that $l_d > \alpha^{-1}$, where $\alpha$ is the absorption coefficient of the semiconductor near the band gap. This condition can be met by using a nanowire geometry for the semiconductor, which allows for a collection length of photogenerated minority carriers that is much shorter than the optical penetration depth required for efficient photon absorption, as shown in Figure 1-9. Orthogonalizing the directions of light absorption and charge carrier
collection within the device thereby decouples these two competing requirements. Such a strategy has proved fruitful in photoelectrochemical architectures composed of a variety of semiconductors.\textsuperscript{28-33}

While such a strategy enables using inexpensive metal-oxide semiconductors for photoelectrochemical applications, it does little to augment the optical response of the semiconductor photoelectrode itself. As most of the stable metal-oxides used for photoelectrochemistry typically exhibit large band gaps ($E_G \sim 3.0$ eV), the efficiency of these devices are ultimately restricted by their inability to harvest visible light. Notable approaches aimed at sensitizing the semiconductor to sub-band gap light will be addressed in the next section.

**Commonly Employed Strategies to Improve Photoelectrochemical Activity**

Although TiO$_2$-based photoelectrochemical cells exhibit activity for solar-driven water splitting, the large optical band gap of TiO$_2$ ($E_G \sim 3.0$ eV) inherently limits its ability to harvest a broad portion of solar radiation, as only a small portion of the solar emission spectrum is composed of UV light (Figure 1-1). However, the robust photochemical stability, ease of processing, appropriate band-edge positions with respect to the H$_2$ and O$_2$ evolving redox half-reactions, and Earth-abundant composition of TiO$_2$-based photoanodes continues to motivate endeavors aimed at augmenting the photoelectrochemical performance of this potentially promising n-type semiconductor in search of more efficient photocatalytic systems.

The two most commonly-employed strategies for improving the capture of solar insolation in wide-band gap photoelectrochemical cells (Figure 1-10) involves: (1) chemical doping of the semiconductor to reduce its band gap through the introduction of defect states, or (2) functionalizing the semiconductor surface with visible-light-
harvesting assemblies (e.g. molecular dyes or quantum dots) to sensitize the semiconductor to sub-band gap light. Unfortunately, each strategy introduces additional deleterious effects that ultimately limit the efficiency of the photoelectrochemical device.

Chemical doping of the semiconductor has been shown to increase the absorption of incident light within the semiconductor through the introduction of defect states within the band gap of the material (Figure 1-10A). Nitrogen (N)-doping is commonly used to substitute for oxygen in the TiO$_2$ lattice, although reducing treatments with hydrogen (H) have also been shown to augment the optical activity of the semiconductor.\textsuperscript{34-38} The introduction of chemical dopants into the semiconductor lattice induces hybridization between O 2p states (which primarily comprise the VB) and N 2p states (introduced by substitutional lattice doping) to provide additional states above the VB maximum.\textsuperscript{35} These new states can be populated by sub-band gap photons ($\hbar\omega < E_G$), which allow the semiconductor to absorb light that would otherwise not be capable of inducing optical transitions between bands. Surface treatments under reducing (H$_2$) conditions have yielded so-called “black” TiO$_2$, which absorbs across a broad range of the solar spectrum with prolonged photocatalytic activity.\textsuperscript{36-38} While the introduction of additional optically-accessible states improves the total number of electron-hole pairs generated within the semiconductor, these charge carriers in these states intrinsically possess weaker reducing/oxidizing capabilities than those within the CB/VB, rendering them less catalytically active.\textsuperscript{38} Furthermore, these states are chemically comprised of highly-localized point defects, which act as trap states within the lattice that prevent free carriers from reaching catalytically-active sites.
An alternative approach to sensitizing the semiconductor to sub-band gap light without imparting lattice defects involves functionalization with a light-harvesting assembly such as a molecular dye or quantum dot (QD). In such a strategy, the photosensitizers acts as an optical antenna to capture light and transfer the excited-state electron to the semiconductor support where charge is collected (Figure 1-10B). The photosensitizer must exhibit a complementary absorption profile at lower energies (visible to IR) than the wide-band gap support and must possess appropriate excited-state electronic levels relative to the semiconductor CB edge to enable the rapid transfer of charges from the photosensitizer to the support prior to relaxation within the light-harvesting assembly (Figure 1-10B). The dense manifold of CB levels of wide band gap semiconductors such as TiO$_2$ or ZnO have been used for dye-sensitized solar cells, dye-sensitized photoelectrosynthesis cells, and QD-sensitized photoelectrochemical cells. Although such a strategy successfully extends light absorption within the device, QDs and molecular dyes are susceptible to irreversible photobleaching under extended working conditions and therefore exhibit shorter operational lifetimes compared to traditional solid-state semiconductors.

**Unique Opportunities for Solar Photoelectrochemistry with Plasmonics**

In light of the limitations inherent in these aforementioned approaches, we present a new strategy involving the use of plasmonic-metal nanostructures to augment the absorption profile of traditional semiconductor-based photoelectrochemical cells. In particular, plasmonic-metal/semiconductor heterostructures have garnered increasing scientific interest due to the intriguing optoelectronic properties that result from these hybrid nanoassemblies. In what follows, we present the unique opportunities offered by plasmonic nanomaterials for applications in solar-to-fuel energy conversion.
Figure 1-1. Air Mass (AM) 1.5G solar emission spectrum. This spectrum shows that the sun emits electromagnetic radiation primarily composed of visible (~43%) and infrared (IR) radiation (~53%), while only a modest fraction (~4%) is composed of ultraviolet (UV) radiation. This is the standard reference spectrum adopted by the American Society of Testing and Materials (ASTM) and is freely available from the National Renewable Energy Lab.
Figure 1-2. Basic requirements of an artificial photosynthetic system for chemical fuel production. A fuel cell (top) combines H\textsubscript{2} and O\textsubscript{2} to generate a flow of electrons and protons across a membrane, producing electrical energy and water as a byproduct. A solar fuel cell (bottom) harvests light to run the electron and proton flow in reverse. Coupling the electrons and protons in the photovoltaic (PV) element to catalysts breaks the molecular bonds of water to form H\textsubscript{2} and O\textsubscript{2}, generating chemical fuels. Reprinted with permission from Lewis et al. Copyright 2010 Proceedings of the National Academies of Sciences.
Figure 1-3. Schematic representation of semiconductor photocatalysis for solar water splitting. A) Colloidal semiconductor photocatalyst augmented with catalysts for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Semiconductor photocatalysis occurs in three elementary steps: (i) light absorption by the semiconductor promotes an electron from the valence band (VB) to the conduction band (CB) to create an excited-state electron-hole pair; (ii) the electrons (e⁻) diffuse to the HER catalyst and the holes (h⁺) diffuse to the OER catalyst; (iii) numerous electrons (2e⁻) and holes (4h⁺) accumulate on the catalysts where the HER and OER occur. B) Band edge potentials and band gaps (Eₕ) of several semiconductor photocatalysts commonly used for the water-splitting reaction plotted on the electrochemical energy scale (V vs. RHE) and the vacuum energy scale (eV) relative to the formal potentials (E⁰) for water reduction E⁰(H⁺/H₂) and water oxidation E⁰(H₂O/O₂) in aqueous solution at pH 0. Adapted with permission from Grätzel et al. Copyright 2001 Nature.
Figure 1-4. Schematic representation of a photoelectrochemical cell. The formal potentials ($E^0$) for water reduction $E^0(H^+/H_2)$ and water oxidation $E^0(H_2O/O_2)$ are indicated, along with the energy levels of the semiconductor CB ($E_{CB}$), VB ($E_{VB}$), flat-band ($E_{fb}$), open-circuit photovoltage ($V_{ph}$), and the quasi-Fermi level of electrons ($E_{F,n^*}$) and holes ($E_{F,p^*}$). Black arrows represent the directions of charge-carrier transport and collection that contributes positively to device efficiency, while dashed-red arrows represent deleterious recombination processes that hinder device performance. A) Photoelectrochemical cell composed of n-type semiconductor photoanode on a conductive glass substrate (e.g. FTO) where water oxidation occurs. The photoanode is electrically wired to an auxiliary cathode (e.g. Pt wire) where water reduction occurs. Absorption of a photon ($\hbar\omega$) creates an electron-hole pair ($e^- - h^+$) in the semiconductor. The holes in the valence band ($E_{VB}$) diffuse to the semiconductor-liquid junction to oxidize $H_2O$ and evolve $O_2$. Electrons are extracted from the semiconductor CB ($E_{CB}$) by the FTO back contact and transferred to the cathode via the external circuit where $H_2O$ reduction occurs to evolve $H_2$. B) Photoelectrochemical cell composed of a p-type semiconductor on a conductive glass substrate where water reduction occurs. The photocathode is electrically wired to an auxiliary anode where water oxidation occurs. Absorption of a photon ($\hbar\omega$) creates an electron-hole pair ($e^- - h^+$) in the semiconductor. The electrons in the conduction band ($E_{CB}$) diffuse to the semiconductor-liquid junction where $H_2O$ reduction occurs to evolve $H_2$. Holes are extracted from the semiconductor ($E_{VB}$) by the FTO back contact and transferred to the anode via the external circuit where $H_2O$ oxidation occurs to generate $O_2$. 
Figure 1-5. Band energetics of a semiconductor-liquid junction in the dark and under illumination. A) Before equilibration in the dark. B) After equilibration in the dark. C) Under illumination. Black arrows represent the directions of charge-carryer transport and collection that contributes positively to device efficiency, while dashed-red arrows represent deleterious recombination processes that hinder device performance. Adapted with permission from Walter et al. Copyright 2010 American Chemical Society.
Figure 1-6. Diagram of the energy levels and free carrier densities in an n-type semiconductor as a function of distance (d) away from the semiconductor-liquid interface. The free-electron density (n_e), free-hole density (n_h) and intrinsic carrier density (n_i) are plotted on a log scale. The dashed black line indicates the extent of the depletion width (W) within the semiconductor. The energy levels of the semiconductor CB (E_CB), semiconductor VB (E_VB), Fermi level (E_F), and Fermi level of the redox couple in solution (E_F, Redox) are also shown. A) Flat-band (E_{fb}) condition. B) Accumulation layer. C) Depletion layer. D) Inversion layer. Adapted with permission from Zhang et al. Copyright 2012 American Chemical Society.
Figure 1-7. Influence of semiconductor nanoparticle diameter ($d$) on the internal field distribution (i.e. band bending) established within the solid. A) For a particle smaller than the width of the space-charge layer ($d < d_{sc}$), there is no internal band bending within the solid because the nanoparticle is too small to support an internal field. B) For nanoparticles larger than the depletion width ($d > d_{sc}$), band bending occurs and this internal field sweeps minority carriers to the semiconductor surface (holes in this example). Meanwhile, the accumulation of majority carriers (electrons) in the conduction band (CB) raises the quasi-Fermi level of the semiconductor until a flat-band condition is reached ($E_{F,n} = E_{fb} = E_{CB}$) and charge transfer occurs to acceptor species ($A/A^-$) in solution. Adapted with permission from Hagfeldt et al. Copyright 1995 American Chemical Society.
Figure 1-8. Recombination pathways for photoexcited carriers within an n-type semiconductor photoanode in contact with a liquid electrolyte with redox couple ($A/A^-$). The electron-hole pairs can recombine through current density ($J$) associated with radiative or non-radiative recombination within the bulk of the semiconductor ($J_{br}$), depletion-region recombination ($J_{dr}$), surface-state recombination current due to defects ($J_{ss}$), tunneling current ($J_t$), or electron-transfer current ($J_{et}$) associated with majority carriers thermally surmounting the interfacial barrier. Electron collection by the back contact and hole injection to the liquid electrolyte are desirable processes (black arrows) that contribute positively to device performance while the recombination pathways (red arrows) hinder device efficiency. Adapted with permission from Walter et al. Copyright 2010 American Chemical Society.
Figure 1-9. The influence of semiconductor geometry on light absorption and charge carrier collection. A) Light absorption in a semiconductor thin-film structure requires that the semiconductor film thickness is commensurate with the light absorption depth ($\alpha^{-1}$) to ensure sufficient absorption of incident light. However, this condition results in a collection length for excited-state carriers far beyond the intrinsic charge-carrier diffusion length ($l_D$) of the material. B) Light absorption within the semiconductor-nanowire geometry orthogonalizes the direction for light absorption and charge separation within the device, such that the nanowire diameter is commensurate with $l_D$, while maintaining an “optically-thick” semiconductor structure. Adapted with permission from Walter et al. Copyright 2010 American Chemical Society.
Figure 1-10. Strategies for enhancing the absorption of visible-light by wide-band gap semiconductors. A) Chemical doping of a wide-band gap semiconductor (e.g. TiO$_2$) with an element like nitrogen (N) provides new 2p orbitals that can mix with the oxygen 2p orbitals that comprise the TiO$_2$ valence band (VB) to alter the resultant band gap ($E_G$) of the material. B) Surface functionalization of the semiconductor electrode with a dye molecule or quantum dot that possesses a smaller HOMO-LUMO gap ($S_0/S_1$) or band gap [$E_G(2)$] than the semiconductor [$E_G(1)$] imparts additional visible-light sensitivity to the wide-band gap semiconductor support. The energy level alignment between the semiconductor and photosensitizer allows for the transfer of charge carriers from the excited state of the molecular dye ($S_1$) or CB of the quantum dot to the CB of the wide-band gap semiconductor.
CHAPTER 2
PLASMONIC NANOSTRUCTURES AND PLASMONIC PHOTOCHEMISTRY

Introduction to Plasmonics

The unique optical properties of plasmonic-metal nanostructures arise as a consequence of a phenomenon known as localized surface plasmon resonance (LSPR). The incidence of visible light exerts a time-dependent electromagnetic force on the conduction electrons that induces a coherent oscillation of charge density waves on the metal nanostructure, known as “surface plasmons.” Polarization of the electron gas relative to the underlying lattice establishes strong electromagnetic near-fields spatially-confined within the local vicinity of the metal nanocrystal (Figure 2-1). The field of “plasmonics” attempts to understand and exploit this unique light-matter interaction for a variety of applications in catalysis, sensing, and biomedicine. To understand the physical mechanisms responsible for LSPR and to predict the ensuing optical properties of the metal nanostructure requires knowledge of its dielectric function, which describes how charges in the solid respond to an applied electric field.

Dielectric Function of Metal Nanocrystals and the Drude Free-Electron Model

The dielectric functions (ε) of metals are highly sensitive to the incident light frequency (ν) and are composed of both real (ε_r) and imaginary (ε_i) components, as given by Equation 2-1:

$$\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$$

(2-1)

where ω is the angular frequency of the incident photon ($\omega = 2\pi\nu$). Qualitatively, the imaginary component (ε_i) of the dielectric function captures the tendency for dephasing of the electron gas with respect to the driving optical field and is related to the damping of the LSPR, while the real component (ε_r) dictates at which frequency the resonance
condition is fulfilled (vide infra). The simplest expression for the dielectric function of metal nanostructures is given by the Drude model, which treats the conduction electrons of the metal as a free electron gas. The response to an applied electric field is obtained by solving the classical equations of motion for a single electron, and then multiplying by the number of electrons per unit volume. This theoretical treatment yields the following expression for the frequency-dependent dielectric function of the metal:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma_b)}$$

(2-2)

where $\omega_p$ is the plasma frequency of the electron gas, $\omega$ is the incident light frequency and $\gamma_b$ is the bulk damping constant. The dielectric response of bulk Au predicted from the Drude model along with that dielectric function obtained from experimental results is shown in Figure 2-2. The material-dependence of the dielectric response is incorporated within the factors ($\omega_p$) and ($\gamma_b$). The plasma frequency of the metal itself is given by Equation 2-3:

$$\omega_p = \sqrt{\frac{n e^2}{\varepsilon_0 m_{\text{eff}}}}$$

(2-3)

where $n$ is the electron density of the material, $\varepsilon_0$ the permittivity of free space, $e$ is the electron charge, and $m_{\text{eff}}$ is the effective mass of the electrons in the material. The bulk damping constant is used to account for electronic losses within the material and is inversely related to the mean free path ($l_{\text{mfp}}$) of the electrons, according to the following expression:

$$\gamma_b = \frac{v_F}{l_{\text{mfp}}}$$

(2-4)
where \( v_F \) is the Fermi velocity. The mean free path of electrons in metals is limited by scattering off lattice defects, phonons, crystal impurities, etc., with the different contributions adding together according to Matthiessen's Rule:

\[
\frac{1}{l} = \sum_i \left( \frac{1}{l_i} \right)
\]

(2-5)

where \( l_i \) represents the mean free paths for the individual processes. For bulk Au, the Fermi velocity is \( v_F = 1.4 \times 10^6 \text{ m s}^{-1} \) and the damping constant is \( \gamma_b = 15 \text{ fs}^{-1} \), which implies a mean free path of approximately \( l_{mfp} = 20 \text{ nm} \) at room temperature (298 K).

For small Au nanoparticles with dimensions less than the bulk \( l_{mfp} \), the damping constant can be modified with the inclusion of an additional term to account for increased collisions with the nanocrystal surface:

\[
\gamma(l_{eff}) = \gamma_b + \frac{A v_F}{l_{eff}}
\]

(2-6)

where \( l_{eff} \) is the effective path length of the electrons (average distance between collisions with the surface), \( A \) is a constant that depends on the electron-surface interaction. The effective path length is given by \( l_{eff} = 4V/S \), where \( V \) is the volume and \( S \) is the surface area of the nanoparticle.

Despite its simplicity, the Drude model gives a good description of the dielectric function of the noble metals in the near-IR to visible region of the spectrum (~0.5—2.1 eV), but fails to adequately capture the photophysics observed in the visible to near-UV portion of the spectrum (~2.1—4.0 eV) due to the presence of interband transitions within the metal. For Au, the onset of interband transitions occurs at ca. 2.4 eV (\( \lambda \sim 500 \text{ nm} \)), which corresponds to the threshold for photoexcitation of electrons from the 5d band to the top of the 6sp band (Figure 2-2, inset). These interband transitions
introduce an additional frequency-dependent damping process in the metal, which can be incorporated into the dielectric function by the inclusion of an additional term:

\[ \varepsilon(\omega) = \varepsilon_{ib}(\omega) + 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma_b)} \]  

(2-7)

where \( \varepsilon_{ib}(\omega) \) contains the contribution from interband transitions to the dielectric function.\(^{49}\) A cursory inspection of the complex dielectric function of Au shows a significant increase in damping at energies greater than 2.4 eV, as evidenced by the increase in the imaginary component (\( \varepsilon_i \)) of the dielectric function (Figure 2-2).

These plasmonic effects are size-dependent. It must be recognized that the basic theory developed by Drude to describe surface plasmons is entirely classical – that is, no quantum effects are considered. Consequently, there exists a certain threshold in the metal nanocrystal size (\( d > 2 \text{ nm} \)) for the appearance of plasmonic effects.\(^{49}\) This restriction arises due to the high conduction electron density required to support surface plasmons. Metal nanoclusters (\( d < 2 \text{ nm} \)) exhibit molecular-like electronic structure as the spacing between states near the Fermi level becomes comparable to the available thermal energy (\( k_B T \)). As these nanoclusters are not metallic in the classical sense, the Drude model fails to adequately describe the dielectric function of very small nanocrystals and nanoclusters.\(^{49}\) Thus, the analysis presented herein is applicable to larger Au (\( d > 2 \text{ nm} \)) nanocrystals above this critical size threshold.

**Optical Properties of Plasmonic-Metal Nanoparticles**

The unique optical properties of plasmonic-metal nanostructures can be described analytically only for the simplest case of an isotropic, spherical nanoparticle, as first shown by Gustav Mie in 1908.\(^{51}\) When the radius, \( a \), of the plasmonic nanoparticle is significantly smaller than the wavelength (\( \lambda \)) of incident light (i.e. \( a/\lambda < \)
0.1), the quasi-static approximation can be used to solve Maxwell’s equations for the
extinction cross-section of a metal sphere ($\sigma_{\text{ext}}$), as given by Equation 2-8:

$$\sigma_{\text{ext}} = \frac{18\pi\varepsilon_m^{3/2}V}{\lambda} \left[ \frac{\varepsilon_i(\lambda)}{(\varepsilon_i(\lambda) + 2\varepsilon_m)^2 + \varepsilon_i(\lambda)^2} \right]$$

(2-8)

where $V$ denotes the particle volume, $\varepsilon_r$ and $\varepsilon_i$ are the real and imaginary components, respectively, of the dielectric function (Equation 2-1) of the metal nanoparticle, $\lambda$ is the wavelength of incident light, and $\varepsilon_m$ represents the dielectric function of the surrounding medium.\textsuperscript{51,52} It is important to note that the extinction cross-section is composed of both absorption and scattering components ($\sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{scat}}$), but in the quasi-static limit ($a/\lambda < 0.1$) the optical response is primarily governed by absorption ($\sigma_{\text{ext}} \approx \sigma_{\text{abs}}$). The scattering cross-section ($\sigma_{\text{scat}}$) of the metal sphere is given by the expression:

$$\sigma_{\text{scat}} = \frac{32\pi^4\varepsilon_m^2V^2}{\lambda^3} \left[ \frac{\left(\varepsilon_r(\lambda) - \varepsilon_m\right)^2 + \varepsilon_i(\lambda)^2}{\left(\varepsilon_i(\lambda) + 2\varepsilon_m\right)^2 + \varepsilon_i(\lambda)^2} \right]$$

(2-9)

where all variables are as previously defined in Equation 2-8.\textsuperscript{51,52} Analysis of these expressions indicates that the resonance condition is roughly fulfilled when $\varepsilon_r \approx -2\varepsilon_m$, as the denominator approaches zero and the extinction or scattering cross-section of the plasmonic metal becomes very large.\textsuperscript{51} These expressions also indicate that the metal should exhibit $\varepsilon_i$ close to zero to support a strong plasmon resonance – that is, large values of $\varepsilon_i$ indicate a weaker plasmon resonance due to significant damping contributions from the dielectric response.\textsuperscript{53} The strength of the plasmon resonance can be described by a quantity known as the quality factor, $Q$:

$$Q = \frac{\omega}{2(\varepsilon_i)^2} \left( \frac{d\varepsilon_i}{d\omega} \right)$$

(2-10)
where all variables are as previously defined in Equation 2-1. The strength of the plasmon resonance is directly proportional to $Q$, and in general, metals should exhibit $Q \sim 10$ or greater for most plasmonic applications.\textsuperscript{53} Many materials sustain surface plasmons, but this resonance condition is typically only satisfied in the visible regime with the noble metals Au, Ag, or Cu.\textsuperscript{51-53} The quality factor for a number of metals across a range of energies is shown in Figure 2-3, which reveals that Al and Ag are superior in the UV, but Au or Cu are better suited to applications in the IR regime.\textsuperscript{53}

As the size of the metal nanocrystal is explicitly included in the expressions for the absorption and scattering cross sections, altering the nanocrystal dimensions significantly affects its optical properties. It is noted that the scattering cross-section scales much more rapidly with particle volume ($\sigma_{\text{scat}} \sim V^2$) than the absorption cross-section ($\sigma_{\text{ext}} \sim V$). Thus, the size of the metal nanocrystal itself exerts a significant influence on the utility of these materials for various applications. Qualitatively the LSPR frequency shifts to lower energies (i.e. red-shift) with increasing size (Figure 2-4). This phenomenon is a retardation effect due to the spatial inhomogeneity associated with the electric field across the entire nanostructure, as the size of the metal nanocrystal becomes comparable to the wavelength of incident light.\textsuperscript{49}

In addition to being material and size dependent, the shape of the metal nanostructure itself also exerts a significant influence on the optical response of the plasmonic metal.\textsuperscript{53-55} As shown in Figure 2-5, manipulating Au nanostructure morphology manifests a marked difference in optical properties of the colloid (compare triangular nanoparticles to nanorods), which allows for continuously tuning the LSPR absorption maximum across the visible and near-IR spectral regimes by adjusting the
architectural parameters of the nanocrystal. Additional terms must be added to the above expression to account for the reduced spatial symmetry of anisotropic nanostructures (e.g. nanorods, nanoprisms) within the incident optical field. However, as the essential physics are illustrated with the simplest example of an isotropic, spherical nanoparticle, further theoretical treatment of more complex morphologies is unnecessary.

When the incident optical excitation matches the LSPR frequency of the metal nanostructure, the driving optical field polarizes the free electron gas of the metal nanocrystal relative to its underlying nuclear framework. Such substantial polarization of surface charge density at the nanoscale establishes a locally enhanced electromagnetic field around the metal nanocrystal that can be orders of magnitude larger than the incident optical field (Figure 2-6A). While highly-enhanced near the nanoparticle surface, these plasmonic near-fields fall off rapidly with distance away from the metal nanocrystal (Figure 2-6B). We consider a spherical nanoparticle of radius, \( a \), irradiated by z-polarized light of wavelength, \( \lambda \). This strong electromagnetic field can be described by solving Maxwell’s equations using classical electrodynamics within the context of the quasi-static approximation (i.e. \( a/\lambda < 0.1 \)). Such a treatment yields the following expression for the electromagnetic field \( (E) \) outside of the metal nanoparticle:

\[
E(x, y, z) = E_0 \hat{z} - \left[ \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \right] a^3 E_0 \left[ \frac{\hat{z} - \frac{3z}{r^3}(x\hat{x} + y\hat{y} + z\hat{z})}{r^3} \right]
\]

where \( E_0 \) is the magnitude of the electric field component of the incident electromagnetic wave, \( \varepsilon(\omega) \) is the dielectric function of the metal nanocrystal, \( \varepsilon_m \) is the dielectric constant of the surrounding medium, and \( r \) is the radial distance away from the metal nanoparticle. Similar to the resonance condition observed in Equation 2-8,
analysis of this expression indicates that the electromagnetic field is enhanced relative to the incident optical field when $\varepsilon \approx -2\varepsilon_m$. This large near-field enhancement has found application in a variety of technologies, and is responsible for Surface Enhanced Raman Spectroscopy (SERS).\textsuperscript{51} As the dielectric function of the metal nanocrystal is frequency-dependent, the material properties of the metal nanocrystal determine at which wavelength this resonance condition is fulfilled.

The LSPR frequency is also sensitive to the dielectric constant of the surrounding medium ($\varepsilon_m$), or refractive index, $n_m$, as both quantities are related according to the relation: $\varepsilon_m = n_m^2$. As such, changes in the refractive index ($n_m$) of the local environment near the nanocrystal induce a shift in the wavelength maximum ($\lambda_{\text{max}}$) at which the LSPR is observed according to the following expression:

$$\Delta \lambda_{\text{max}} = m\Delta n \left[ 1 - \exp \left( -\frac{2d}{l_d} \right) \right]$$

(2-12)

where $m$ is the bulk-refractive index response of the nanoparticles, $\Delta n$ is the change in refractive index induced by the adsorbate, $d$ is the effective adsorbate thickness, and $l_d$ is the characteristic electromagnetic-field decay length.\textsuperscript{51} This relationship serves as the basis for molecular sensing via plasmonic near-fields, as a red-shift (blue-shift) in the LSPR frequency ($\lambda_{\text{max}}$) is observed upon an increased (decreased) refractive index ($n_m$) of the surrounding medium.\textsuperscript{51} Such effects must be considered when interfacing plasmonic-metal nanostructures with other materials (e.g. semiconductors, insulators) to ensure that the dielectric function of the surrounding medium does not dramatically alter the desired optical response of the metal nanostructure in the composite system.
Photophysics of Plasmonic-Metal Nanoparticles

Resonant optical excitation of a plasmonic nanocrystal initiates a cascade of complex photophysical processes that shape the temporal evolution of hot carriers in plasmonic-metal nanostructures, depicted schematically in Figure 2-7. In the dark, a single Fermi level ($E_F$) is established within the metal and the occupation of electronic levels is given by the Fermi-Dirac distribution:

$$f(E) = \frac{1}{e^{(E-E_F)/k_BT}+1}$$

(2-13)

where $E$ is the energy of the electronic level, $\mu$ is the chemical potential ($E_F$), $k_B$ is Boltzmann’s constant, and $T$ is the absolute temperature (in Kelvin) of the system. At equilibrium conditions in the dark only states up to $E_F$ are occupied and a single temperature $T_{(1)}$ describes the system. Absorption of a photon by the plasmonic nanostructure excites the collective oscillation of surface plasmons on the metal nanostructure, depositing electromagnetic energy into the electron gas (Figure 2-7A). Plasmons may be damped either radiatively via the emission of a photon or non-radiatively through the creation of electron-hole (e-h) pairs via Landau damping (Figure 2-7B). The branching ratio between these two decay channels is determined by the radiance of the plasmon mode, and is predicted to be size-dependent: hot carrier production via Landau damping is the dominant decay channel in smaller ($d < 25$ nm) metal nanostructures while re-emission of a photon (i.e. photon scattering) begins to dominate at larger ($d > 50$ nm) sizes. These plasmons quickly dephase with respect to the driving optical field via Landau damping processes that transfer a plasmon quantum into a single electron-hole pair excitation on an ultrafast timescale ($t \sim 1—100$ fs) to create a so-called “hot” electron distribution. As the LSPR energy ($\hbar\omega_{\text{LSPR}}$) for most
plasmonic metals is ca. $\hbar \omega_{\text{LSPR}} \approx 1.0-4.0$ eV, these hot electrons may possess energies anywhere from $E_F$ up to $E_F + \hbar \omega_{\text{LSPR}}$ with the hot holes located anywhere from $E_F$ down to $E_F - \hbar \omega_{\text{LSPR}}$. This "hot" electron distribution is so named to indicate that the electronic temperature ($T_e$) has not yet equilibrated with the lattice temperature ($T_l$) due to the substantial disparity in heat capacities between the electron gas ($C_e$) and the phonon bath ($C_{\text{ph}} \approx 100 C_e$). These hot electrons quickly ($t \sim 100$ fs—1 ps) redistribute this energy amongst the lower-energy electrons via electron-electron scattering processes to eventually establish an excited-state, Fermi-Dirac-like electron distribution described by the higher effective electronic temperature $T_{e(2)}$ (Figure 2-7C). The hot carriers then relax on longer timescales ($t \sim 1-10$ ps) as the elevated electronic temperature equilibrates with the phonon bath via electron-phonon coupling. The dynamics of this process are well described by the so-called "two-temperature model," in which $T_l$ and $T_e$ are time-dependent and the redistribution of energy is governed by a set of coupled differential equations. This energy transfer process ultimately elevates the temperature of the metal nanocrystal itself, which is subsequently transferred to the surrounding environment ($t \sim 100$ ps—10 ns). Heat transfer across the metal surface depends on both the material properties of the nanocrystal itself and the thermal conductivity of the surrounding environment (Figure 2-7D). The various decay channels and their associated timescales must be appropriately manipulated to adequately harness these electron dynamics for photocatalysis.

**Plasmonic-Metal Nanoparticles for Solar Energy Conversion**

The integration of plasmonic-metal nanostructures into semiconductor-based photoelectrochemical devices has the potential to offer numerous enhancements to the composite device. The number of plasmonic enhancement mechanisms that must
be considered in a given photocatalytic system depends upon the specific material properties of the individual building blocks comprising the plasmonic composite. The four principle enhancement mechanisms that must be considered in plasmonic photocatalysis are illustrated in Figure 2-8: (1) resonant photon scattering, (2) resonant energy transfer, (3) hot electron transfer, and/or (4) local photothermal heating. Mechanism (1) serves to increase the optical path length for resonant photons within the plasmonic-metal/semiconductor composite through enhanced light scattering. Such a strategy essentially employs these nanostructures as “mirrors” to scatter light through the semiconductor multiple times before leaving the device (Figure 2-8A). This mechanism is only significant in systems employing large \( d \geq 50 \) nm plasmonic-metal nanostructures as the scattering cross section scales directly with the volume of the metal nanoparticle itself. Mechanism (2) exploits the locally-enhanced electromagnetic fields near the surface of a plasmonic-metal nanostructure during excitation of its LSPR (Figure 2-8B), since the optical transition rate of a semiconductor photocatalyst is proportional to the magnitude of these local EM fields \( |E|^2 \). This near-field mechanism requires that the LSPR frequency of the metal nanoparticle coincide with the threshold for band gap excitation within the semiconductor to effectively couple incident light into these enhanced near-field modes. Mechanism (3) harnesses the hot electron distribution generated on plasmonic-metal nanostructures during optical excitation to harvest visible light via a plasmonic photosensitization scheme analogous to that employed in dye-sensitized solar cells (Figure 2-8C). This approach requires intimate physical contact between the plasmonic metal and the semiconductor in order to facilitate plasmon-mediated electron
transfer (PMET) from the metal nanocrystal to the energetically-accessible CB levels of the semiconductor support. Mechanism (4) occurs after the creation of hot e-h pairs via Landau damping. This hot carrier distribution rapidly relaxes as it equilibrates with the metal lattice through electron-phonon coupling ($t \sim$fs—ps), thereby elevating the surface temperature of the metal nanoparticle relative to its environment (Figure 2-8D). This localized thermal energy is subsequently released to the nearby surroundings via heat transfer across the metal/solution interface on longer timescales ($t \sim$ps—ns). In the presence of surface-adsorbed species this spatially-confined heat source can serve to thermally-activate chemical reactions and/or decompose inorganic chemical precursors for nanomaterials fabrication.

It must be recognized that these plasmonic processes may coexist in a given system, requiring careful control over the material properties of each individual constituent in the plasmonic composite to conclusively elucidate the enhancement mechanism operative within the device. Of these possible mechanisms, we specifically explore the interaction between plasmonic near-fields and semiconductor photoelectrodes on photoelectrochemical performance (mechanism 2) and evaluate the potential for harvesting hot electrons from plasmonic nanostructures (mechanism 3) for visible-light-driven water splitting. The specific points to consider for each strategy are elaborated upon below.

**Plasmon-Mediated Electron Transfer in Metal/Semiconductor Heterojunctions**

Upon formation of a metal/semiconductor heterojunction, the difference in Fermi levels ($E_F$) between the two materials induces a transfer of charge until a single Fermi level is established within the heterostructure. The semiconductor is assumed to be free of surface states and the influence of any surface dipoles induced by adsorbed
surface species is neglected. For an n-type semiconductor (e.g. TiO$_2$) in contact with a large work function metal (e.g. Au), electrons will flow from the semiconductor to the metal until an interfacial Schottky barrier ($\varphi_B$) is formed at the metal/semiconductor interface,$^{16}$ as shown in Figure 2-9. This transfer of charge induces a positive space-charge layer within the semiconductor, which extends to a certain depth beneath the surface known as the depletion width, $W$.\textsuperscript{14-16} This preponderance of positive charge induces an upward band bending within the space-charge layer of the semiconductor (Figure 2-9B).\textsuperscript{16} The Schottky barrier height ($e\varphi_B$) is given by the following expression:

$$e\phi_B = e\phi_m - e\chi_s$$  \hspace{1cm} (2-14)

while the potential across the space-charge layer ($e\varphi_{SC}$) is given by:

$$e\phi_{SC} = e\phi_B - (E_{CB} - E_F)$$  \hspace{1cm} (2-15)

where all variables have been previously defined.$^{15}$ It must be noted that the final position of $E_F$ within the composite system and the potential across the space-charge layer ($\varphi_{SC}$) depend on the relative positions of the two Fermi levels before the materials are brought into physical contact.$^{15}$ This space-charge layer is critical for sustaining plasmon-driven charge separation, as the band bending near the metal/semiconductor interface repels electrons in the semiconductor CB away from the heterojunction.$^{13-16}$

While it was assumed that the semiconductor is free of surface states, this is not strictly true in all cases, and therefore Equation 2-14 may not give the actual Schottky barrier height established in real systems. If the n-type semiconductor possesses a high-density of isoenergetic surface states within the band gap, it may be able to transfer charges without significantly affecting the occupation of levels (i.e. $E_F$ remains constant at the surface). Therefore, electrons transferred from the surface states to the
metal do not affect the interfacial barrier height – it is entirely determined by the properties of the semiconductor surface and the contact potential occurs across a very small region at the interface.\textsuperscript{15} Such a situation is known as “Fermi-level pinning.”

Hot carrier transfer across a plasmonic-metal/semiconductor Schottky barrier can be described as consisting of a series of three sequential steps (Figure 2-9C): (1) hot electrons are generated in the metal film via photon absorption, lifting electrons from states below the metal Fermi level by the incident photon energy ($\sim E_F + h\nu$); (2) a fraction of these hot carriers move toward the metal/semiconductor interface. As these electrons are assumed to behave as free electrons and possess an initial momentum distribution that is isotropic, only those that possess the appropriate direction in $k$-space will reach the barrier; (3) hot electrons arriving at the metal/semiconductor interface with a kinetic energy greater than the interfacial barrier height have a probability of traversing the barrier, but may still be reflected. This follows from the requirement that these electrons must conserve their energy, and therefore their momentum tangential to the interface upon transmission through the barrier.\textsuperscript{50,56} As such, electrons can only emit across the Schottky barrier when their $k$-vector lies within the emission cone in $k$-space and their energy exceeds that of the barrier height ($q\phi_B$).\textsuperscript{56} The internal quantum transmission probability ($\eta$) of hot electrons across the interfacial Schottky barrier can be approximated by using the modified Fowler expression:

$$\eta = C_F \left( \frac{h\nu - q\phi_B}{h\nu} \right)^2$$

(2-16)

where $C_F$ is the device-specific Fowler emission constant, $q\phi_B$ is the Schottky barrier height, and $h\nu$ is the energy ($E = h\nu$) of the incident photon.\textsuperscript{94} It must be noted that such a model was developed to describe hot electron transfer across semi-infinite planar
interfaces, which do not apply to plasmons confined within metal nanocrystals. In such systems, the hot electrons do not behave as free carriers because their trajectories are bound by the physical dimensions of the nanocrystal.\textsuperscript{56,89} The restrictions on momentum conservation are lifted, and the crystal momentum is no longer a good quantum number due to the uncertainty principle.\textsuperscript{56} As such, confinement effects in nanocrystal geometries enable the possibility of geometry-assisted intraband transitions without involving phonons, and thus allow the generation of hot electrons with energies high above the metal Fermi level.\textsuperscript{89} Nevertheless, previous studies have shown excellent agreement between experimental hot electron emission and Fowler’s simple theoretical model, indicating the general validity of the model to nanoscale systems.\textsuperscript{94}

The use of noble metals as light harvesting elements offers several advantages relative to organic dyes or quantum dots. First, the large optical cross-sections of plasmonic nanostructures enable them to harvest incident photons from a region larger than their geometrical cross-section.\textsuperscript{56,57} In fact, the optical cross-section of a plasmonic-metal nanostructure can be up to five orders of magnitude larger than their molecular analogues,\textsuperscript{57} and are therefore expected to provide improved light-harvesting efficiency as compared to more traditional Ruthenium-based molecular photosensitizers. Secondly, the unique ability to continuously tune the LSPR absorption maximum ($\lambda_{\text{max}}$) throughout the solar emission spectrum (UV—IR) by simply adjusting the physical parameters of the nanostructure offers the possibility of creating panchromatic photosensitizers with complementary optical characteristics across the entire solar spectrum.\textsuperscript{53-55} Third, the use of a noble metal such as Au imparts significant chemical stability to the device.\textsuperscript{79-83} Such robust photochemical stability is in stark
contrast to that observed for molecular dyes and quantum dots, which are susceptible to photo-bleaching and/or photocorrosion under extended operation. Despite much promise, challenges associated with harvesting these hot carriers from plasmonic-metal nanostructures still remain. The relatively short lifetime of hot electrons (t \sim \text{ps}) within plasmonic nanostructures requires a strategy for quickly capturing these carriers prior to thermalization with the phonon bath.

Plasmonic-Metal Nanoparticles as Optical Antennas

The large optical cross-section of metal nanocrystals offers the potential for augmenting the absorption profile of a semiconductor photocatalyst by taking advantage of the strong near-field enhancement provided by plasmonic nanostructures. As shown in Figure 2-6A, optical excitation of the plasmonic-metal’s LSPR induces a local enhancement of electromagnetic fields near the nanoparticle surface that can be orders of magnitude (~10³) larger than that of the incident photon flux. These surface fields are spatially inhomogeneous and rapidly decay away from the metal surface within ~20—30 nm (Figure 2-6B). When a semiconductor is brought within close proximity of these plasmonic-metal nanostructures it encounters these enhanced near-fields. The optical transition rate (\Gamma) from the VB to the CB within a semiconductor can be approximated with Fermi’s Golden Rule:

\[ \Gamma = \frac{2\pi}{\hbar} \left| \langle \Psi_f | \hat{H} | \Psi_i \rangle \right|^2 \rho(E) \]  

(2-17)

where the initial state, \( \Psi_i \), is located in the semiconductor VB and the final state, \( \Psi_f \), is located in the semiconductor CB, \( \rho(E) \) represents the joint density of states between the VB and CB, and \( \hat{H}' \) is the operator connecting these states. In the case of a photon-
assisted optical transition, this operator can be written in the form of the electromagnetic interaction Hamiltonian, as given by:

$$H' = \langle \Psi_{i(VB)} | H_{EM} | \Psi_{f(CB)} \rangle = -\left( \frac{e}{m_e c} \right) \langle \Psi_{i} | \mathbf{A}(\mathbf{r}, \tau) \cdot \mathbf{p} | \Psi_{f} \rangle$$  \hspace{1cm} (2-18)

where $e$ is the charge of an electron, $m_e$ is the reduced mass of the electron, $c$ is the speed of light in a vacuum, $\mathbf{A}$ is the vector potential of the electromagnetic wave (at position, $\mathbf{r}(x, y, z)$ and time, $\tau$), and $\mathbf{p}$ is the momentum vector.\textsuperscript{111} The vector potential is related to the electric fields of the incident photon according to the relationship:

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} = \frac{i\omega}{c} \mathbf{A}$$  \hspace{1cm} (2-19)

where $\mathbf{E}$ is the electric field vector of the electromagnetic wave and all other variables are as previously defined.\textsuperscript{111} As such, the electric field of the incident photon itself mediates the transition from VB to CB. Thus, the optical transition rate within a semiconductor photocatalyst is proportional to the magnitude of these local electromagnetic fields (i.e. $|\mathbf{E}|^2$), and the plasmonic nanoparticle effectively serves as an optical nanoantenna to increase the probability for photon absorption within the semiconductor.\textsuperscript{65-77} Such a strategy is particularly useful for augmenting photocatalysts, as these enhanced near-fields serve to preferentially couple incident light into the semiconductor near the solid/liquid junction (Figure 2-10). Concentrating the incident photon flux near the semiconductor surface serves to selectively produce e-h pairs within the space-charge layer of the semiconductor where the surface potential helps to separate charge carriers. Preferentially producing charge carriers near the semiconductor surface also reduces the average diffusion distance these carriers must travel before reaching the solid/liquid junction where they can participate in
photochemistry.\textsuperscript{57-59} This mechanism thereby improves the probability for photochemical reactions relative to recombination, enhancing photocatalytic activity.\textsuperscript{65-77} Panchromatic light-harvesting devices are envisioned by tailoring the LSPR frequency to amplify the absorption profile of the semiconductor in regions of the solar spectrum that would otherwise be inefficiently harvested by the device.

It must be noted that this plasmonic resonant energy transfer-based enhancement mechanism requires that the LSPR frequency of the metal nanoparticle coincide with the threshold for band gap excitation within the semiconductor to effectively couple these enhanced near-fields with the incident light (i.e. far-field radiation).\textsuperscript{57-59} The reaction rate enhancement is therefore proportional to the optical overlap between the illumination source, the LSPR frequency of the metal and the absorption spectrum of the semiconductor, as given by the overlap integral:

\[
\frac{r}{r_0} \propto \int I_0(\lambda) A_{SC}(\lambda) E_{LSPR}(\lambda) d\lambda
\]  

(2-20)

where \(I_0\) is the illumination source intensity, \(A_{SC}\) is the absorption spectrum of the semiconductor, and \(E_{LSPR}\) is the LSPR energy of the metal, and \(\lambda\) is the wavelength of incident light.\textsuperscript{65} To exclusively evaluate this near-field enhancement mechanism and exclude the possibility of PMET between the plasmonic metal and the nearby semiconductor requires an insulating electronic barrier.\textsuperscript{57} It is emphasized, however, that nanoscale precision over the metal—semiconductor separation distance is required to ensure close physical proximity for encountering these enhanced near-fields, while preventing the nearby metal from quenching the excited-state of the semiconductor photocatalyst. Difficulties associated with such stringent material requirements have
hindered the unambiguous assignment of enhanced plasmonic photocatalysis to this near-field mechanism.

**Challenges Associated with Elucidating the Plasmonic Enhancement Mechanism**

Although the incorporation of plasmonic nanoparticles into semiconductor-based photoelectrochemical cells represents a promising approach towards enhancing the conversion of visible light into chemical energy, the mechanics of these processes remain poorly understood within the burgeoning field of plasmon-enhanced photoelectrochemical water splitting.\textsuperscript{57-61} In many instances of plasmon-enhanced photocatalysis reported to date, a multitude of mechanisms have been invoked to explain the enhancements observed in the composite device.\textsuperscript{75,76} Thus, carefully-designed material systems are required to separately investigate the individual plasmonic enhancement mechanisms that contribute to the overall photocatalytic activity observed in the composite system.

The work reported herein uses two distinct material systems to elucidate the fundamental photophysical processes and chemical interactions governing the use of hot carriers and enhanced electromagnetic near-fields in photoelectrochemical systems for solar-to-fuel energy conversion. A photoelectrochemical system composed of Au nanoparticles anchored to TiO\textsubscript{2} nanowires was constructed to evaluate the potential for harvesting hot electrons from Au nanoparticles for solar photochemistry. The temporal evolution of hot electrons following PMET was probed using photoelectrochemical techniques to study these charge carrier dynamics \textit{in situ}. These hot electrons were then harnessed for photocatalysis to produce H\textsubscript{2} from water using visible light. The fate of these hot electrons within the semiconductor photocatalyst was further followed via electron paramagnetic resonance (EPR) spectroscopy to identify the structural sites
within the semiconductor support involved in the PMET process. The influence of plasmonic near-fields was studied using a Cu$_2$O-based photocathode containing Au@SiO$_2$ (core@shell) nanoparticles. The plasmonic device was found to exhibit a ~3 times increase in photoelectrochemical performance, enabling a ~40% reduction in semiconductor material required for efficient photocatalytic operation. Systematic variation of the SiO$_2$ shell thickness (5—22 nm) enabled unambiguous isolation of the near-field effects, proving that this was the sole mechanism responsible for the enhanced performance of the plasmonic photocathode. Taken together, these studies illustrate the potential merits of integrating plasmonic-metal nanostructures into semiconductor-based photoelectrochemical cells for enhanced artificial photosynthetic constructs.
Figure 2-1. Localized surface plasmon resonance (LSPR) of metal nanocrystals under optical excitation. The electron gas (illustrated in green) is polarized relative to the metal lattice (grey sphere) under the incidence of the incident electromagnetic wave (where $k_{\text{photon}}$ indicates the wavevector of the photon). Notice that the wavelength of incident light is much larger than the metal nanocrystal, such that at any given instant the metal nanocrystal experiences a quasi-static electromagnetic field. Adapted with permission from Willets et al. Copyright 2007 Annual Review of Physical Chemistry.
Figure 2-2. Dielectric function of Au. The real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) components of the complex dielectric function for Au from experimental data (blue curve) are plotted in comparison to the dielectric function predicted from the Drude model (red dashed curve). The Drude model reproduces the experimental spectra well until the onset of interband transitions (~2.4 eV) occurring within the Au, which introduce additional damping processes that modify the dielectric response. Inset shows a cartoon representation of the band structure of Au, where $E_F$ denotes the Fermi level and $\omega_{ib}$ is the frequency at which the onset of interband transitions is observed ($\omega_{ib} \approx 2.4$ eV) from the 5d-band to the 6sp-band. Reprinted with permission from Willets et al. Copyright 2011 American Chemical Society.
Figure 2-3. Quality factor ($Q$) of the plasmon resonance at a given metal/air interface across the UV-visible-near IR spectrum. A higher $Q$-factor indicates a stronger plasmon resonance less affected by damping. The shaded area denotes the region of interest for many plasmonic applications. Reprinted with permission from Rycenga et al. Copyright 2011 American Chemical Society.

Figure 2-4. Extinction spectra of Au nanoparticles with increasing size. As the nanoparticle size increases, the LSPR wavelength maximum ($\lambda_{\text{max}}$) shifts to lower energies (red-shift). Reprinted with permission from Hartland et al. Copyright 2011 American Chemical Society.
Figure 2-5. Influence of Au nanocrystal morphology on optical properties. TEM images of A) Au nanospheres, B) Au nanorods, and C) Au nanoprisms with corresponding digital photograph of glass vials containing nanostructures dispersed in aqueous solution shown below. D) Extinction spectra of these Au nanostructures dispersed in aqueous solution showing the distinctive optical properties of the nanospheres (A, red curve), the nanorods (B, blue curve) and the nanoprisms (C, green curve). Adapted with permission from DuChene et al. Copyright 2013 American Chemical Society.
Figure 2-6. Plasmonic near-fields. A) Near-field distribution around a single Au nanoparticle under optical excitation ($\lambda = 525$ nm) immersed in a water medium showing the electric-field enhancement (i.e. $|E/E_0|^2$) relative to the incident photon ($E_0$) with wavevector, $k$. B) Plot of the electric-field enhancement $|E/E_0|^2$ as a function of distance ($d$) away from the surface of the Au nanoparticle shown in (A). Inset depicts the line segment along which the field enhancement is plotted.
Figure 2-7. Hot carrier dynamics in metal nanocrystals. A) Excitation of a localized surface plasmon deposits optical energy into the nanoparticle. B) Hot electrons are created above the $E_F$ and hot holes are created below $E_F$ immediately following Landau damping processes ($t \sim 100$ fs), creating a highly non-thermalized distribution of hot electron-hole pairs. C) Hot carriers redistribute their energy via electron-electron scattering processes on a timescale from $t \sim 0.1$—1 ps. D) Heat is finally transferred to the surrounding environment on a longer timescale ($t \sim 100$ ps—1 ns) via thermal conduction. Adapted with permission from Brongersma et al. Copyright 2015 Nature Nanotechnology.
Figure 2-8. Plasmonic enhancement mechanisms in semiconductor photocatalysis. A) Plasmon-enhanced light absorption via enhanced resonant photon ($\hbar \omega$) scattering within the semiconductor photocatalyst (blue), which can be further enhanced through the use of a plasmonic reflective backing layer (dark grey). B) Plasmon-enhanced light absorption via plasmonic near-fields, which concentrate the photon flux within the photocatalyst to boost the probability for light absorption within the semiconductor. C) Plasmon-mediated electron transfer (PMET) from a plasmonic metal (grey) to a semiconductor conduction band (blue) in three steps: (i) generation of hot electron-hole pairs via photon absorption, (ii) transfer of hot electrons to semiconductor photocatalyst, (iii) surface reaction to produce H$_2$ from water. D) Plasmon-driven photothermal effects near the surface of metal nanocrystals under optical excitation. Plasmonic hot spots confine optical radiation within nanoscale volumes that are capable of reaching local temperatures far beyond that obtained in the bulk solution. These nanoscale environments enable chemical reactions to occur near the nanoparticle surface that are not feasible in the bulk solution. Adapted with permission from Linic et al. Copyright 2011 Nature Materials.
Figure 2-9. Band alignment diagram and hot electron transmission from a plasmonic-metal nanoparticle to an n-type semiconductor. A) Band diagram in the dark prior to physical contact, denoting the level of the semiconductor CB ($E_{CB}$), semiconductor VB ($E_{VB}$), band gap ($E_G$), electron affinity ($\chi_s$), Fermi level ($E_F$) of both phases, and the work function of the metal ($\phi_M$) with respect to the vacuum level ($E_{vac}$). B) Band alignment between materials after physical contact, showing the presence of an interfacial Schottky barrier ($\phi_B$) and accompanying depletion width ($W$) with a single Fermi level ($E_F$) of the composite system. C) Hot electron transfer across an interfacial Schottky barrier $\phi_B$ via internal photoemission as described by the Fowler theory involving the following three steps: (1) absorption of a photon ($h\nu$) creates hot electron-holes pairs in the metal nanocrystal; (2) the hot electrons move towards the metal/semiconductor interface; (3) a fraction of these hot carriers arriving at the heterojunction transmit across the interfacial Schottky barrier.
Figure 2-10. Scheme of plasmon-enhanced light absorption within a semiconductor nanowire under resonant optical excitation. Incident light simultaneously excites the LSPR of the Au@SiO$_2$ (plasmonic-metal core@dielectric shell) nanoparticles and the band gap of the Cu$_2$O nanowires. The plasmonic near-fields (red shading) serve to focus the incident photon flux near the semiconductor-liquid junction to increase the production of electron-hole (e$^-$—h$^+$) pairs within the Cu$_2$O nanowires and enhance the photocatalytic reaction rate. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Harvesting Hot Electrons from Au/TiO₂ Heterostructures for Solar Photocatalysis

Solar photocatalysis for chemical fuel production represents a promising approach to sustainably satisfy escalating global energy demands. Unfortunately, current photocatalysts exhibit limited solar-to-fuel efficiencies due to the daunting temporal disparity between the brief excited-state lifetimes of photogenerated electron-hole pairs \( (t \sim \text{ps} - \mu \text{s}) \) and the prolonged timescales required to facilitate multi-electron photocatalytic reactions \( (t \sim \text{ms} - \text{s}) \) at the semiconductor/liquid junction. This so-called “kinetic bottleneck” constitutes a significant hindrance to the eventual realization of efficient photosynthetic devices for solar energy conversion. Recently, the thoughtful integration of plasmonic nanostructures (e.g. Au and Ag) into traditional photoelectrochemical architectures has been shown to endow the plasmonic composite with substantial enhancements in photocatalytic performance. Plasmonic nanoparticles are particularly well-suited to augment solar photocatalysts due to their unique optical properties, derived from a phenomenon known as localized surface plasmon resonance (LSPR). Following optical excitation, these localized surface plasmons rapidly decohere with respect to the applied optical field and predominantly relax non-radiatively through electron-electron scattering processes. This decay channel yields highly energetic electrons via Landau damping, transiently populating electronic states above the metal Fermi level \( (E_F) \), and briefly establishing a so-called “hot” electron distribution. If plasmonic-metal nanostructures are proximal to a semiconductor with a dense manifold of conduction band (CB) states (e.g. TiO₂, ZnO, SrTiO₃, etc.), the hot electrons can be directly injected into the energetically accessible...
CB levels of the semiconductor.\textsuperscript{56,57} This plasmon-mediated electron transfer (PMET) process enables these plasmonic nanoparticles to serve as visible-light-harvesting assemblies when physically anchored to a semiconductor scaffold.\textsuperscript{78-84}

Although PMET occurs on an ultrafast timescale ($t < 240 \text{ fs}$),\textsuperscript{91,92} the temporal evolution of these transferred electrons within the semiconductor CB after PMET warrants further study. It must be recognized that the average lifetime of hot electrons within the semiconductor CB represents a critical catalytic parameter, as these photoexcited electrons must persist long enough to facilitate chemical reactions at the semiconductor surface. Previous dynamics studies were conducted in air using femtosecond pulsed-laser excitation, and thus did not adequately capture the excited-state dynamics relevant to photoelectrochemical systems operating in solution.\textsuperscript{60} Knowledge of these hot electron dynamics within a plasmonic device under simulated solar conditions is therefore crucial to the further optimization and eventual exploitation of the PMET process in artificial photosynthetic constructs.

To that end, we used a plasmonic photoelectrochemical cell to elucidate the dynamics of hot electrons within Au/TiO\textsubscript{2} heterojunctions during \textit{in situ} (i.e. aqueous solution) operation. A wide band gap semiconductor (i.e. TiO\textsubscript{2}) was specifically selected to ensure unambiguous assignment of the visible-light response to the plasmonic nanoparticles while the TiO\textsubscript{2} nanowires served solely as the conduit for hot electron transport (\textit{vide infra}). The photodeposition of Au nanoparticles directly onto highly oriented single-crystalline TiO\textsubscript{2} nanowires provides a semiconductor support of sufficient physical dimensions and electronic quality to facilitate the formation of an interfacial Schottky barrier and sustain a depletion width within the solid. The band
bending associated with this Schottky barrier is expected to hinder back electron transfer and promote interfacial charge separation across the plasmonic-metal/semiconductor heterojunction. This device architecture further renders the plasmonic composite electronically addressable, providing an ideal platform to probe the PMET process under realistic working conditions. These studies unambiguously confirm that visible-light excitation of the Au/TiO₂ photoanode induces PMET from the Au nanoparticles to the CB of the TiO₂ nanowires. These plasmonic photoanodes delivered superior photoelectrochemical performance under simulated solar conditions as a result of increased visible-light collection via this plasmonic photosensitization strategy. Significantly, we monitored the lifetime of these hot electrons within the semiconductor CB in situ and found that the PMET process yields excited-state electrons with prolonged lifetimes compared to those of electrons excited directly within the TiO₂ via UV light. These long-lived electrons were subsequently harnessed for visible-light-driven hydrogen (H₂) evolution from water, demonstrating the utility of PMET for solar photocatalysis.

**Experimental Methods**

**Materials**

Fluorine-doped tin oxide (FTO) glass substrates (TEC 15) were purchased from Hartford Glass Co. (Hartford City, IN). Titanium(IV) butoxide (97%), tetrachloroauric acid (HAuCl₄), methanol (MeOH), and 2-propanol were purchased from Sigma Aldrich (St. Louis, MO). Acetone, hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Fisher Scientific (Hampton, NH). All chemicals were used as received without further purification. All glassware was cleaned with aqua regia solution, followed by copious rinsing with Nanopure™ H₂O (Barnstead, 18.2 MΩ cm) prior to use. Caution!
Aqua regia is highly corrosive/toxic. Handle with care and use appropriate personal protection equipment.

**Synthesis of TiO$_2$ Nanowire Arrays for n-type Photoanode**

Titanium dioxide (TiO$_2$) nanowire arrays were fabricated according to a previously reported method.$^{112}$ The fluorine-doped tin oxide (FTO) substrate was ultrasonically cleaned via immersion in a 30 mL solution consisting of 10 mL acetone, 10 mL 2-propanol, and 10 mL Nanopure™ H$_2$O for 1 h. The substrate was rinsed with Nanopure™ H$_2$O, dried in air, and placed at an angle (conductive side facing down) against the sidewall of a 40 mL Teflon®-lined autoclave. In a separate 100 mL beaker, 15 mL Nanopure™ H$_2$O and 15 mL concentrated HCl (38 wt.%) were combined, followed by the addition of 500 μL of Ti(IV) butoxide. The solution was stirred for 5 min and poured into the 40 mL Teflon®-lined autoclave containing the FTO substrate. The hydrothermal synthesis was then conducted in an oven at 150 °C for 18 h. After synthesis, the FTO substrate was removed, washed copiously with Nanopure™ H$_2$O, and allowed to dry in ambient air.

**Synthesis of Au/TiO$_2$ Nanowire Arrays**

A photochemical growth solution was prepared by adding 200 μL of methanol (MeOH) to 4.8 mL of Nanopure™ H$_2$O in a 50 mL beaker. The TiO$_2$ nanowire array was immersed in this solution, and 250 μL of 10 mM HAuCl$_4$ was added to achieve a final gold (Au) concentration of 0.475 mM HAuCl$_4$. The contents of the beaker were irradiated for 5 min with a 500 W Hg (Xe) lamp (Newport Corp.) equipped with a beam turning UV dichroic mirror (λ = 280-400 nm) (Newport Corp.). Following illumination, the growth solution was poured out and the substrate, now purple in color, was immersed in Nanopure™ H$_2$O. Brief sonication (~5 s) was used to remove any Au nanoparticles not
strongly bound to the TiO$_2$ nanowires. The substrate was further rinsed with copious amounts of Nanopure™ H$_2$O and allowed to dry in air.

**Materials Characterization**

Scanning electron microscopy (SEM) analysis of the TiO$_2$ nanowire arrays was conducted on an FEI Nova Nano 430 SEM operated at 15 kV at the Nanoscale Research Facility at the University of Florida (UF). X-ray diffraction (XRD) patterns of the TiO$_2$ nanowires on the FTO glass substrate were obtained using an X’Pert powder diffractometer (PANalytical Systems) with Cu Kα radiation ($\lambda = 1.5406$ Å) located at the Major Analytical Instrumentation Center (MAIC) at UF. To prepare the Au/TiO$_2$ materials for structural analysis by transmission electron microscopy (TEM), the nanowires were mechanically removed from the FTO substrate with a razor blade, dispersed in Nanopure™ H$_2$O, and subjected to sonication for 2 min in order to disperse the nanowires. TEM samples were prepared by dropping 6 μL of the Au/TiO$_2$ heterostructure suspension onto a Holey Carbon 400 mesh Cu grid (Ted Pella, Inc.) and allowed to dry in ambient air. TEM analysis was then performed using a JEOL 200CX TEM (housed at MAIC, UF) operated at 200 kV. Additional high-resolution transmission electron microscopy (HRTEM) images were acquired using a JEOL 2100F HRTEM equipped with a Schottky field-emission gun (FEG) with Cs = 1.0 mm operated at 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging was conducted on a Cs-corrected Hitachi HD-2700C equipped with a Cold-FEG operated at 200 kV. Images were acquired using a probe convergence semi-angle of 23 mrad and the inner collection angle of the ADF detector was 53 mrad. Energy dispersive X-ray spectroscopy (EDS) mapping of the Au/TiO$_2$ heterostructures
was obtained with a probe convergence angle of 28 mrad. Both instruments are located at Brookhaven National Lab, Upton, NY.

**Photoelectrochemical Experiments**

The photoelectrochemical characteristics were investigated via the construction of a three-electrode electrochemical cell controlled by a potentiostat (EC Epsilon, Bioanalytical Systems, Inc.). The nanowire photoanode served as the working electrode, with a platinum (Pt) wire as the auxiliary electrode, and a Ag/AgCl (saturated KCl) reference electrode all immersed in 1.0 M NaOH (pH 13.6) as the supporting electrolyte. The working electrode area was 2 cm$^2$ for each experiment. All potentials are reported relative to the Reversible Hydrogen Electrode (RHE), which represents the potential of the Standard Hydrogen Electrode (SHE) adjusted for the pH of the solution with the following equation:

$$E_{RHE} = E_{Ag/AgCl} + (0.059 \text{ V pH}^{-1} \times \text{pH}) + E_{o}^{o}_{Ag/AgCl}$$

(3-1)

where $E_{RHE}$ is the converted potential vs. RHE, $E_{Ag/AgCl}$ is the experimental potential measured relative to the Ag/AgCl reference electrode, and $E_{o}^{o}_{Ag/AgCl}$ is the standard potential of the Ag/AgCl reference electrode relative to the RHE at 25 °C (0.1976 V$_{RHE}$). The photoanodes were illuminated through the FTO glass substrate with simulated sunlight from an ozone-free 300 W Xe lamp (Newport Corp.) equipped with an air mass (AM) 1.5G filter (Newport Corp.). All photoelectrochemical measurements were conducted at an incident power of 1-sun ($I_0 = 100 \pm 10$ mW cm$^{-2}$) unless otherwise indicated. Any numbers given after the ± sign throughout the text indicate the standard deviation (SD) about the mean value. Chronoamperometry [$J_{ph}(t)$], power-dependent photocurrent [$J_{ph}(I_0)$], and bias-dependent photocurrent [$\Delta J_{ph}(E_{appl})$] experiments were

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conducted using the three-electrode configuration (*vide supra*) while the photoanode was potentiostatically poised at different potentials ($E_{\text{appl}} = 0.20$-$1.80$ $V_{\text{RHE}}$; $\Delta E_{\text{appl}} = 0.2$ V) during illumination. The photocurrent action spectrum [$J_{\text{ph}}(\lambda)$] was investigated using a set of band pass filters ($\lambda = 420$-$680$ nm) with a bandwidth of $\Delta \lambda = 20$ nm ± $10$ nm (Thor Labs, Inc.). The plasmonic photovoltage action spectrum [$\Delta V_{\text{ph}}(\lambda)$] was investigated with a series of long pass ($\lambda = 300$, 360, 395, 495, 515, 550, 610, 715 nm) and short pass ($\lambda = 400$, 500, 600 nm) optical filters (Thor Labs, Inc. and Edmund Optics, Inc.) in order to isolate specific regions of the lamp spectrum. All experiments were performed on three independently fabricated photoanodes, all of which exhibited similar photoelectrochemical characteristics. The data presented is for the best performing plasmonic (Au/TiO$_2$) and control (TiO$_2$-only) device.

**Photoluminescence Measurements**

Photoluminescence (PL) measurements were carried out using a Horiba Aramis Raman system, which is a software-selectable multi-wavelength Raman/PL system located at NRF (UF). The PL spectra were collected by using a 325 nm laser with a grating of 2400 g/mm to excite the band gap transitions of the TiO$_2$ nanowires. The samples were focused using a 40x objective lens. The laser spot size used for each measurement was ca. 150 $\mu$m in diameter with an incident power of 0.6 mW and an acquisition time of 10 s. PL spectra were acquired on pristine TiO$_2$-only and Au/TiO$_2$ devices prior to photoelectrochemical measurements. All PL measurements were acquired from at least 3 different spots selected at random on each device. All PL emission spectra were then averaged to mitigate any signal variability associated with irregularities in film composition.
Visible-Light-Driven Photocatalytic H$_2$ Production Experiments

An air-tight electrochemical cell was used to monitor the evolution of H$_2$ (g) from a water/methanol solution (pH 13.3) composed of 1.0 M NaOH/methanol (3/1 v/v %). We chose methanol as a sacrificial reagent (i.e. hole scavenger) in order to isolate the water reduction step from the overall water-splitting process. The solution and reactor cell were purged via N$_2$ bubbling of the solution/reactor system under vigorous magnetic stirring for 20 min to remove any dissolved O$_2$ (g) prior to each photoelectrochemical experiment. The plasmonic Au/TiO$_2$ working electrode (area = 2 cm$^2$) was poised at $E_{\text{appl}} = 1.20$ V$_{\text{RHE}}$ during irradiation with visible light ($\lambda > 515$ nm) from a 300 W Xe lamp ($I_0 = 3.0 \pm 0.2$ W/cm$^2$) to investigate the photocatalytic activity associated with excitation of the plasmonic Au nanoparticles. The evolution of H$_2$ (g) was then confirmed through headspace gas analysis with a gas chromatograph (Shimadzu GC-2014) equipped with a 60/80 Mol Sieve 5A column (Supelco) and a thermal conductivity detector maintained at 35 °C with Ar (g) as the carrier gas. A 200 μL sample volume was extracted from the reactor headspace at 1 h intervals using a microliter syringe and injected directly into the column. The integrated peak area was compared to that of a standard H$_2$ curve in order to convert the peak area into the number of moles of H$_2$ produced. The photoelectrochemical stability of the plasmonic photoanode was evaluated by repeatedly subjecting the device to identical experimental conditions ($E_{\text{appl}} = 1.20$ V$_{\text{RHE}}$ with $\lambda > 515$ nm at $I_0 = 3.0 \pm 0.2$ W/cm$^2$) on 4 consecutive days while monitoring the H$_2$ evolution rate over time.
Results and Discussion

Morphology and Optical Properties of Au/TiO₂ and TiO₂ Photoanodes

A plasmonic photoanode was assembled from a vertically aligned TiO₂ nanowire array, which served as the semiconductor support for the subsequent photochemical deposition of plasmonic Au nanoparticles (see Experimental Methods section for details). The wide band gap of rutile TiO₂ ensures that these nanowires serve solely as the conduit for hot electron transport upon optical excitation of the Au nanoparticles with visible light (~2.4 eV). Relative to planar semiconductor configurations, this nanowire topology has been shown to improve photoelectrochemical performance by orthogonalizing the directions for light absorption and charge transport within the device.³⁰⁻⁴³ Inspection by scanning electron microscopy (SEM) showed that the TiO₂ nanowires were perpendicularly oriented on the fluorine-doped tin oxide (FTO) glass substrate with average lengths (l) of 2.2 ± 0.2 μm and diameters (d) of 200 ± 50 nm (Figure 3-1). X-ray diffraction (XRD) indicated that these nanowires were monocrystalline and composed exclusively of the rutile phase (Figure 3-2A), consistent with a prior report.¹¹² The optical properties of the TiO₂ nanowires on the FTO substrate were characterized by diffuse-reflectance spectroscopy, which showed that these rutile TiO₂ nanowires respond to wavelengths of visible light (λ < 415 nm) but primarily absorb in the UV region (Figure 3-3). Tauc plot analysis indicated that the rutile TiO₂ nanowires exhibit a band gap of \( E_G \approx 3.0 \) eV (Figure 3-3D). Photoluminescence (PL) spectra of the TiO₂ nanowire arrays exhibit a broad peak centered at ca. 3.2 eV, indicating that PL emission primarily occurs via free carrier recombination near the band edge (Figure 3-2B). This limited sub-band PL gap emission coupled with the high crystallinity of the
TiO$_2$ nanowires further suggests a low number of surface defects and/or trap states below the TiO$_2$ CB edge.

Plasmonic-metal/semiconductor (Au/TiO$_2$) heterostructures was then constructed via photochemical deposition, which allows for physically grafting Au nanoparticles directly onto the TiO$_2$ nanowires without surfactants or chemical linkers. This method was chosen to facilitate strong electronic coupling at the metal-semiconductor interface and ensure the maximum probability for PMET in these plasmonic photoanodes. A dramatic change in the photoanode color was observed following the photodeposition of Au nanoparticles, concomitant with the emergence of a dominant spectral feature indicative of the LSPR of the Au nanoparticles (Figure 3-3). Analysis of these Au/TiO$_2$ heterostructures by SEM (Figure 3-4) and energy dispersive X-ray spectroscopy (Figure 3-5) revealed that the Au nanoparticles ($d = 20 \pm 5$ nm) were distributed along the TiO$_2$ support but were predominantly located at the terminus of each nanowire. Given the importance of the metal-semiconductor interface to the PMET mechanism,$^{56,57}$ the crystallographic orientation at the Au-TiO$_2$ heterojunction was inspected by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and high-resolution transmission electron microscopy (HRTEM). As shown in Figure 3-6, a coherent interface was established at the Au-TiO$_2$ heterojunction by the photodeposition method, confirming that this approach provides intimate physical contact between the plasmonic-metal nanostructure and the semiconductor support. PL spectra were further collected under UV excitation to demonstrate the feasibility for interfacial charge transfer across the Au-TiO$_2$ heterojunction. Indeed, Figure 3-2B shows that the PL emission is completely quenched after the photodeposition of Au nanoparticles onto the TiO$_2$
nanowires. These Au/TiO$_2$ heterostructures are therefore anticipated to constitute an ideal photoelectrochemical platform for probing the PMET process in plasmonic-metal/semiconductor photoelectrodes.

**Photoelectrochemical Studies of Au/TiO$_2$ and TiO$_2$ Photoanodes**

A suite of photoelectrochemical experiments were then performed using a three-electrode electrochemical cell consisting of a plasmonic Au/TiO$_2$ photoanode (working), Pt wire (auxiliary), and Ag/AgCl (reference) electrode immersed in a supporting electrolyte of 1.0 M NaOH (see Experimental Methods section for details). All electrode potentials ($E$) are reported relative to the reversible hydrogen electrode (RHE) through use of Equation 3-1, which represents the potential of the standard hydrogen electrode (SHE) adjusted for the pH of the supporting electrolyte.$^{113}$ The photoelectrochemical properties of the TiO$_2$-only photoanodes were first examined by linear sweep voltammetry at a scan rate of 20 mV s$^{-1}$ under dark conditions and under simulated solar irradiation (AM 1.5G at 1-sun $I_0 = 100$ mW cm$^{-2}$), as shown in Figure 3-7. The TiO$_2$ nanowire array exhibits negligible dark current ($J_{\text{dark}}$) along the potential sweep but produces significant anodic photocurrent ($J_{\text{ph}} = 0.13$ mA cm$^{-2}$) at 1.20 V$_{\text{RHE}}$ (V vs. RHE) under AM 1.5G irradiation (Figure 3-7A). The linear sweep voltammogram was repeated under periodic excitation ($t = 5$ s on/off) to confirm the $J_{\text{ph}}$ originates from light absorption by the TiO$_2$ nanowires (Figure 3-7A). The apparent flat-band potential ($E_{\text{fb}}$) of the TiO$_2$ photoanode can be estimated from the value of the “turn-on” voltage ($E_{\text{on}} = 0.15$ V$_{\text{RHE}}$), defined as the potential at which the current ($J$) changes sign from cathodic to anodic for an n-type semiconductor.$^{113}$ From the voltammogram we estimate $E_{\text{fb}} \approx 0.1$ V$_{\text{RHE}}$, similar to that previously reported for rutile TiO$_2$ nanowires.$^{38,112}$
It is noted that the band gap of rutile TiO$_2$ ($E_G \sim 3.0$ eV) technically enables the absorption of visible light (Figure 3-2C). Although essentially all of the AM 1.5G activity is derived from UV excitation ($\lambda < 400$ nm) of the TiO$_2$ nanowires, a small fraction of photoelectrochemical activity is derived from visible-light irradiation ($\lambda > 400$ nm) (Figure 3-7B, blue curve). However, it is clear that the TiO$_2$ nanowires exhibit a negligible $J_{ph}$ at $\lambda > 435$ nm (2.9 eV) compared to the dark current ($J_{dark}$) (Figure 3-7B, green curve), confirming that the nanowires do not exhibit significant visible-light activity below the band gap of rutile TiO$_2$ ($E_G \sim 3.0$ eV). These nanowires thereby serve solely as a conduit for hot electron transport under optical excitation of the Au nanoparticles ($\lambda > 495$ nm), as these photon energies are insufficient to directly excite the underlying TiO$_2$ support.

As shown in Figure 3-8A, the introduction of Au nanoparticles onto the TiO$_2$ nanowires endowed the plasmonic composite with increased $J_{ph}$ at all values along the potential sweep under simulated solar conditions. No significant change in the turn-on potential $E_{on} = 0.15$ V$_{RHE}$ was observed, suggesting a similar value of $E_{fb}$ for both photoanodes. The value of $E_{fb}$ was further estimated from the point at which the open-circuit voltage ($V_{oc}$) obtained under optical excitation plateaus with increasing incident power ($I_0$). As the $E_{fb}$ of the semiconductor enforces the limiting $V_{oc}$ that can be obtained by the photoanode under illumination, the plateau of $V_{oc}$ under increased power indicates the value of $E_{fb}$. From these data, we estimate a value of $E_{fb} = 0.11$ V$_{RHE}$ (Figure 3-8B), similar to that obtained from the value of $E_{on} = 0.15$ V$_{RHE}$ (Figure 3-8A). Chronoamperometry was further used to demonstrate the reproducibility of the plasmonic enhancement under AM 1.5G irradiation ($I_0 = 0.1$ W cm$^{-2}$) while poised at $E_{appl} = 1.20$ V$_{RHE}$ (Figure 3-8C). A reproducible $J_{ph}$ response was observed for both
devices, with the plasmonic photoanode \( J_{ph} = 116 \pm 1 \, \mu A \, cm^{-2} \) consistently above that of the control \( J_{ph} = 94 \pm 1 \, \mu A \, cm^{-2} \). The influence of incident light power \( I_0 \) on the \( J_{ph} \) response from these devices was then examined with the photoanodes potentiostatically poised at \( E_{appl} = 1.20 \, V_{RHE} \), as shown in Figure 3-8D. It is noted that the plasmonic device exhibits increased \( J_{ph} \) compared to the control, but both devices eventually plateau with increased power \( I_0 > 0.5 \, W \, cm^{-2} \). This limiting \( J_{ph} \) behavior is attributed to rapid depletion of redox species (e.g. \( OH^- \)) near the photoanode surface under an increased photon flux.\(^{114-116}\) A series of optical filters were then used to construct a photoelectrochemical action spectrum \([ J_{ph} (\lambda) ]\) to correlate the device performance with the optical properties (Figure 3-9). The direct correlation between the IPCE and the optical response of the Au nanoparticles indicates that the device enhancement occurs via the PMET mechanism.

**Photoelectrochemical Studies of PMET in Au/TiO\(_2\) Photoanodes**

Controlled potential electrolysis was used to evaluate the reproducibility of hot electron injection by interposing a 515 nm long pass filter \( (\lambda > 515 \, nm) \) between the plasmonic device and the excitation source. This approach permits the selective excitation of the Au nanoparticles while excluding any contribution from direct interband transitions within the TiO\(_2\) support (Figure 3-3 and Figure 3-7B). The plasmonic Au/TiO\(_2\) photoanode was potentiostatically poised at \( E_{appl} = 1.20 \, V_{RHE} \) and illuminated by periodic \( (t = 3 \, s \, on/off) \) visible-light excitation at an incident power of \( I_0 = 100 \, mW/cm^2 \). As shown in Figure 3-10A (blue curve), the plasmonic device exhibits a prompt and reproducible \( J_{ph} \sim 1.1 \pm 0.1 \, \mu A \, cm^{-2} \) when exposed to periodic visible-light irradiation, indicating facile charge injection within the Au/TiO\(_2\) heterostructures. In contrast, the TiO\(_2\)-only reference device produced no measureable \( J_{ph} \) above \( J_{dark} \) when irradiated.
with sub-band gap irradiation (Figure 3-10A, red curve). These results confirm that the $J_{ph}$ elicited from the plasmonic Au/TiO$_2$ device is attributable to hot electron injection via optical excitation of the Au nanoparticles. Significantly, it is noted that these plasmonic photoanodes delivered reproducible $J_{ph}$ responses over the course of the investigation (~9 months), displaying superior photoelectrochemical stability relative to narrow band gap semiconductor-based devices.

The power dependence of the PMET process was evaluated with the plasmonic photoanode poised at $E_{appl} = 1.20$ V$_{RHE}$ (Figure 3-10B). Although these results show an initially linear dependence on the incident photon flux, the $J_{ph}$ plateaus at increased light intensities ($I_0 \geq 150$ mW cm$^{-2}$). The linear dependence precludes a two-photon absorption mechanism, and the saturation behavior is attributed to rapid depletion of the redox electrolyte near the photoanode surface under increased incident power.$^{114-116}$ The influence of $E_{appl}$ on the PMET process was then investigated by taking the difference between the steady-state light and dark currents ($\Delta J_{ph} = J_{light} - J_{dark}$) for a given value of $E_{appl}$ (Figure 3-10C). Notably, a larger onset potential ($E_{on}$) was observed under visible-light excitation ($E_{on} \sim 0.7$ V$_{RHE}$) than under AM 1.5G illumination ($E_{on} \sim 0.15$ V$_{RHE}$), suggesting that greater band bending is requisite for charge injection via the PMET mechanism.$^{114}$

To further probe the energetics of these hot electrons during the PMET process, the $V_{oc}$ was monitored as a function of incident photon energy to construct a photovoltage ($V_{ph} = V_{oc,light} - V_{oc,dark}$) action spectrum [$V_{ph}(\lambda)$]. The occupancy of CB states within the semiconductor during optical excitation is given by the quasi-Fermi level ($E_F^+$) of the device, which can be monitored externally via the $V_{oc}$ of the
photoelectrochemical cell. Under open-circuit conditions, the photovoltage ($V_{ph}$) corresponds to the increase of the quasi-Fermi level under illumination ($E_{F,n^*}$) with respect to the value obtained under equilibrium conditions in the dark ($E_{F,n} = E_{F,Redox}$), as given by the following equation:

$$V_{ph} = \frac{E_{F,n}^* - E_{F,Redox}}{q} = \frac{k_B T}{q} \ln\left(\frac{n}{n_0}\right)$$

(3-2)

where $E_{F,Redox}$ corresponds to the Fermi level of the electrolyte, $k_B$ is the Boltzmann constant, $T$ is the temperature (in Kelvin), $q$ is the (unsigned) charge of an electron, $n$ is the free electron concentration under illumination and $n_0$ represents the free electron concentration in the dark. We emphasize that no increase in $E_{F}^*$ was observed for the TiO$_2$-only device when it was illuminated with visible light, consistent with the chronoamperometric results (Figure 3-10A). This lack of visible-light activity enables utilization of the $V_{ph}$ as a photoelectrochemical probe to monitor the generation of hot electrons in the plasmonic photoanode, as shown in Figure 3-10D. No significant difference in $\Delta V_{ph}$ between these photoanodes ($\Delta V_{ph}(\lambda) = (Au/TiO_2) V_{ph}(\lambda) - (TiO_2) V_{ph}(\lambda)$) was observed in the UV regime ($\lambda \leq 400$ nm) because direct excitation of the TiO$_2$ support with UV light dominates the overall $V_{ph}$ of the device. There is, however, a clear distinction assignable to the Au nanoparticle LSPR in the visible regime, with the maximum $\Delta V_{ph}$ occurring at $\sim 2.4$ eV, qualitatively corresponding to $\lambda_{max}$ of the plasmonic device (Figure 3-3C). A decline in $\Delta V_{ph}$ toward lower photon energies is observed as the hot electrons produced at longer wavelengths have less available energy to surmount the Schottky barrier ($\phi_B$). Taken together, these photoelectrochemical characteristics demonstrate that visible-light excitation induces
PMET from the Au nanoparticles to the otherwise-vacant CB states of the TiO$_2$
anowire support, enabling these plasmonic photoanodes to harvest visible light.

**Examining Hot Electron Lifetimes in Au/TiO$_2$ Photoanodes in situ**

The relaxation dynamics of the hot electrons within the TiO$_2$ CB were then
examined via the well-established open-circuit voltage decay (OCVD) method.$^{117-119}$ In
this technique, the photoelectrochemical cell is irradiated until a photostationary
condition is achieved, whereby the rates of charge accumulation and recombination
equilibrate, corresponding to the observed $V_{ph}$. The temporal profile of $V_{oc}$ is then
monitored upon termination of the excitation source, as CB electrons are scavenged by
adsorbed surface species (e.g. dissolved O$_2$) or relax via recombination with holes
trapped in the VB.$^{117-119}$ Subsequent analysis of the $V_{oc}$ transient via the OCVD
approach yields the average lifetime of the photogenerated carriers ($\tau_n$) within the
device, according to the following expression:

$$
\tau_n = - \frac{k_B T}{q} \left( \frac{dV_{oc}}{dt} \right)^{-1}
$$

(3-3)

where $\tau_n$ represents the average electron lifetime,$^{117}$ and all other variables are as
previously defined (*vide supra*). It should be recognized that this measurement
preferentially probes the slow recombination kinetics ($t \sim ms$—s) of interfacial charge
transfer processes occurring at the semiconductor/liquid junction.$^{117,118}$ Consequently,
this approach lends unique insight into the extended dynamics of long-lived surface
electrons capable of facilitating multi-electron reduction reactions, as these processes
transpire on similarly prolonged timescales.$^6$

Since irradiation of the Au/TiO$_2$ photoanode with visible light enables the
selective excitation of the Au nanoparticles, monitoring the $V_{oc}$ decay in the plasmonic
device permits an evaluation of $\tau_n$ for hot electrons within the TiO$_2$ CB in situ (i.e. under aqueous conditions). A gradual increase in $V_{oc}$ is observed upon exposure of the plasmonic device to visible light (Figure 3-11A, blue curve), indicative of PMET from the Au nanoparticles to the CB of the TiO$_2$ nanowires. As hot electrons accumulate within the TiO$_2$ CB, the $E_F^*$ of the semiconductor increases, and subsequently the $V_{oc}$ of the plasmonic photoanode shifts to more negative potentials.\textsuperscript{120} Therefore, the extended $V_{oc}$ transient ($\Delta t \sim$50 s) observed during optical excitation offers insight into the transmission probability for hot electrons at the metal-semiconductor interface. We attribute this feature to the presence of a Schottky barrier ($\varphi_B \sim$1.0 eV)$^{95,121}$ at the Au-TiO$_2$ heterojunction, which is expected to impede hot electron transmission into the TiO$_2$ CB. Despite this barrier, a steady-state condition was eventually established, at which point the excitation source was extinguished in order to monitor the relaxation dynamics of these transferred electrons. A prolonged $V_{oc}$ decay of hot electrons was then observed over the course of several minutes ($\Delta t \sim$250 s) as these carriers recombined and eventually equilibrated with $E_{F,\text{Redox}} \sim$0.84 $V_{RHE}$ (indicated by the dashed black line in Figure 3-11A).

To compare the lifetimes of the hot electrons transferred to the TiO$_2$ CB via the PMET process to those of excited-state electrons generated directly within the semiconductor, the TiO$_2$-only photoanode was illuminated with UV light under open-circuit conditions. This approach allows the PMET dynamics in the Au/TiO$_2$ device to be distinguished from the intrinsic optical transitions within the TiO$_2$ support. A substantial distribution of electron-hole pairs was generated via UV excitation of the TiO$_2$ nanowires and a significant $V_{ph}$ of $\sim$0.69 V was promptly established (Figure 3-11A, red curve).
Upon termination of the UV excitation, the $V_{oc}$ rapidly decreased ($\Delta t \sim 90$ s) back to that obtained in the dark as the CB electrons readily recombined with dissolved species in solution (i.e. $O_2$) or holes trapped in the VB.

A quantitative description of these charge carrier dynamics emerges upon analysis of the $V_{oc}$ transients via the OCVD approach. As shown in Figure 3-11B, the hot electrons transferred to the TiO$_2$ CB via PMET exhibited lifetimes that were 1-2 orders of magnitude longer ($\tau_n \sim 10^3$ s) than those of CB electrons originating within the TiO$_2$ nanowires themselves ($\tau_n \sim 10^1$ s). Moreover, the relatively short-lived distribution ($\tau_n \sim 0.1$ s), indicative of rapid recombination following UV excitation of the TiO$_2$ nanowires, was not observed for the hot electrons transferred to the TiO$_2$ CB via the PMET process. We note that the lifetimes of CB electrons within the TiO$_2$-only device are in accord with prior values obtained with the OCVD method; however, the singular nature of the prolonged $V_{oc}$ transient observed in the Au/TiO$_2$ device is unique, and implies a substantially reduced tendency for recombination following the PMET process.

It is emphasized that such an extended average lifetime for hot electrons has not been previously observed, and we speculate that this results from the significant Schottky barrier ($\varphi_B \sim 1.0$ eV) established at the metal-semiconductor interface via photochemical deposition. Although this energetic barrier ($\varphi_B$) tempers the transmission of hot electrons into the TiO$_2$ CB (as evidenced by the extended transient rise in $V_{oc}$), once the barrier has been breached, the depletion layer within the semiconductor promotes charge separation by sweeping hot electrons away from the Au-TiO$_2$ interface. Accordingly, the TiO$_2$ used in our study plays an important role in the long
lifetimes we observed via the OCVD approach. Previous dynamics studies were conducted on nanoparticle-based \((d \sim 10–25 \text{ nm})\) TiO\(_2\) films,\(^{91,99}\) which are incapable of supporting any internal field distribution and thereby preventing the creation of a depletion layer within the semiconductor.\(^{13,14}\) In contrast, our device is composed exclusively of rutile-phase TiO\(_2\) nanowires, with dimensions on the \(\sim 0.2–1 \mu\text{m}\) scale, which should be sufficient to support a depletion layer within the nanowires.\(^7,13,32\)

Therefore, the size and composition of the semiconductor support used in our investigation should facilitate the formation of a Schottky barrier \((\phi_B)\) and concomitant space-charge layer, which serves to drive these hot electrons away from the Au-TiO\(_2\) interface after PMET. Recombination is further suppressed by the absence of unoccupied states within the TiO\(_2\) VB \(\text{(i.e. holes)}\) under visible-light irradiation. This deficiency of vacant VB states constrains the number of relaxation channels available to these transferred electrons, effectively prolonging the charge-separated state, since the only accessible recombination pathway requires traversing back through the depletion layer to cross the interface. In contrast, the direct excitation of the TiO\(_2\) nanowires with UV irradiation generates CB electrons that are not physically separate from VB holes, encouraging geminate recombination upon termination of the light source. Thus, the salient feature of the PMET process involves the spatial isolation of the hot electrons in the TiO\(_2\) CB from the holes left behind on the Au nanoparticles.

**Extended Discussion of the Open-Circuit Voltage Decay (OCVD) Method**

It is important to clarify the nature of the charge carriers probed in the OCVD technique, as this methodology has clear distinctions with respect to other dynamic techniques, such as ultrafast transient absorption spectroscopy.\(^{91,118}\) The OCVD measurement simultaneously samples from the entire distribution of both free and
trapped electrons as the Fermi level moves through the exponential distribution of states within the band gap of the semiconductor.\textsuperscript{118} Therefore, this technique does not allow for separating the individual contributions from both free (CB states) and trapped (bulk/surface defect states) electrons to the observed excited-state lifetime. It should be noted, however, that as the Fermi level in the semiconductor decreases, the proportion of electrons in free and trapped states changes, such that the initial $V_{oc}$ timescales correspond to a greater contribution from free electrons in CB states, while later $V_{oc}$ timescales contain a greater contribution from bulk/surface trap states.\textsuperscript{5} The utility of the OCVD technique arises from the ability to monitor the entire distribution of both free and trapped carriers while the device is immersed in aqueous solution. This provides unprecedented insight into the dynamics of these long-lived excited-state electrons that are capable of participating in chemical reactions with adsorbed surface species.

Although trap states also contribute to the overall lifetimes being measured,\textsuperscript{117,118} we do not expect the difference in electron lifetime between the TiO$_2$-only and the Au/TiO$_2$ devices to be a consequence of trap-mediated recombination for a number of reasons. First, previous reports have demonstrated that these highly-oriented rutile TiO$_2$ nanowire arrays possess a substantially-reduced number of defects compared to nanoparticle-based films.\textsuperscript{13,32,82} The monocrystalline nature of the rutile TiO$_2$ nanowires used in this study imply a relatively low number of defects exist in the bulk of the semiconductor (Figure 3-2A). Secondly, PL measurements indicate very few trap states below the TiO$_2$ CB edge (Figure 3-2B). We therefore suspect that bulk traps play a minimal role in the electron trapping processes, leaving surface defects as the likely source of available trap states.\textsuperscript{8} However, if surface traps were responsible for the
prolonged average lifetimes observed in the Au/TiO₂ device under visible light, we would expect similarly prolonged lifetimes in the TiO₂-only device following UV light irradiation. Such a feature was not observed. Although surface traps are inevitable in both TiO₂-only and Au/TiO₂ devices, we actually anticipate a lower number of surface defects in the plasmonic device; photochemical deposition of the Au nanoparticles directly onto the semiconductor surface is likely to preferentially passivate these surface defects, as they constitute photocatalytic active sites where excited-state electrons exist for prolonged periods. Therefore, the Au/TiO₂ device is expected to exhibit a reduced number of surface traps than the TiO₂-only device, making it unlikely that surface traps and bulk trap states are responsible for the substantial difference in excited-state lifetime observed between these two systems. We therefore conclude that the Schottky barrier is responsible for reducing the recombination probability and extending the excited-state lifetime of these hot electrons in our Au/TiO₂ system following PMET. Indeed, recent studies of hot electron lifetimes within the TiO₂ CB via X-ray absorption spectroscopy support our conclusion, as long-lived hot electrons were observed on Ti states highly-localized near semiconductor surface. These studies further demonstrating the merits of using plasmonic-metal/semiconductor heterojunctions to prolong the hot electron lifetime within the semiconductor support.

**Influence of Hole Scavenger on PMET in Au/TiO₂**

Although it has been demonstrated that the oxidation of water is feasible with Au/TiO₂ heterostructures under visible-light excitation, the considerable thermodynamic challenges associated with oxidizing water require additional modification with OER catalysts to efficiently drive overall water splitting. To alleviate these kinetic constraints from the PMET process, we studied the photoelectrochemical properties of
the plasmonic photoanodes in an electrolyte composed of 10% methanol (v/v %) as a hole scavenger in 1.0 M NaOH solution. The influence of $E_{\text{appl}}$ on the PMET process in the presence of methanol was investigated by taking the difference between the steady-state light and dark currents ($\Delta J_{\text{ph}} = J_{\text{light}} - J_{\text{dark}}$) for a given value of $E_{\text{appl}}$. As shown by the voltammogram in Figure 3-12A, the introduction of the hole scavenger induces two noticeable changes in the photoelectrochemical response of the system. First, the addition of methanol leads to a substantial increase (~4 times) in the $J_{\text{ph}}$ across the entire potential window (Figure 3-12A, red points) compared to the pure NaOH electrolyte (Figure 3-12A, blue points). Secondly, the value of $E_{\text{on}}$ is shifted by ca. 250 mV to more negative potentials ($E_{\text{on}} = 0.45 \text{ V}_{\text{RHE}}$). Such substantial improvements in photoelectrochemical performance accompanied by the introduction of a hole scavenger indicate the limited oxidation ability of the hot holes generated in the Au nanoparticles. By alleviating the kinetic and thermodynamic barriers to hot hole transfer from the Au nanoparticles to solution, the PMET process from Au to TiO$_2$ is markedly improved. As the Fermi level of Au ($E_F \sim 0.5 \text{ V}_{\text{RHE}}$) is thermodynamically capable of oxidizing water under alkaline conditions [$E^0(\text{O}_2/\text{H}_2\text{O}) = 0.43 \text{ V}_{\text{RHE}}$ at pH 13.6], it is likely that this limited oxidation ability primarily stems from the daunting kinetic barriers associated with the OER.

Controlled potential electrolysis was used to further evaluate the reproducibility of the $J_{\text{ph}}$ response in the presence of methanol. The plasmonic Au/TiO$_2$ photoanode was potentiostatically poised at $E_{\text{appl}} = 1.20 \text{ V}_{\text{RHE}}$ (V vs. RHE) and illuminated by periodic ($t = 3 \text{ s on/off}$) visible-light excitation at an incident power of 1 sun ($I_0 = 100 \text{ mW cm}^{-2}$). As shown in Figure 3-12B, the plasmonic device exhibits a prompt and reproducible $J_{\text{ph}} = \ldots$
4.0 ± 0.1 μA cm$^{-2}$ when exposed to periodic visible-light irradiation in the presence of the hole scavenger methanol, which represents a 4-fold device enhancement in comparison to that obtained in the absence of a hole scavenger ($J_{ph} = 1.1 ± 0.1 \mu A cm^{-2}$). Power-dependent photocurrent measurements $J_{ph}(I_0)$ further show that the plasmonic photoanode delivers marked improvements in $J_{ph}$ upon the addition of methanol to the system at all incident powers before eventually plateauing at ca. $I_0 > 0.5 W cm^{-2}$ (Figure 3-12C). These results further support that hot hole transfer to solution limits PMET from Au to TiO$_2$ in the 0.1 M NaOH electrolyte.

The photovoltage action spectrum $\Delta V_{ph}(\lambda)$ obtained from these plasmonic photoanodes shows that the overall $V_{ph}$ is improved with the addition of methanol to the electrolyte (Figure 3-12D), indicating that more hot electrons accumulate within the TiO$_2$ CB in the presence of a hole scavenger capable of quickly quenching the charge vacancies left behind on the Au nanoparticles. Notably, the action spectrum shows a significant enhancement in $V_{ph}$ at lower photon energies (red points) as compared to the pure NaOH electrolyte (Figure 3-12D, blue points). The increased $J_{ph}$ at reduced photon energy ($\lambda > 610$ nm) indicates that a greater proportion of hot electrons are capable of transferring to the TiO$_2$ CB and contributing to the $V_{ph}$ in the presence of the hole scavenger methanol.

The influence of the hole scavenger methanol on the hot electron lifetime was then studied by examining the dynamics of the $V_{oc}$ transients, as shown in Figure 3-13. There are several notable exceptions from the dynamics observed in the absence of methanol. First, the extended transient rise observed under visible-light excitation ($\lambda > 515$ nm) in the pure NaOH electrolyte (Figure 3-13A, blue curve) was not observed
upon the addition of methanol (Figure 3-13A, red curve), indicating that the hot electron accumulation within the TiO$_2$ CB occurs much more rapidly in the presence of a hole scavenger. Secondly, the overall $V_{ph}$ obtained with the addition of methanol is ca. 2 times greater than that observed in the pure NaOH electrolyte (Figure 3-13A). These two differences further indicate that the PMET process is substantially improved if the hot holes left behind on the Au nanoparticles can be readily quenched to reduce the recombination probability. Upon termination of the light source, a transient decay was observed over a similarly prolonged period as observed in the pure NaOH electrolyte ($\Delta t \sim 300$ s). However, the $V_{oc}$ declines much more rapidly at the initial point at which the irradiation is ceased ($t = 200—230$ s) before slowing to a similar decay rate observed in the absence of methanol ($t > 230$ s). Analysis of this transient by the OCV technique shows that the hot electrons transferred to the TiO$_2$ CB via PMET exhibited similarly prolonged lifetimes ($\tau_n \sim 10^3$ s) as that observed in the pure NaOH electrolyte (Figure 3-13B). Notably, however, a relatively short-lived distribution ($\tau_n \sim 0.1$ s) was observed in the presence of methanol that was not observed in the pure NaOH electrolyte (Figure 3-13B, red curve). Such a result indicates that the recombination rate of hot electrons in the TiO$_2$ CB with Au nanoparticles is dependent on the relative energy difference between the quasi-Fermi level of the hot electrons in the semiconductor CB ($E_{F}^{*}$) and the Fermi level of the plasmonic-metal nanostructure ($E_F$). As more hot electrons accumulate within the semiconductor CB, the extent of band bending within the semiconductor is diminished. The internal fields within the semiconductor that help to sweep hot electrons away from the interface are reduced accordingly. Thus, the extent to which hot electrons accumulate within the TiO$_2$ CB strongly affects their
recombination dynamics across the metal-semiconductor heterojunction. Taken together, these additional photoelectrochemical studies in the presence of methanol demonstrate that hot hole transfer from the Au nanoparticles to solution limits the PMET process in Au/TiO$_2$ photoanodes. As such, these results illustrate the importance of maximizing the efficiency of both water reduction and oxidation to achieve an efficient plasmon-driven photocatalytic system for solar water splitting.

**Harvesting Hot Electrons for Visible-Light-Driven H$_2$ Production**

The PMET mechanism offers intriguing possibilities from a photocatalytic perspective, as this process procures a steady source of charge carriers with excited-state lifetimes commensurate with the extended timescales required to catalyze inherently sluggish, multi-electron reactions (e.g. water splitting). Accordingly, we envisioned that a strategy based on the PMET mechanism should enable these plasmonic photoanodes to perform concerted redox reactions if these hot electrons could be appropriately harnessed to drive a photocatalytic process. Since long-lived photoexcited electrons are vital to water-splitting photochemistry,$^{17-19}$ we evaluated the photocatalytic activity of these plasmonic devices for visible-light-mediated ($\lambda > 515$ nm) H$_2$ evolution from water while potentiostatically poised at $E_{appl} = 1.20$ V$_{RHE}$ (see Experimental Methods section for details). Photoelectrochemical experiments confirm that these hot electrons are catalytically suitable for water reduction, facilitating H$_2$ evolution at a rate of $0.9 \pm 0.1 \mu$mol H$_2$ cm$^{-2}$ h$^{-1}$ in the presence of methanol as a sacrificial reagent (Figure 3-14A). The plasmonic photoanodes were also found to exhibit excellent photoelectrochemical stability when subjected to repeated 5 h photocatalytic cycling experiments on 4 consecutive days, as shown in Figure 3-14B.
Such robust H\textsubscript{2} production over $t > 24$ h indicates the long-term viability of these plasmonic photoelectrochemical cells for solar energy conversion.

It should be noted that water reduction with rutile TiO\textsubscript{2} requires an external bias to proceed since the CB of rutile TiO\textsubscript{2} resides at a slightly positive potential compared to that of the H\textsuperscript{+/H\textsubscript{2}} redox couple.\textsuperscript{4} However, under identical experimental conditions in the dark ($E_{\text{appl}} = 1.20$ V\textsubscript{RHE}), no H\textsubscript{2} was detected from the plasmonic Au/TiO\textsubscript{2} photoanode after 5 h, confirming that the applied bias alone is insufficient to evolve H\textsubscript{2} from this system in the dark (Figure 3-15A). Visible-light excitation ($\lambda > 515$ nm) of the TiO\textsubscript{2}-only photoanode also fails to produce H\textsubscript{2} under otherwise identical experimental conditions ($E_{\text{appl}} = 1.20$ V\textsubscript{RHE} and $I_0 = 3.0 \pm 0.2$ W cm\textsuperscript{-2}), confirming the role of the Au nanoparticles in the photocatalytic process (Figure 3-15B). These studies demonstrate the singular characteristics of hot electrons for promoting visible-light-driven photocatalytic reactions. It is anticipated that the PMET mechanism employed herein can be applied to various solar-driven redox processes, providing new opportunities for solar photochemistry.

**Summary of Results**

In summary, we have demonstrated the utility of photoelectrochemical techniques for probing hot electron dynamics in Au/TiO\textsubscript{2} heterostructures within a plasmonic photoelectrochemical cell under simulated solar conditions (aqueous solution, diffuse low-power light). The incorporation of Au nanoparticles imparts significant visible-light activity to the plasmonic photoanode, unambiguously confirming the existence of PMET in these plasmonic Au/TiO\textsubscript{2} heterostructures. Moreover, we discovered that the lifetimes of the hot electrons transferred to the TiO\textsubscript{2} CB are 1-2 orders of magnitude longer than those of CB electrons generated directly within the semiconductor support via UV excitation. Such marked differences are attributed to the
presence of the Schottky barrier established at the metal-semiconductor interface, which impedes charge carrier recombination and prolongs the excited-state lifetimes of the hot electrons after they are transferred to the TiO$_2$ CB. We further demonstrate that these long-lived photogenerated electrons can be harnessed to promote visible-light-driven H$_2$ evolution from water in the presence of a sacrificial reagent. These results highlight the merits of the PMET strategy for substantially extending the excited-state lifetimes of charge carriers within photoelectrochemical devices, while simultaneously sensitizing the semiconductor scaffold to sub-band gap light. We anticipate improved photocatalytic efficiencies for a variety of kinetically hindered chemical reactions if plasmonic metal-semiconductor heterostructures can be appropriately engineered to exploit the PMET process.
Figure 3-1. Physical characterization of TiO$_2$ nanowire arrays on FTO substrates. A) Digital image showing the white color of the TiO$_2$ nanowires. B) Low-magnification SEM image displaying the highly oriented arrangement of the nanowires on the FTO glass substrate. C) High-magnification SEM image of the TiO$_2$ nanowire array. D) Cross-sectional view of the TiO$_2$ nanowire array showing the height of the nanowires. E) Cross-sectional view of the TiO$_2$ nanowire array showing the height of the nanowires. F) Cross-sectional view of the TiO$_2$ nanowire array showing the height of the nanowires. Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
Figure 3-2. Structural and optical characterization of TiO$_2$ and Au/TiO$_2$ nanowire arrays on FTO substrates. A) X-ray diffraction pattern of Au/TiO$_2$ (blue), TiO$_2$ (red) and the bare FTO glass substrate (black) shown for reference. The diffraction peaks indicative of rutile TiO$_2$ are labeled and the rest are due to the FTO substrate, as indicated by an asterisk (*). B) Photoluminescence (PL) spectra of Au/TiO$_2$ (blue) and TiO$_2$ (red) photoanodes under 325 nm laser excitation at 0.6 mW showing that PL emission primarily occurs near the band edge ($E_G$ ~3.2 eV). With the addition of Au nanoparticles the PL signal is completely quenched, indicating facile charge transfer between Au and TiO$_2$ as a consequence of the direct physical contact established at the interface by the photodeposition method. Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
Figure 3-3. Optical properties of TiO$_2$ and Au/TiO$_2$ photoanodes. A) Digital photograph of TiO$_2$-only photoanode showing white color of TiO$_2$. B) Digital photograph of plasmonic Au/TiO$_2$ photoanode showing the purple color of the device following photochemical deposition of Au nanoparticles. C) Absorbance spectra (Kubelka-Munk) of TiO$_2$-only (red) and plasmonic Au/TiO$_2$ (blue) devices obtained by diffuse-reflectance spectroscopy showing optical properties throughout the UV-visible spectrum ($\lambda = 350$—750 nm). These spectra show a strong peak in the UV-blue region ($\lambda < 410$ nm) for both devices due to the band gap excitation of the TiO$_2$ nanowire support; however, the Au-TiO$_2$ device (blue) exhibits a new feature in the visible part of the spectrum with a peak maximum at $\lambda = 562$ nm due to the LSPR of the Au nanoparticles. D) Tauc plot of the TiO$_2$-only device to confirm the band gap of the rutile TiO$_2$ nanowires is ca. $E_g \approx 3.0$ eV. Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
Figure 3-4. Physical characterization of plasmonic Au/TiO$_2$ nanowire arrays on FTO substrates. A) Digital image of Au/TiO$_2$ nanowire array showing purple color indicative of Au nanoparticles. B) Low-magnification SEM image displaying the distribution of Au nanoparticles on the TiO$_2$ nanowires. C) High-magnification SEM image of the TiO$_2$ nanowire array showing the distribution of Au nanoparticles. D) SEM image of cross-sectional view of the TiO$_2$ nanowire array showing the height of the nanowires. E) SEM image of cross-sectional view of the TiO$_2$ nanowire array showing the distribution of Au nanoparticles along the length of the nanowires. F) SEM image of cross-sectional view of the TiO$_2$ nanowire array showing the distribution of Au nanoparticles along the length of the nanowires. Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
Figure 3-5. Elemental mapping of Au/TiO₂ heterostructures. A) HAADF-STEM image of the Au-TiO₂ heterojunction showing the mapped region. B) Energy dispersive X-ray spectroscopy (EDS) map indicating the presence of elemental gold, Au (red). C) EDS map indicating the presence of elemental oxygen, O (blue). D) EDS map indicating the presence of elemental titanium, Ti (green). Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
Figure 3-6. Structural analysis of the Au-TiO$_2$ interface of a typical plasmonic photoanode. A) HAADF-STEM image of a single Au-TiO$_2$ heterojunction demonstrating epitaxial relationship at the metal-semiconductor interface. B) HAADF-STEM image of a single Au-TiO$_2$ heterojunction showing direct physical contact at the interface. C) HAADF-STEM image of a single Au-TiO$_2$ heterojunction showing significant interfacial contact area between materials. D) HRTEM image of a single Au-TiO$_2$ heterojunction. Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
Figure 3-7. Linear sweep voltammetry and action spectra of TiO₂ photoanode. Linear sweep voltammetry (LSV) of the TiO₂-only photoanode under different excitation conditions. All LSVs were acquired at a scan rate of 20 mV/s with an incident power of 1-sun (100 mW/cm²). A) LSV under chopped AM 1.5G illumination at 1-sun power (red) and in the dark (black). From the LSV curve, the value of the apparent flat-band potential (Eₖb) can be estimated from the value of the turn-on voltage (Eₜₕₐₜₖ), which is Eₖb ≈ Eₜₕₐₜₖ = 0.15 V_RHE under AM 1.5G illumination. B) LSV action spectrum of the TiO₂-only photoanode under various excitation conditions with different short pass and long pass filters. A cursory inspection of these two plots reveals that essentially all of the AM 1.5G activity is derived from UV (λ < 400 nm) excitation of the TiO₂ nanowires, whereas only limited activity is observed under visible (λ > 400 nm) light. Moreover, it is clear that the TiO₂ nanowires exhibit a negligible J_ph at λ > 435 nm (2.9 eV) compared to the dark current (J_dark), confirming that the TiO₂ nanowires do not exhibit significant visible-light activity below the band gap. This is consistent with the band gap for rutile TiO₂ (E_G ~3.0 eV), which implies that only λ < 418 nm should be capable of exciting the TiO₂ nanowires. Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
Figure 3-8. Photoelectrochemical properties of control TiO\textsubscript{2}-only (red) and plasmonic Au/TiO\textsubscript{2} (blue) photoanodes. A) Linear sweep voltammograms (20 mV s\textsuperscript{-1}) of control and plasmonic photoanodes under periodic AM 1.5G irradiation. A turn-on voltage ($E_{on}$) of 0.15 V\textsubscript{RHE} was observed for both devices. B) Influence of light intensity ($I_0$) on the open-circuit voltage ($V_{oc}$) of photoanodes; the plateau indicates a flat-band potential ($E_{fb}$) of ca. 0.11 V\textsubscript{RHE} for both devices. C) Chronoamperometry [$J_{ph}(t)$] recorded during periodic (t = 3 s on/off) AM 1.5G excitation. D) Influence of incident light power ($I_0$) on photocurrent ($J_{ph}$) while poised at $E_{appl} = 1.20$ V\textsubscript{RHE}. All errors bars represent standard deviation.
Figure 3-9. Photoelectrochemical action spectrum $J_{\text{ph}}(\lambda)$ of TiO$_2$-only (red) and plasmonic Au/TiO$_2$ (blue) photoanodes. A series of band pass filters (from 420—720 nm with $\Delta\lambda = 20 \pm 10$ nm) were used to assess the influence of incident light wavelength on these photoanodes. It is clear from these data that the Au/TiO$_2$ device exhibits a marked enhancement in visible-light collection at wavelengths commensurate with the LSPR of the Au nanoparticles. All errors bars represent standard deviation.
Figure 3-10. Photoelectrochemical study of PMET in Au/TiO₂ photoanodes. A) Chronoamperometric response [J_{ph}(t)] recorded during periodic visible-light excitation demonstrating (PMET) in the plasmonic device (blue) but no response from TiO₂ (red). B) Influence of incident light power [J_{ph}(I₀)] on PMET. C) Influence of applied bias [ΔJ_{ph}(E_{appl})] on PMET. D) Photovoltage action spectrum difference [ΔV_{ph}(λ)] between the plasmonic (Au/TiO₂) and control (TiO₂-only) photoanodes. All error bars represent standard deviation. Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
Figure 3-11. Comparison of excited-state lifetimes between the TiO$_2$-only (red) and the plasmonic Au/TiO$_2$ photoanode (blue) following exposure to UV ($\lambda < 400$ nm) or visible-light ($\lambda > 515$ nm) excitation, respectively. A) Chronopotentiometry $[V_{oc}(t)]$ profile obtained during excitation/termination of irradiation. The dashed black line represents the $V_{oc}$ baseline obtained in the dark ($E_{F,\text{Redox}}$). B) Average carrier lifetime ($\tau_n$) within the photoanode as determined by the open-circuit voltage decay (OCVD) method. Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
Figure 3-12. Photoelectrochemical properties of plasmonic Au/TiO$_2$ photoanodes in the presence (red) or absence (blue) of methanol. A) Influence of applied bias ($E_{\text{appl}}$) on device photocurrent ($J_{\text{ph}}$). B) Controlled potential electrolysis during periodic visible-light excitation demonstrating PMET. C) Influence of incident light power [$J_{\text{ph}}(I_0)$] on PMET. C) Influence of applied bias [$\Delta J_{\text{ph}}(E_{\text{appl}})$] on PMET. D) Photovoltage action spectrum difference [$\Delta V_{\text{ph}}(\lambda)$] between the plasmonic (Au/TiO$_2$) photoanodes in the presence (red) or absence (blue) of methanol as a hole scavenger. All error bars represent standard deviation.
Figure 3-13. Comparison of excited-state lifetimes within the Au/TiO₂ device in the presence (red) and absence (blue) of the hole scavenger methanol (MeOH) following exposure to visible-light (λ > 515 nm) excitation. A) Chronopotentiometry [V_{oc}(t)] profile obtained during excitation/termination of irradiation. The dashed black line represents the V_{oc} baseline obtained in the dark (E_{F,Redox}). B) Average carrier lifetime (τ_n) within the photoanodes as determined by the open-circuit voltage decay (OCVD) method.
Figure 3-14. Plasmon-driven H₂ production from plasmonic Au/TiO₂ photoanode under visible-light illumination in the presence of methanol as a sacrificial reagent. A) Average H₂ production over time under visible-light excitation (λ > 515 nm) at an incident power of 3.0 ± 0.2 W cm⁻² for 5 h while the photoanode was poised at $E_{\text{appl}} = 1.20$ V_RHE. The dashed line represents a linear fit to the experimental data ($R^2 = 0.992$) in order to determine the rate ($k$) of H₂ evolution. B) Photocatalytic cycling experiments for H₂ evolution demonstrating the photoelectrochemical stability of the plasmonic photoanode. Vertical dashed lines represent the point at which the experiment was terminated (after 5 h) and subsequently repeated the following day. Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
Figure 3-15. Photocatalytic H\(_2\) evolution control experiments. A) The influence of applied bias (\(E_{\text{appl}}\)) on the H\(_2\) evolution activity. The plasmonic device does not evolve H\(_2\) from water in the dark, demonstrating that the applied bias alone is insufficient to accomplish the overall water-splitting process. Only when the LSPR of the Au nanoparticles is excited with visible light (\(\lambda > 515\) nm) can H\(_2\) be produced from the Au/TiO\(_2\) device. B) Photocatalytic activity of the plasmonic Au/TiO\(_2\) photoanode (blue) compared to the TiO\(_2\)-only control photoanode (red) under visible-light (\(\lambda > 515\) nm) excitation at 3.0 ± 0.2 W cm\(^{-2}\) for 5 h while the photoanode was poised at \(E_{\text{appl}} = 1.20\) V\(_{\text{RHE}}\). These results demonstrate that the plasmonic Au nanoparticles are required for H\(_2\) gas evolution under visible-light irradiation. Adapted with permission from DuChene et al. Copyright 2014 Angewandte Chemie International Edition.
CHAPTER 4
SPECTROSCOPIC STUDIES OF PMET IN PLASMONIC-METAL/SEMICONDUCTOR HETEROSTRUCTURES

Photoelectrochemical techniques allow for evaluating the energetics of the PMET process and for probing the dynamics of hot electrons within the TiO\textsubscript{2} CB after PMET occurs, but are incapable of identifying the structural sites within the semiconductor support where hot electrons reside. Knowledge of the catalytically active sites involved in the PMET process is required to establish the structure-function relationships necessary for the eventual realization of efficient plasmonic photocatalysts.\textsuperscript{60-62} While the initial photophysics (\(t \sim \text{fs} - \text{ps}\)) of PMET from a plasmonic metal to an n-type semiconductor support (e.g. Au/TiO\textsubscript{2}) have been approached via ultrafast transient absorption spectroscopy,\textsuperscript{91,92} relatively little is known about the ensuing electronic landscape eventually established (\(t \sim \text{s} - \text{min}\)) on plasmonic photocatalysts under steady-state reaction conditions \textit{in operando} (i.e. low-power, continuous-wave irradiation).\textsuperscript{60,124} As the charge density distribution at the surface of metal-semiconductor heterostructures exerts a profound influence on their catalytic activity,\textsuperscript{125} more precise knowledge of the temporal evolution and subsequent spatial distribution of these hot carriers over timescales commensurate with catalysis (\(t \sim \text{ms} - \text{min}\)) is critical to the eventual implementation of plasmonic photocatalysts for solar energy conversion.

Here, \textit{in situ} electron paramagnetic resonance (EPR) spectroscopy was employed to follow the fate of hot electrons transferred to TiO\textsubscript{2} via the PMET process and identify the structural sites within the semiconductor support where hot electrons reside after PMET occurs. EPR spectroscopy is uniquely suited to elucidate the mechanics of the interfacial electron transfer process in plasmonic photocatalysts as the EPR signals obtained from photoexcited carriers exhibit distinct spectroscopic
signatures indicative of their local electronic environment.\textsuperscript{126-137} EPR spectroscopy works by the same principles governing any other type of spectroscopy: photon-mediated transitions occur between spin states in a paramagnetic species when resonance is achieved between the splitting of spin levels induced by the applied magnetic field ($B_0$) and the energy of the incident electromagnetic wave ($\hbar\omega$).\textsuperscript{126} The low frequency of electromagnetic radiation required for EPR experiments (i.e. microwaves) naturally lends itself to the study of semiconductor photochemistry, as irradiation with high-frequency light (UV or visible) is feasible without causing interference with the microwave source.\textsuperscript{127} Indeed, EPR has proven to constitute a powerful tool for studying photochemistry in colloidal semiconductor photocatalysts (e.g. TiO$_2$)\textsuperscript{127-131} and has recently been applied to the study of plasmonic photocatalysts (e.g. Cu/TiO$_2$, Au/TiO$_2$).\textsuperscript{132-137} Furthermore, as EPR signals originate from hot carrier distributions established on plasmonic photocatalysts under steady-state conditions ($t \sim \text{min}$), these spectroscopic studies elucidate the ensuing charge density distribution eventually established on plasmonic photocatalysts under reaction conditions. As such, the timescale of these measurements are commensurate with the multi-step reactions requisite for catalysis ($t \sim \text{ms—s}$), lending unprecedented insight into the mechanics of plasmon-driven charge separation under steady-state conditions relevant to photocatalytic systems. Comparison with another system that prevents PMET (i.e. Au/SiO$_2$) illustrates the critical role of interfacial electronic structure in sustaining plasmon-driven charge separation over prolonged periods to enable catalysis. Taken together, these studies offer new insight into the design of plasmonic-metal/semiconductor heterostructures for photocatalytic applications.
Experimental Methods

Materials

Commercial (P25) titanium dioxide (TiO$_2$) nanoparticle supports were obtained from Degussa. These nanoparticles are ca. 25 nm in diameter and composed of a mixed phase of ~25% rutile and 75% anatase. Tetrachloroauric acid (HAuCl$_4$), methanol (MeOH), ammonium hydroxide (28% NH$_3$ in H$_2$O), and the SiO$_2$ supports (100-200 mesh silica gel) were purchased from Sigma Aldrich (St. Louis, MO). All chemicals were used as received without further purification. All glassware was cleaned with aqua regia solution, followed by copious rinsing with Nanopure™ H$_2$O (Barnstead, 18.2 MΩ cm) prior to use. Caution! Aqua regia is highly corrosive/toxic. Handle with care and use appropriate personal protection equipment.

Synthesis of Au/TiO$_2$ and Au/SiO$_2$ Heterostructures

Plasmonic-metal/semiconductor (Au/TiO$_2$) heterostructures were synthesized according to a deposition-precipitation method (DP) commonly employed in the literature to prepare Au/TiO$_2$ heterostructures. Briefly, 1 g of TiO$_2$ powder (P25, Degussa) was added to 100 mL of Nanopure™ H$_2$O in a 250 mL round-bottom flask and quickly sonicated (~30 s) to disperse the TiO$_2$ powder. An aliquot of 25 mM HAuCl$_4$ was then added to prepare 1 wt.% Au on P25 supports or 5 wt.% Au on P25 supports. The aqueous solution of HAuCl$_4$ and P25 were then placed in an oil bath heated to 323 K and stirred vigorously for 30 min. An appropriate amount (~1 mL) of ammonium hydroxide solution (10% NH$_3$ in H$_2$O) was added drop-wise to adjust the pH of the system to pH 9. The solution was stirred at 323 K for another 2 h, after which time it was removed from the oil bath and allowed to cool. The solid was collected by centrifugation at 10,000 RPM for 10 min, washed with Nanopure™ H$_2$O three times, and dried.
overnight for 12 h at 323 K. The powder was then calcined at 473 K for 4 h the next day. The sample was stored in a glass vial for future use. For a comparison photocatalyst, we also used the same DP method outlined above to deposit 5 wt.% Au onto SiO₂ supports (100-200 mesh silica gel, Aldrich), which is labeled as Au/SiO₂.

Materials Characterization

Ultraviolet–Visible (UV–Vis) extinction spectrum of the Au/TiO₂ photocatalyst was measured using a Shimadzu UV-2600 spectrophotometer with diffuse reflectance integrating sphere accessory. Transmission electron microscopy (TEM) was operated at 200 kV on a JEOL 200CX TEM, which is located at the Major Analytical Instrumentation Center (MAIC) at the University of Florida (UF). Medium-angle annular dark field scanning transmission electron microscopy (MAADF-STEM) imaging was conducted on a Cs-corrected Hitachi HD-2700C equipped with a cold-field emission electron gun located at Brookhaven National Lab, Upton, NY. The microscope was operated at 200 kV with a probe convergence semi-angle of 23 mrad. The contrast of the MAADF image, acquired by an annular dark-field detector with collection angles of 53-260 mrad, is primarily sensitive to atomic number and sample thickness. The oxidation states of the Au nanoparticles were characterized by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II). In XPS experiments, the system uses a focused monochromatic Al Kα X-ray (1486.6 eV) excitation source and a spherical section analyzer. Adventitious carbon was used as a binding energy reference at 284.8 eV to correct for any specimen charging effect. A 50 W X-ray beam was focused to a 200 μm diameter area on the sample. The X-ray beam is incident normal to the sample and the photoelectron detector is at 45° off-normal.
**EPR Spectroscopy Studies of Photocatalysts**

EPR experiments were performed on a Bruker ELEXSYS E580 CW/pulsed or a Bruker ELEXSYS-II E500 CW X-band spectrometer equipped with a super high-Q cavity (ER 4123SHQE), and an ESR900 Oxford Instruments helium flow cryostat for low temperature experiments. All spectra were collected with the following instrumental parameters: 100 kHz modulation frequency, 3 G modulation amplitude, 41.96 ms conversion time, 6.325 or 20 mW microwave power, and 60 dB receiver gain. A small amount of photocatalyst sample (~25—50 mg) was loaded into a glass capillary tube and placed in the cavity of the resonator. In most experiments the sample was under atmospheric conditions, but experiments were also conducted under inert atmosphere for comparison. Optical excitation of the sample was performed with an ozone-free 300 W Xe lamp (Newport Corp.) equipped with a long pass filter (λ_{inc} > 495 nm) or a UV dichroic mirror (λ_{inc} = 280—400 nm) through the optical port of the resonator. The power incident upon the sample surface was I_0 = 350 ± 50 mW cm^{-2}. Simulated spectra were generated in collaboration with U. Twahir using the EasySpin toolbox in MATLAB.

**Results and Discussion**

**Physical Morphology and Optical Properties of Photocatalysts**

Plasmonic-metal/semiconductor (Au/TiO_2) heterostructures were constructed via a deposition-precipitation (DP) method to load Au nanoparticles (5 wt.% Au) onto TiO_2 nanoparticle supports (Degussa P25). Inspection of these heterostructures with medium-angle annular dark-field scanning transmission electron microscopy (MAADF-STEM) reveals that the Au nanoparticles are well dispersed on the TiO_2 support and exhibit an average diameter (d) of 4.4 ± 1.0 nm, as shown in Figure 4-1A and B. Analysis of the Au nanoparticle oxidation state by X-ray photoelectron spectroscopy
(XPS) indicated that these nanoparticles exclusively consist of metallic \( \text{Au}^{(0)} \) (Figure 4-2). It is noted, however, that these \( \text{Au} \) nanoparticles exhibit binding energies consistent with a partial-negative surface charge (\( \text{Au}^{x-} \)), indicative of charge transfer from the underlying \( \text{TiO}_2 \) support to the \( \text{Au} \) nanoparticles. This partial-negative character suggests that an interfacial Schottky barrier (\( \varphi_B \)) is established at the \( \text{Au}-\text{TiO}_2 \) heterojunction by the DP method. As the PMET process requires intimate physical contact between the plasmonic-metal and the semiconductor support, this synthetic approach was used to ensure direct physical contact at the \( \text{Au}-\text{TiO}_2 \) interface without intervening chemical linkers or surfactants. Indeed, high-resolution transmission electron microscopy (HRTEM) demonstrates that a direct interface was formed at the \( \text{Au}-\text{TiO}_2 \) heterojunction via the DP method (Figure 4-1C and D). Intimate physical contact between components is further anticipated to establish an interfacial Schottky barrier (\( \varphi_B \approx 1.0 \text{ eV} \))\textsuperscript{95,121} at the \( \text{Au}-\text{TiO}_2 \) heterojunction that is critical for providing a pathway to physically separate hot electrons across the interface via PMET. A dramatic change in color from white to dark purple was observed upon addition of the plasmonic \( \text{Au} \) nanoparticles onto the \( \text{TiO}_2 \) support (Figure 4-3, inset). The optical properties of these \( \text{Au}/\text{TiO}_2 \) heterostructures along with the bare P25 \( \text{TiO}_2 \) support were then characterized by diffuse reflectance spectroscopy. The plasmonic \( \text{Au}/\text{TiO}_2 \) photocatalysts exhibit a pronounced feature in the visible spectrum attributable to the LSPR of the \( \text{Au} \) nanoparticles (\( \lambda_{\text{max}} = 556 \text{ nm} \)) while the onset of interband transitions within the \( \text{TiO}_2 \) support itself occurs in the UV (\( \lambda < 400 \text{ nm} \)) regime (Figure 4-3A). Tauc plot analysis demonstrates that the \( \text{TiO}_2 \) support exhibits a band gap of \( E_G \approx 3.1—3.2 \text{ eV} \) (Figure 4-3B).
For comparison, Au/SiO$_2$ heterostructures were also prepared by the DP method to provide Au nanoparticles of similar size ($d = 5.6 \pm 1.0$ nm) as the Au/TiO$_2$ system but on an insulating dielectric support (Figure 4-4). The SiO$_2$ support was specifically chosen because it is well known that PMET is energetically unfeasible in Au/SiO$_2$ heterostructures while PMET readily occurs in the Au/TiO$_2$ system.$^{93}$ Figure 4-5A shows that the optical properties of the Au-SiO$_2$ heterostructures exhibit a feature in the visible spectrum attributable to the LSPR of the Au nanoparticles ($\lambda_{\text{max}} = 531$ nm) in a similar position as that observed in the Au/TiO$_2$ system ($\lambda_{\text{max}} = 556$ nm). The oxidation state of the Au nanoparticles on the SiO$_2$ support was further characterized by XPS, as shown in Figure 4-5B and Figure 4-6. In contrast to that observed for Au/TiO$_2$, the Au nanoparticles on the insulating SiO$_2$ support exhibit binding energies fully consistent with metallic Au$^{(0)}$ at 84.1 eV, indicating no charge transfer between the underlying SiO$_2$ support and the Au nanoparticles (Figure 4-5B). These two heterostructure systems (Au/TiO$_2$ and Au/SiO$_2$) thereby serve as the ideal counterparts to elucidate the influence of interfacial electronic structure on plasmon-driven charge separation in plasmonic photocatalysts under visible-light excitation.

**Low-Temperature EPR Spectroscopy of Photocatalysts**

The EPR spectra of TiO$_2$ and Au/TiO$_2$ photocatalysts were first investigated under low-temperature conditions prior to room-temperature measurements (see Experimental Methods section for details). Figure 4-7A presents the low temperature ($T = 90$ K) EPR spectra of Au/TiO$_2$ and TiO$_2$-only photocatalysts in the dark (black curves) and under visible-light excitation ($\lambda_{\text{inc}} > 495$ nm) (blue curve) or UV-light irradiation ($\lambda_{\text{inc}} = 280—400$ nm) (red curve), respectively. A manual offset was applied along the ordinate axis to facilitate comparison of these spectra. As the spectral features of
photoexcited TiO$_2$ nanoparticles are well known from previous EPR studies,\textsuperscript{127-131} the TiO$_2$-only system serves as a benchmark for establishing the origin of the EPR signals observable from the plasmonic Au/TiO$_2$ photocatalysts. Two distinct features are observed in the dark spectra of both samples (Figure 4-8, black curves), attributable to electrons trapped in oxygen vacancies (V$_o$) and the presence of Ti$^{3+}$ sites due to the intrinsic lattice defects of the solid itself.\textsuperscript{127} Little difference was observed between these samples in the dark, although a slight reduction in signal amplitude from V$_o$ was observed in the Au/TiO$_2$ system, suggesting that the deposition of Au nanoparticles by DP method preferentially passivates the V$_o$ sites on the surface of the TiO$_2$ support.

Optical excitation of the TiO$_2$ support with UV irradiation initiates charge separation within the semiconductor, as evidenced by the emergence of a wealth of EPR signals across a broad range of g-values from $g \sim 1.82$—2.07 (Figure 4-8A). These spectra can be roughly divided into two segments, as trapped electrons produce signals on one side of the spectrum ($g \leq 2.01$) while trapped holes exhibit $g$-values on the other side of the spectrum ($g \geq 2.01$).\textsuperscript{127-129} We assign these features to electrons trapped at V$_o$ or Ti$^{3+}$ lattice sites, holes trapped in the TiO$_2$ valence band (VB) to form O$^-$ lattice sites, and the formation of superoxide (O$_2^-$) species, consistent with prior reports.\textsuperscript{127-134} While it is possible to generate O$_2^-$ species via electron-mediated reduction of adsorbed O$_2$ molecules or via hole-mediated oxidation of surface-bound OH$^-$ species, experiments conducted under a He atmosphere indicate that the formation pathway likely proceeds via hole-driven photochemistry.\textsuperscript{133} It is further noted that the presence of residual adsorbed OH$^-$ species on the surface of the photocatalysts was confirmed by
Fourier transform infrared spectroscopy (FTIR) (Figure 4-9). Experiments remain ongoing to conclusively assign the photocatalytic origin of these O$_2^-$ species.

Simulations were subsequently performed to reconstruct the experimentally observed spectra and confirm the signal assignments in the dark (Figure 4-10) and under optical excitation (Figure 4-11). Deconvolution of these spectra into their respective components (denoted by roman numerals i-vi) demonstrates that low-temperature EPR spectroscopy not only distinguishes between Ti$^{3+}$ lattice sites in the anatase and rutile phases, but is also differentiates between those sites located within the bulk of the lattice and those on the semiconductor surface (Figure 4-11). Such chemical and spatial sensitivity reveals that optical excitation of TiO$_2$ preferentially promotes the occupation of electrons at anatase Ti$^{3+}$ surface sites, while a significant proportion of VB holes oxidize surface-bound OH$^-$ species to produce superoxide species (O$_2^-$).$^{133}$ Parsing the separate contributions from individual spin systems to the collective spectra observed experimentally thereby allows for identifying where these charge carriers reside within the semiconductor lattice.

By understanding the wealth of spectroscopic information contained within the TiO$_2$ samples under UV excitation, we have a spectroscopic fingerprint by which to interpret the features observed upon visible-light irradiation of the Au/TiO$_2$ photocatalysts, as shown in Figure 4-7A (blue curve) and Figure 4-8B. Similar EPR features emerge upon visible-light irradiation of the Au/TiO$_2$ photocatalysts, as the hot electrons transferred to the TiO$_2$ CB via PMET are subsequently trapped at similar Ti$^{3+}$ centers within the semiconductor support. It is noted, however, that in general all the features observed in the Au/TiO$_2$ samples are less intense than observed in the TiO$_2$
system, indicating that the Schottky barrier at the Au-TiO$_2$ heterojunction limits hot electron transfer to the semiconductor support. Nevertheless, we observe EPR signals from electrons trapped at Ti$^{3+}$ lattice sites within both TiO$_2$ phases, indicative of hot electron transfer to the TiO$_2$ support.\textsuperscript{133,134} It is noted that no change in the EPR spectrum was observed for the bare TiO$_2$-only photocatalysts under visible-light irradiation, confirming that the EPR signals observed in the Au/TiO$_2$ heterostructures originate from hot electrons transferred to the TiO$_2$ CB via the PMET process. Simulation of these spectra and subsequent deconvolution into their respective components (signals i-vi) provides insight into the different contributions from individual spin systems to the aggregate EPR spectra (Figure 4-12). A cursory examination of Figure 4-12B reveals a distinct preference for the hot electrons to reside at Ti$^{3+}$ sites associated with the rutile phase (signal ii) as opposed to those found within the anatase phase (signal iv). Such a result is not unexpected given the difference in CB level between these two phases (~0.2 eV),\textsuperscript{138} suggesting that only a fraction of the hot electrons transferred to the TiO$_2$ CB possess the additional energy required to occupy levels associated with the anatase phase.\textsuperscript{139,140} In stark contrast, direct optical excitation of the TiO$_2$ support with UV light primarily promotes the occupation of Ti$^{3+}$ lattice sites within the anatase phase relative to the rutile phase (Figure 4-12B). Indeed, EPR studies have previously indicated that such an electron transfer pathway exists in P25-based photocatalysts, whereby electrons first accumulate within the CB of the rutile phase before eventually transferring to the anatase phase to initiate surface reactions.\textsuperscript{128,29,132}
Unambiguous attribution of these EPR signals to the PMET process is given through comparison with Au/SiO$_2$ heterostructures. It has previously been shown that Au nanoparticles anchored to SiO$_2$ supports are capable of driving plasmonic photochemistry with adsorbed surface molecules via the production of hot carriers. With the only significant difference between the Au/TiO$_2$ and Au/SiO$_2$ systems being the electronic properties of the underlying support (semiconductor vs. insulator), Au/SiO$_2$ heterostructures are ideally suited to study the influence of an interfacial Schottky barrier on plasmon-driven charge separation. The EPR spectra of Au/SiO$_2$ heterostructures in the dark (black curve) and under visible-light irradiation (green curve) along with the background signal from the sample cavity itself (grey curve) are shown in Figure 4-13A. A manual offset was applied along the ordinate axis to clearly separate all three spectra that would otherwise be indistinguishable, as they are each congruent. The analogous spectra obtained from Au/TiO$_2$ heterostructures is also shown in Figure 4-13B for comparison. These data demonstrate that no EPR signals were observable from the Au/SiO$_2$ system under otherwise identical experimental conditions (either dark or visible light) to that employed for the Au/TiO$_2$ heterostructures. As resonant optical excitation of plasmonic Au nanoparticles occurs in both systems, the complete absence of EPR features observed under both dark and light conditions in the Au/SiO$_2$ system confirms that the signals observed from the Au/TiO$_2$ system originate solely from hot carriers transferred to the semiconductor support, and not from hot carriers generated on the Au nanoparticles themselves, consistent with a previous report. Thus, a Schottky barrier is required to physically separate these hot carriers and prolong their lifetime to enable detection by EPR spectroscopy.
Room-Temperature EPR Spectroscopy of Photocatalysts

EPR experiments were then conducted at room temperature ($T = 298$ K) to probe this PMET process under photocatalytic conditions. Again the Au/TiO$_2$ (visible light) and TiO$_2$-only (UV light) EPR spectra exhibit identical features, albeit with significantly reduced resolution at higher temperature (Figure 4-7B). Under dark conditions, the spectra from the Au/TiO$_2$ samples exhibit a single feature indicative of electrons trapped at $V_0$ centers, though the reduced sensitivity at room temperature precludes observation of other features. The TiO$_2$-only sample exhibits similar features in the dark, though the signals from trapped electrons are significantly better resolved. Upon the incidence of UV light ($\lambda = 280—400$ nm), the TiO$_2$ sample shows signals associated with electrons trapped at $V_0$ and holes trapped in the TiO$_2$ VB, along with the formation of O$_2^-$ species (Figure 4-7B, red curve). Unfortunately, all the spectroscopic features related to electrons trapped at Ti$^{3+}$ sites are lost, consistent with previous studies showing that electrons trapped at these sites typically exhibit lifetimes that are too short-lived at room temperature to reliably observe by EPR. A complete assignment of EPR signals was achieved through simulation of the EPR spectra and elucidation of their associated g-values (Figure 4-14). By comparison, visible-light irradiation ($\lambda > 495$ nm) of the plasmonic Au/TiO$_2$ photocatalysts produces similar signals (Figure 4-7B, blue curve), confirming the occurrence of PMET is observable under photocatalytic conditions.

These results thereby demonstrate the applicability of using EPR spectroscopy to probe the PMET process in plasmonic-metal/semiconductor heterostructures in situ.

Correlating EPR Signals with Photocatalytic Activity

EPR spectroscopy has proven capable of distinguishing between hot electrons trapped at either rutile or anatase Ti$^{3+}$ lattice sites, as well as between those electrons
trapped at Ti$^{3+}$ sites within the semiconductor lattice (Ti$^{3+}$ interstitials) and those on the semiconductor surface arising from under-coordinated Ti surface atoms. To ascertain which of these sites are chemically accessible, the photocatalysts were immersed in solutions composed of either H$_2$O or methanol prior to performing EPR experiments to provide adsorbed surface species capable of scavenging trapped carriers.

While previous results show that EPR spectroscopy is capable of probing the PMET process at room temperature, the reduced spectral sensitivity at elevated temperatures limits its applicability to monitor subtle changes in the complex EPR spectra of these samples. With the majority of signals arising from Ti$^{3+}$ centers, these sites must be spectroscopically accessible to differentiate between different trapping sites within the semiconductor support. As such, further experimental studies were conducted under low temperatures ($T = 90$ K) to provide the necessary sensitivity to elucidate differences between these spectra. Although conducted at 90 K, suspensions were first formed at room temperature and thoroughly mixed via sonication to cover the semiconductor surface with thin-films of adsorbed molecules prior to freezing the sample. Monitoring changes in EPR spectra in the presence or absence of these surface molecules reveals which sites are chemically accessible and therefore capable of participating in photochemistry. Initial experiments were conducted with bare TiO$_2$ samples under UV light irradiation, as direct optical excitation of the semiconductor generates substantially more charge carriers within TiO$_2$ that are observable by EPR than generated from Au/TiO$_2$ via the PMET process.

Under dark conditions, the addition of either water or methanol to the TiO$_2$ photocatalysts subtly alters their EPR spectrum in the dark. The features arising from
electrons trapped in $V_o$ sites are slightly more pronounced with the addition of water, as compared to methanol, relative to the dark (Figure 4-15). However no new features arise with the addition of surface adsorbed species, and the same features observed in the dry powder samples are retained in the solvated samples. Upon UV irradiation of the TiO$_2$ photocatalysts, charge separation within the semiconductor is evidenced by the emergence of several new features (Figure 4-15). While ostensibly similar to that observed for the dry powder sample, closer inspection of these EPR spectra reveals that the presence of water or methanol induces several notable differences to the features observable under UV light. The changing spectral profile of the EPR spectrum indicates a shift in the relative populations of charge carriers at specific trap states within the semiconductor in the presence of these adsorbed surface species. Full simulations of the experimental spectra are currently underway to deconvolute individual contributions from the separate spin systems and fully elucidate the subtle differences between the photophysics of TiO$_2$ photocatalysts under inert atmosphere and in the presence of reactant molecules. The influence of adsorbed surface species on the PMET process is also being studied to ascertain which of these trap states involved in hot electron transfer are responsible for the photocatalytic activity observed from these systems under visible-light irradiation.

**Summary of Results**

In summary, we have shown that *in situ* EPR spectroscopy is a powerful tool for probing the PMET process in Au/TiO$_2$ heterostructures under realistic operating conditions. As these EPR signals originate from hot carrier distributions established on plasmonic photocatalysts under steady-state conditions ($t \sim$min), these spectroscopic studies elucidate the ensuing charge density distribution eventually established on
plasmonic photocatalysts *in operando*. As such, the timescale of these measurements are commensurate with the multi-step reactions requisite for catalysis \((t \approx \text{ms} - \text{s})\), lending unprecedented insight into the mechanics of plasmon-driven charge separation under steady-state conditions relevant to photocatalytic systems. Our studies demonstrate that hot electrons preferentially transfer to the rutile phase instead of the anatase phase of the underlying TiO\(_2\) support, in contrast to that observed in the pure TiO\(_2\)-only system. Such a finding implies that the semiconductor support must be properly chosen to ensure optimal activity in plasmonic-metal/semiconductor photocatalysts. Advanced electron microscopy studies are currently underway to chemically map the spatial distribution of Ti\(^{3+}\) defects within these plasmonic photocatalysts and correlate the structural features of the photocatalyst with local variations in chemical composition. It is anticipated that these studies will improve our fundamental understanding of the structure-function relationships governing catalytic activity in plasmonic photocatalysts and inform the design of more efficient artificial photosynthetic constructs for solar-to-fuel energy conversion.
Figure 4-1. Structural characterization of Au/TiO₂ heterostructures. A) MAADF-STEM image of 5 wt.% Au/TiO₂ heterostructures showing the Au nanoparticle size distribution. B) MAADF-STEM image showing Au nanoparticles dispersed on TiO₂ (P25) supports. Inset shows a size distribution histogram of the Au nanoparticles (d = 4.4 ± 1.0 nm) obtained by the DP method. C) HRTEM image showing the direct physical contact established at the Au-TiO₂ interface by the DP method. D) HRTEM image showing intimate physical contact at the interface. Images courtesy of Dr. A. C. Johnston-Peck at the Center for Functional Nanomaterials, Brookhaven National Lab, Upton, NY.
Figure 4-2. X-ray photoelectron spectroscopy (XPS) of Au/TiO$_2$ photocatalysts. A) Gold (Au) 4f region. B) Titanium (Ti) 2p region. C) Carbon (C) 1s region. D) Oxygen (O) 1s region.
Figure 4-3. Optical properties of Au/TiO$_2$ heterostructures (blue) and TiO$_2$-only (red) nanoparticle support. A) Absorbance spectra (Kubelka-Munk) of plasmonic and control heterostructures obtained by diffuse reflectance spectroscopy. B) Tauc plot of TiO$_2$-only (P25) support. As the P25 support constitutes a mixture of anatase (indirect band gap) and rutile (direct band gap) phases, this semiconductor exhibits a band gap ($E_g$) of ca. 3.1—3.2 eV.
Figure 4-4. Structural characterization of Au/SiO₂ heterostructures. A) HRTEM image of 5 wt.% Au-SiO₂ heterostructures showing the Au nanoparticle size distribution. B) HRTEM image showing Au nanoparticles dispersed on SiO₂ supports. Inset shows a size distribution histogram of the Au nanoparticles (d = 5.6 ± 1.0 nm) obtained by the DP method. C) HRTEM image showing the Au-SiO₂ nanoparticles obtained by the DP method. D) High-magnification HRTEM image showing the direct physical contact at the Au-SiO₂ interface.
Figure 4-5. Comparison of Au nanoparticle optical properties and oxidation state between Au/TiO$_2$ and Au/SiO$_2$ heterostructures. A) Absorbance (Kubelka-Munk) spectra of Au/SiO$_2$ (green) and Au/TiO$_2$ (blue) for comparison obtained by diffuse reflectance measurements, showing the prominent LSPR peak of Au nanoparticles in both samples. The $\lambda_{\text{max}}$ of Au/SiO$_2$ is blue-shifted ($\lambda_{\text{max}} = 531$ nm) relative to Au/TiO$_2$ ($\lambda_{\text{max}} = 556$ nm). Inset shows digital photographs of powder samples of either Au/SiO$_2$ (left image) or Au/TiO$_2$ (right image) heterostructures. B) X-ray photoelectron spectroscopy of the Au 4f region from Au/SiO$_2$ heterostructures (green) and Au/TiO$_2$ heterostructures (blue) for comparison. A shift is noted to lower binding energies in the Au/TiO$_2$ samples, suggesting the presence of an interfacial Schottky barrier at the Au/TiO$_2$ heterojunction that does not form in the Au/SiO$_2$ system.
Figure 4-6. X-ray photoelectron spectroscopy (XPS) of Au/SiO$_2$ photocatalysts. A) Gold (Au) 4f region. B) Silicon (Si) 2p region. C) Carbon (C) 1s region. D) Oxygen (O) 1s region.
Figure 4-7. EPR spectra of Au/TiO₂ (blue) and P25 TiO₂ (red) photocatalysts under visible-light irradiation ($\lambda > 495$ nm) or UV-light irradiation ($\lambda = 320-400$ nm), respectively, as well as in the dark (black curve for both samples). A) Low-temperature ($T = 90$ K) EPR spectra of plasmonic and control photocatalysts in the dark and under visible or UV-light irradiation, respectively. B) Room-temperature ($T = 298$ K) EPR spectra of plasmonic and control photocatalysts in the dark and under visible or UV-light irradiation.
Figure 4-8. Low-temperature ($T = 90$ K) EPR spectra of control and plasmonic photocatalysts. A) EPR spectra of P25 TiO$_2$-only photocatalysts in the dark (black) and under UV-light (red) irradiation ($\lambda = 320$—400 nm) and B) EPR spectra of plasmonic Au/TiO$_2$ photocatalysts in the dark (black) and under visible-light (blue) irradiation ($\lambda > 495$ nm).
Figure 4-9. FTIR spectra of Au/TiO\textsubscript{2} photocatalysts (blue) and P25 TiO\textsubscript{2} photocatalysts (red) at room temperature ($T = 298$ K). A) FTIR spectra of photocatalysts in the region where surface-adsorbed hydroxyl (OH\textsuperscript{-}) species are commonly observed on TiO\textsubscript{2} surfaces. B) Close-up view of the OH region shown in (A).
Figure 4-10. Simulated low temperature ($T = 90$ K) EPR spectra of A) P25 TiO$_2$ and B) Au/TiO$_2$ photocatalysts in the dark. The dark spectra (black curve) can be further deconvoluted into its respective components (i—iii), where signal (i) originates from electrons trapped at oxygen vacancies ($V_O$), signal (ii) originates from electrons trapped at Ti$^{3+}$ sites in the rutile phase (R) and signal (iii) originates from electrons trapped at Ti$^{3+}$ sites in the anatase (A) phase. Simulations courtesy of U. Twahir.
Figure 4-11. Simulated low temperature ($T = 90$ K) EPR spectra of A) P25 TiO$_2$ and B) Au/TiO$_2$ photocatalysts under UV-light irradiation ($\lambda = 320-400$ nm) or visible-light irradiation ($\lambda > 495$ nm), respectively. The EPR spectra (black curve) can be further deconvoluted into its respective components (i—vi). Signal (i) originates from electrons trapped at oxygen vacancies ($V_O$), signal (ii) originates from electrons trapped at Ti$^{3+}$ sites in the rutile (R) phase, signal (iii) originates from electrons trapped at Ti$^{3+}$ sites in the anatase (A) phase at the bulk lattice sites, signal (iv) originates from electrons trapped at Ti$^{3+}$ sites in the anatase (A) phase located at or near the TiO$_2$ surface, signal (v) originates from superoxide species ($O_2^-$), and signal (vi) originates from holes trapped at lattice oxygen sites ($O^-$) in the TiO$_2$ valence band (VB). Simulations courtesy of U. Twahir.
Figure 4-12. EPR spectra of Au/TiO$_2$ (blue) and TiO$_2$ (red) photocatalysts under light and dark (black) conditions with corresponding deconvolution of total spectra into relative signal components. A) Low-temperature ($T = 90$K) EPR spectra of Au/TiO$_2$ (blue) and TiO$_2$ (red) photocatalysts under visible-light irradiation ($\lambda > 495$ nm) or UV-light irradiation ($\lambda = 320-400$ nm), respectively. B) Plot of the individual % contributions from each signal (i—vi) to the overall experimental spectra shown in (A). Deconvolution of these spectra through simulations reveal six different EPR signals (i—vi) originating from distinct sites within the photocatalysts: signal (i) originates from electrons trapped at oxygen vacancies ($V_O$), signal (ii) originates from electrons trapped at Ti$^{3+}$ sites in the rutile phase, signal (iii) originates from electrons trapped at Ti$^{3+}$ sites in the anatase phase at the bulk lattice sites, signal (iv) originates from electrons trapped at Ti$^{3+}$ sites in the anatase phase located at or near the TiO$_2$ surface, signal (v) originates from superoxide species ($O_2^-$), and signal (vi) originates from holes trapped at lattice oxygen sites ($O^-$) in the TiO$_2$ valence band (VB). Simulations courtesy of U. Twahir.
Figure 4-13. Low-temperature EPR spectra of Au-SiO$_2$ and Au/TiO$_2$ photocatalysts. A) EPR spectra of Au/SiO$_2$ heterostructures under dark (black) and under visible-light irradiation ($\lambda > 495$ nm) (green). For clarity, a manual offset was applied to the ordinate axis to show that only the background spectrum from the EPR cavity itself (grey curve) is observable in the Au/SiO$_2$ system. B) EPR spectra of Au/TiO$_2$ heterostructures in the dark (black) and under visible-light irradiation ($\lambda > 495$ nm) (blue) shown for comparison with the Au/SiO$_2$ system (A).
Figure 4-14. Simulated room temperature \((T = 298 \text{ K})\) EPR spectra of A) P25 TiO\(_2\) and B) Au/TiO\(_2\) photocatalysts under UV-light irradiation \((\lambda = 320—400 \text{ nm})\) or visible-light irradiation \((\lambda > 495 \text{ nm})\), respectively. The EPR spectra (black curve) can be further deconvoluted into its respective components \((i—vi)\), where signal \((i)\) originates from electrons trapped at oxygen vacancies \((V_O)\), signal \((v)\) originates from superoxide \((O_2^-)\) species, and signal \((vi)\) originates from holes trapped at lattice oxygen sites \((O^-)\) within the TiO\(_2\) valence band \((VB)\). Simulations courtesy of U. Twahir.
Figure 4-15. Low-temperature EPR spectra of P25 TiO₂ photocatalysts in the presence of adsorbed surface species. A) EPR spectra of P25 TiO₂ photocatalysts in methanol in the dark (grey curve) or under UV-light irradiation (λ = 280-400 nm) (bright blue curve) shown relative to the dry powder sample in the dark (black curve) or under UV light (red curve) for comparison. B) EPR spectra of P25 TiO₂ photocatalysts in water in the dark (grey curve) or under UV-light irradiation (λ = 280-400 nm) (purple curve) shown relative to the dry powder sample in the dark (black curve) or under UV light (red curve) for comparison. These data demonstrate subtle differences between the EPR spectra obtained from dry P25 TiO₂ powder and TiO₂ nanoparticles coated with adsorbed surface species.
CHAPTER 5
ISOLATING THE NEAR-FIELD ENHANCEMENT MECHANISM IN P-TYPE PHOTOCATHODES

Cuprous oxide (Cu₂O) p-Type Photocathodes for Solar Hydrogen Production

Solar water splitting via a photoelectrochemical cell represents a sustainable route to energy production by harvesting solar insolation and storing it in the form of chemical bonds (e.g. H₂) for discharge on demand.¹⁻⁹ Cuprous oxide (Cu₂O) is a promising p-type semiconductor for photoelectrochemical H₂ production because it consists of Earth-abundant elements, possesses a direct optical band gap ($E_g$) of ca. 2.0 eV, boasts long minority-carrier (electrons) diffusion lengths ($l_d$ ~50 nm), and exhibits a so-called “built-in” overpotential for H₂ evolution.¹⁴¹⁻¹⁵⁷ Despite these auspicious properties, exploration of Cu₂O-based devices for photoelectrochemical applications has been hindered by their inherent instability within aqueous electrolytes under cathodic operation.¹⁴¹⁻¹⁴⁸ Although atomic layer deposition (ALD) of metal oxide thin films onto p-type photocathodes has proven useful for passivating the semiconductor surface against photocorrosion,¹⁴⁹⁻¹⁵¹ the development of simpler methods for achieving sustained photoelectrochemical operation continues to constitute a burgeoning area of applied research.¹⁵²⁻¹⁵⁷ Another serious limitation of Cu₂O-based photocathodes stems from their intrinsically weak optical response; the abrupt decrease in absorption coefficient at energies below ~2.5 eV substantially restricts the range of solar insolation that can be efficiently collected with this semiconductor.¹⁴⁴⁻¹⁵¹ Attempts to mitigate this constraint by fabricating thicker semiconductor films have met with limited success as this approach ultimately restricts device performance by adversely affecting charge carrier collection.¹¹⁴,¹¹⁵ Innovative approaches to augment the optical cross section of the semiconductor without significantly altering the internal device
architecture are therefore required to achieve viable solar-to-fuel conversion efficiencies.

**Plasmonic-Metal Nanostructures as Optical Antennas**

Plasmonic-metal nanostructures (e.g. Au and Ag) offer intriguing opportunities for solar photocatalysis due to their unique ability to confine freely propagating optical radiation into subwavelength volumes.\(^{47,51-53}\) Optical excitation at their localized surface plasmon resonance (LSPR) frequency induces a local enhancement (\(\sim 10^3\)) of electromagnetic (EM) fields near the nanoparticle surface that can markedly boost the absorption cross section of a nearby semiconductor photocatalyst.\(^{57-60}\) Panchromatic light-harvesting devices are envisioned by tailoring the LSPR frequency to amplify the absorption profile of the semiconductor in regions of the solar spectrum that would otherwise be inefficiently collected by the device.\(^{63-77}\) Although promising, the pursuit of plasmonic photocatalysts is plagued by the daunting complexity of such systems.\(^{57-63}\) Numerous plasmonic processes may coexist spatiotemporally,\(^{48,49,56}\) resigning most studies to invoke a multitude of mechanisms to explain the enhancements observed in the plasmonic composite. This inability to properly distinguish between different enhancement mechanisms has curtailed the development of a comprehensive set of plasmonic principles to guide the efficient augmentation of semiconductor-based devices with plasmonic-metal nanostructures.

We construct a plasmon-enhanced photocathode composed of Au@SiO\(_2\) (plasmonic-metal core@dielectric shell) nanoparticles integrated within Cu\(_2\)O nanowire networks to specifically isolate the impact of the enhanced EM near-fields on the light-harvesting efficiency of a p-type semiconductor. To exclude resonant photon scattering, the plasmonic-metal core is comprised of a small Au nanoparticle possessing a
negligible scattering cross section.\textsuperscript{57,58} Encapsulation within a dielectric silica (SiO\textsubscript{2}) shell serves both to electrically isolate the metal nanoparticle from the Cu\textsubscript{2}O nanowires and to chemically isolate the Au nanoparticle surface from the surrounding electrolyte.\textsuperscript{57,72} This core@shell motif therefore prevents direct charge transfer between the plasmonic-metal nanoparticles and their surrounding environment while permitting the enhanced EM fields to permeate the dielectric shell and interact with the nearby semiconductor.\textsuperscript{57} As the EM field intensity rapidly decays with increasing distance from the Au surface,\textsuperscript{57,158-160} minor adjustments in SiO\textsubscript{2} shell thickness enable significant attenuation of the local EM fields experienced by the Cu\textsubscript{2}O nanowires. This composite system thereby constitutes an ideal test bed to systematically probe the influence of the EM near-fields from plasmonic-metal nanoparticles on a p-type semiconductor within a working photoelectrochemical cell. The results of these detailed studies demonstrate the merits of incorporating plasmonic-metal nanostructures into semiconductor-based devices and reveal general plasmonic design rules for engineering more efficient artificial photosynthetic constructs.

**Experimental Methods**

**Materials**

Copper\textsuperscript{(II)} sulfate (CuSO\textsubscript{4}), trisodium citrate (Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7}), and sodium hydroxide (NaOH) were purchased from Fisher Scientific (Hampton, NH). Sodium tartrate dibasic dihydrate (Na\textsubscript{2}C\textsubscript{4}H\textsubscript{4}O\textsubscript{6}•2H\textsubscript{2}O), α-D-glucose (C\textsubscript{6}H\textsubscript{12}O\textsubscript{6}), tetrachloroauric acid trihydrate (HAuCl\textsubscript{4}•3H\textsubscript{2}O), sodium borohydride (NaBH\textsubscript{4}), L-ascorbic acid (C\textsubscript{6}H\textsubscript{8}O\textsubscript{6}), hexadecyltrimethylammonium bromide (CTABr), tetraethoxysilane (TEOS), acetone (C\textsubscript{3}H\textsubscript{6}O), 2-propanol (C\textsubscript{3}H\textsubscript{8}O), and 12 nm SiO\textsubscript{2} nanoparticles (No. 718483) were purchased from Sigma Aldrich (St. Louis, MO). The fluorine-doped tin oxide (FTO) glass
substrates (TEC 15) were purchased from Hartford Glass Co. (Hartford City, IN). All materials were used as received without further purification. Nanopure™ H$_2$O (Barnstead, 18.2 MΩ cm) was used for the preparation of all solutions. All glassware was cleaned with aqua regia solution and copious rinsing with Nanopure™ H$_2$O prior to use. Caution! Aqua regia is highly corrosive and toxic. Handle with care and use appropriate personal protection equipment.

**Synthesis of Cu$_2$O Nanowires**

The synthesis of Cu$_2$O nanowires was conducted in accordance with a previous report.$^{161}$ Three aqueous solutions labeled Solution A, Solution B, and Solution C were freshly prepared in Nanopure™ H$_2$O (18.2 MΩ cm) each day the synthesis was conducted. Solution A was a 2 mM Cu$^{(II)}$SO$_4$ solution, Solution B was composed of 8 mM sodium tartrate in 14 mM NaOH (pH ~8) solution, and Solution C was a 0.1 mM α-D-glucose solution. The solutions were mixed together according to the volume ratio 1:1:2 (A:B:C) in 5:5:10 mL volumes inside a 30 mL glass vial with a screw-on cap. The vials were sealed and placed in an oven and heated at 96° C for 75—90 min. After this time, the solution changed color from a pale blue solution to a vibrant yellow color, signifying the reduction of Cu$^{(II)}$ to Cu$^{(I)}$ and the growth of Cu$_2$O nanowires. The vials were removed from the oven, allowed to cool naturally to room temperature (~1 h), centrifuged three times at 10,000 RPM for 15 minutes to clean Cu$_2$O nanowires, and finally redispersed in Nanopure™ H$_2$O for future use. This procedure was repeated many times to compile enough nanowires for the eventual fabrication of Cu$_2$O nanowire-based photocathodes.
Synthesis of Au@SiO$_2$ (Core@Shell) Nanoparticles

The synthesis of Au nanoparticles consisted of several steps, and was based on two previous reports \cite{ref1, ref2}. Initially, small Au nanoparticles were created via the traditional NaBH$_4$ reduction of HAuCl$_4$ in the presence of sodium citrate to yield small Au nanoparticle "seeds" with diameters of 3-5 nm \cite{ref1}. The Au seed solution was prepared by adding 1 mL of 10 mM HAuCl$_4$ and 1 mL of 10 mM sodium citrate to 37 mL of Nanopure™ H$_2$O in a glass beaker. A 1 mL aliquot of an ice-cold 100 mM NaBH$_4$ solution was then added all at once to this solution under vigorous stirring and allowed to react for 2—3 h prior to use. A subsequent seed-mediated growth step converted these small seeds into larger Au nanoparticles via controlled secondary growth according to a previous literature report \cite{ref1}, but with slight modification. A 9 mL growth solution composed of 10 mM CTABr and 0.25 mM HAuCl$_4$ was then prepared in a 16 mL glass vial, followed by the addition of 50 μL of 0.1 M ascorbic acid (freshly prepared) under rapid magnetic stirring. After the solution turned colorless, signifying the reduction of Au$^{(III)}$ to Au$^{(I)}$, a 1 mL aliquot of the citrate-stabilized Au seeds was injected all at once under rapid magnetic stirring. The reaction was allowed to proceed for 10—20 min until a vibrant purple color is achieved, at which point the stir bar was removed and the solution was stored for further use. This secondary growth step enlarges the Au nanoparticles to 10 ± 1 nm in diameter, and these nanoparticles then serve as the substrate for the subsequent deposition of silica (SiO$_2$) shells. We note that our procedure uses a 10 mM CTABr growth solution instead of the 100 mM CTABr solution initially reported \cite{ref1} because we found that this lower concentration allows for controlled enlargement of the Au nanoparticles without the concomitant production of unwanted Au nanorods \cite{ref2}. Conformal SiO$_2$ shells were then deposited onto the Au nanoparticle
surface via our previously reported procedure. Briefly, the 10 nm Au nanoparticles were first centrifuged once for 15 min at 14,000 RPM and redispersed in Nanopure™ H₂O to remove excess CTABr from the solution (a critical step for achieving conformal SiO₂ shells). A 4 mL aliquot of the washed Au nanoparticles was then added to a 16 mL glass vial with a magnetic stir bar. To this solution, we added 100 μL of 1.0 M NaOH to raise the pH of the growth solution to pH ~10, followed by the addition of 20 μL of tetraethoxysilane (TEOS) under rapid magnetic stirring. The addition of TEOS was repeated x times (where x = 1—8) in 60 min intervals to achieve a final SiO₂ shell thickness from 5 nm to 22 nm.

**Photocathode Device Preparation**

Photocathodes were prepared by drop-casting the previously prepared Cu₂O nanowire and Au@SiO₂ nanoparticle solutions onto clean FTO glass substrates. The FTO substrates were first cleaned via ultrasonication for 1 h in a solution of 1:1:1 (by volume) Nanopure™ H₂O:2-propanol:acetone. The substrates were then copiously rinsed with Nanopure™ H₂O, and then dried with a stream of compressed air. Photocathodes were then prepared by drop-casting aliquots of the nanoparticle suspensions directly onto the clean FTO glass substrates. Variability in device construction was minimized by using a single “master” solution of Cu₂O nanowires at a fixed concentration for the preparation of all photocathodes. This preparation method enabled remarkable photoelectrochemical reproducibility between photocathodes, with ca. 5% variability observed between devices. This fabrication process also provided a simple method of controlling the Cu₂O film thickness (1—5 μm) by varying the total volume of solution drop-casted onto the FTO substrate. All plasmonic devices (Cu₂O/Au@SiO₂) were prepared in triplicate from the same master Cu₂O nanowire.
solution used for control devices with a “master” Au@SiO$_2$ nanoparticle solution used for each different SiO$_2$ shell thickness investigated. Prior to all photoelectrochemical experiments, the photocathodes were subjected to a mild heat treatment at 120 °C for 30 min to improve the adhesion between the nanowires and the FTO glass substrate.

**Photoelectrochemical Characterization**

The photoelectrochemical characteristics of these materials were investigated via the construction of a three-electrode electrochemical cell controlled by a potentiostat (EC Epsilon, Bioanalytical Systems, Inc.). The Cu$_2$O nanowire photocathode served as the working electrode, with a Ag/AgCl (saturated KCl) reference electrode and a platinum (Pt) wire auxiliary electrode all immersed in 0.10 M Na$_2$SO$_4$ (pH 6) as the supporting electrolyte. All potentials are reported relative to the Reversible Hydrogen Electrode (RHE), which represents the potential of the Standard Hydrogen Electrode (SHE) adjusted for the pH of the solution with the following equation:

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + (0.059 \, \text{V pH}^{-1} \times \text{pH}) + E_{\text{Ag/AgCl}}^\circ
\]

(5-1)

where $E_{\text{RHE}}$ is the converted potential vs. RHE, $E_{\text{Ag/AgCl}}$ is the experimental potential measured relative to the Ag/AgCl reference electrode, and $E_{\text{Ag/AgCl}}^\circ$ is the standard potential of the Ag/AgCl reference electrode relative to the RHE at 25 °C (0.1976 V$_{\text{RHE}}$).\textsuperscript{113} All photoelectrochemical experiments were repeated in triplicate on three independently fabricated photocathodes. Photoanodes were illuminated through the FTO glass substrate with simulated sunlight using an ozone-free 300 W Xe lamp (Newport Corp.) equipped with an air mass (AM) 1.5G filter (Newport Corp.). It should be noted that all measurements were conducted at an incident power of $I_0 = 100 \pm 10$ mW/cm$^2$ (1-sun intensity) unless indicated otherwise. Chronoamperometry [$J_{\text{ph}}(t)$] and
power-dependent photocurrent \([J_{\text{ph}}(I_0)]\) experiments were conducted using the three-electrode configuration mentioned above while a particular applied potential \((E_{\text{appl}} = -0.50—1.0 \text{ V}_{\text{RHE}})\) was maintained by the potentiostat during illumination. Incident photon-to-charge conversion efficiency (IPCE) measurements were conducted using a set of band pass filters \((\lambda = 400-700 \text{ nm})\) with a bandwidth of \(\Delta \lambda = 20 \text{ nm} \pm 10 \text{ nm} \) (Thor Labs, Inc.) coupled with an AM 1.5G optical filter. The measured \(J_{\text{ph}}\) at each irradiation wavelength was then converted into an IPCE value according to equation:

\[
\text{IPCE} (\%) = \left( \frac{J_{\text{ph}} \times 1240 \text{ eV nm}^{-1}}{I_0 \times \lambda} \right) \times 100
\]

(5-2)

where \(J_{\text{ph}}\) is the measured photocurrent density (in mA cm\(^2\)), \(I_0\) is the power density of light incident upon the device (mW cm\(^2\)), \(\lambda\) is the wavelength of incident light (nm), and the value 1240 eV nm\(^{-1}\) is a conversion factor between photon energies expressed in eV and wavelength (in nm). Any numbers given after the ± sign throughout the text indicate the standard deviation (SD) about the mean value.

**Photoluminescence Studies**

Photoluminescence (PL) measurements were carried out using a Horiba Aramis Raman system, which is a software-selectable multi-wavelength Raman/PL system located at NRF (UF). The PL spectra were collected by using a 532 nm laser with a grating of 1800 g/mm to simultaneously excite the band gap transitions of the \(\text{Cu}_2\text{O}\) nanowires and the LSPR of the Au nanoparticles. The samples were focused using a 100x objective lens. The laser spot size used for each measurement was ca. 5 μm in diameter with an incident power of 0.6 mW and an acquisition time of 5 s. PL spectra were acquired on pristine \(\text{Cu}_2\text{O}\)-only and \(\text{Cu}_2\text{O}/\text{Au@SiO}_2\) devices prior to photoelectrochemical measurements. All PL measurements were acquired from at least
9 different spots selected at random on each device. All PL emission spectra were then averaged to mitigate any signal variability associated with irregularities in film composition. Furthermore, each device condition investigated (control or plasmonic) was examined in duplicate to further ensure accurate representation of the PL enhancement factor for the various devices.

**Discrete Dipole Approximation Simulations**

The program DDSCAT v7.1 developed by Draine and Flatau was used for all calculations. The wavelength-dependent extinction, scattering, and absorption cross sections were calculated for each Au@SiO₂ geometry, and electromagnetic field distributions were visualized around each particle under 525 nm light irradiation. The dielectric functions for Au and SiO₂ were taken from previous literature reports. The core@shell morphology was modeled by two concentric spheres immersed in a pure water medium with refractive index, $n = 1.333$. For all simulations, light propagated in the $x$-direction and was polarized in the $y$-direction. OriginLab, a scientific graphing and data analysis software package, was used to plot the raw data and visualize the EM field distribution around a single nanoparticle.

**Results and Discussion**

**Structural Characterization of Cu₂O Nanowires**

The Cu₂O nanowires were synthesized according to a hydrothermal method that yields high aspect ratio nanowires with diameters ($d$) of $80 \pm 10$ nm and typical lengths ($l$) of 10—25 μm (Figure 5-1A to C). Keeping the nanowire diameter ($d \sim 80$ nm) commensurate with the minority carrier diffusion length ($l_d \sim 50$ nm) is expected to maximize electron injection at the semiconductor-electrolyte interface while maintaining an uninterrupted corridor for majority carrier (holes, $h^+$) extraction along the Cu₂O.
Scanning electron microscopy (SEM) revealed that these nanowires form large-scale interconnected nanowire networks on the fluorine-doped tin oxide (FTO) glass substrate, as shown in Figure 5-1D to F. The high internal surface area and large open channels of this interwoven structure are expected to facilitate electrolyte diffusion throughout the semiconductor network during photoelectrochemical operation. Further characterization of these materials with X-ray diffraction (XRD) and Raman spectroscopy verified that these nanowires were composed of the Cu$_2$O phase (Figure 5-2). The crystal planes of individual nanowires were then indexed to those of Cu$_2$O by high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analysis (Figure 5-3). Closer inspection of individual nanowires by HRTEM revealed the presence of an amorphous layer ca. 2 nm thick adhered to the Cu$_2$O nanowire surface, as shown in Figure 5-3 B and D. Subsequent investigation of the chemical composition of this amorphous layer by scanning transmission electron microscopy-electron energy loss spectroscopy (STEM-EELS) identified this substance to be highly enriched in carbon (C) and oxygen (O) relative to the Cu$_2$O nanowire core (Figure 5-4). We attribute the origin of this C/O layer to the α-D-glucose used in the initial synthesis of the Cu$_2$O nanowires, which persisted along the length of the nanowires despite repeated washing of the sample. It is noted that X-ray photoelectron spectroscopy (XPS) experiments also identified the presence of a carbon species on the Cu$_2$O nanowire surface (Figure 5-5) consistent with glucose-derived carbon coatings.

**Morphology of Au@SiO$_2$ (Core@Shell) Nanoparticles**

Small Au nanoparticles ($d = 10 \pm 1$ nm) served as the plasmonic core (Figure 5-6) for the subsequent deposition of conformal SiO$_2$ shells via previously published
methods\textsuperscript{162,163} to yield Au@SiO\textsubscript{2} (core@shell) nanoparticles. This approach circumvents tedious surface functionalization steps while enabling precise control over SiO\textsubscript{2} shell thickness from 5 nm to 25 nm (Figure 5-7). Since it is expected that a near-field enhancement strategy will be most effective at wavelengths where the Cu\textsubscript{2}O absorption coefficient is small (\(\lambda \sim 520—600\) nm), spherical Au nanoparticles exhibiting a maximum LSPR absorption (\(\lambda_{\text{max}}\)) at 521 nm were chosen to ensure sufficient spectral overlap with the optical response of the Cu\textsubscript{2}O nanowires (Figure 5-8). A slight red shift in \(\lambda_{\text{max}}\) was observed from 521 nm to 525 nm upon the deposition of a 5 ± 2 nm SiO\textsubscript{2} shell onto the Au nanoparticle core (Figure 5-8B and Figure 5-9A). This red shift is attributable to the increased refractive index of SiO\textsubscript{2} (\(n = 1.45\)) compared to water (\(n = 1.31\)).\textsuperscript{167} After synthesis of the desired core@shell motif, these Au@SiO\textsubscript{2} nanoparticles were intimately mixed with the Cu\textsubscript{2}O nanowires during device assembly to confer the maximum plasmonic enhancement to the Cu\textsubscript{2}O/Au@SiO\textsubscript{2} photocathode.

**Optical Properties of Photocathodes**

The optical properties of the control (Cu\textsubscript{2}O-only) and plasmonic (Cu\textsubscript{2}O/Au@SiO\textsubscript{2}) photocathodes were characterized as thin films with diffuse reflectance spectroscopy, as shown in Figure 5-9B. The broad extinction feature above 2.5 eV (\(\lambda < 500\) nm) is attributed to the interband transitions of the Cu\textsubscript{2}O nanowires (Figure 5-9B, red line). It is noted that the abrupt change in the optical cross-section of the Cu\textsubscript{2}O nanowires is evidenced by the steady decline in extinction towards longer wavelengths of the visible spectrum (\(\lambda \sim 520—600\) nm). Tauc analysis reveals the band gap (\(E_{\text{G}}\)) of the Cu\textsubscript{2}O nanowires used in our study was ca. 2.14 eV (Figure 5-9C), in agreement with prior reports (\(E_{\text{G}} = 2.0—2.2\) eV).\textsuperscript{141-150}
The optical characteristics of the plasmonic photocathodes (Cu$_2$O/Au@SiO$_2$) retain the peaks attributable to the interband transitions of the Cu$_2$O nanowires, but exhibit an additional spectroscopic feature in the visible region centered at $\lambda_{\text{max}} = 525$ nm due to the LSPR of the Au@SiO$_2$ nanoparticles (Figure 5-9B, blue line). Although the overall extinction was enhanced throughout the entire visible spectrum, it must be emphasized that the most substantial improvements occurred in the spectral region commensurate with the LSPR of the Au nanoparticles ($\lambda \sim 500—600$ nm). This increased extinction at longer wavelengths imparts a more balanced absorption profile to the plasmonic system throughout the visible region than originally obtained with the Cu$_2$O-only device. These results suggest that the substantial optical cross section of the plasmonic nanoparticles effectively augments the weak optical response of the Cu$_2$O nanowires near the band edge ($h\nu \sim 2.0—2.4$ eV).

**Photoelectrochemical Properties of Control and Plasmonic Photocathodes**

The photoelectrochemical properties of the photocathodes were then investigated via an electrochemical cell in a standard three-electrode configuration with a supporting electrolyte (pH $\sim 6$) composed of 0.10 M Na$_2$SO$_4$ (see Experimental Methods for details). The p-type Cu$_2$O photocathode served as the working electrode (working area of 2 cm$^2$), with a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. All electrode potentials ($E_{\text{appl}}$) are reported relative to the Reversible Hydrogen Electrode (RHE) using Equation 5-1. The photoelectrochemical stability of the Cu$_2$O nanowires was first evaluated via chronoamperometry with the photocathodes potentiostatically poised at 0 V$_{\text{RHE}}$(V vs. RHE) while subjected to periodic ($t = 2$ s on/off) AM 1.5G irradiation at 3-sun intensity ($I_0 = 300 \pm 10$ mW cm$^{-2}$). As shown in Figure 5-10A, the Cu$_2$O device displayed reproducible and stable cathodic photocurrents ($J_{\text{ph}} =$
−42 ± 3 μA cm−2) for 20 min, indicating superior photoelectrochemical stability relative to most Cu2O-based photocathodes.141-150 It was recently demonstrated that Cu2O can be rendered electrochemically stable through passivation of the semiconductor surface with carbon-based coatings derived from glucose precursors.156,157 The considerable stability observed during controlled potential electrolysis over 20 min indicates that the α-D-glucose initially used to synthesize the Cu2O nanowires confers a similar carbon layer (Figure 5-3 and Figure 5-4) capable of stabilizing the semiconductor surface against photocorrosion and enabling extended operation in aqueous environments. Extended photoelectrochemical operation over 1 h further confirms the stability of the Cu2O-based photocathodes (Figure 5-11). These C-coated Cu2O nanowires thereby constitute the basis for a robust photoelectrochemical platform to study plasmonic enhancement mechanisms in p-type photocathodes.

A comparison of photoelectrochemical activity for the plasmonic device (Cu2O/Au@SiO2) and the control device (Cu2O-only) is presented in Figure 5-10B to G. The Au@SiO2 nanoparticles with the thinnest SiO2 shell of 5 ± 2 nm (Figure 5-9A, inset) were used for all plasmonic photocathodes unless otherwise specified. The optimal Au@SiO2 nanoparticle loading was first investigated to determine a suitable ratio between the plasmonic metal and semiconductor components for achieving the maximum photocurrent (Jph) from the plasmonic device. The initial addition of Au@SiO2 nanoparticles induces a monotonic increase in Jph at 0 V RHE until 0.5 ± 0.1 wt.%, at which point a plateau is reached up to ~1.0 ± 0.1 wt.% before a rapid decline in device performance was observed with further loading of 1.8 ± 0.1 wt.% (Figure 5-10B). We attribute this reduction at increased Au@SiO2 nanoparticle loading to photonic
competition between Au nanoparticles and Cu$_2$O nanowires for incident light, as both components absorb similar regions of the solar spectrum (Figure 5-9). This observation is also consistent with a recent theoretical model developed to interpret this empirical phenomenon, which is based on the changing spatial location of the enhanced near-fields within the device as a function of metal nanoparticle loading.$^{168}$ The optimized Au@SiO$_2$ loading of 0.5 ± 0.1 wt.% was adopted for all subsequent photoelectrochemical experiments. As shown in Figure 5-10C, the Cu$_2$O photocathodes were found to display a turn-on potential ($E_{on}$) of ca. 0.4 V$_{RHE}$, in agreement with previous reports.$^{141-150}$ The incorporation of the Au@SiO$_2$ nanoparticles did not induce any change in $E_{on}$ of the plasmonic device, but did impart a significant increase in $J_{ph}$ at all values of $E_{appl}$ along the potential sweep (Figure 5-10C). In particular, these voltammograms reveal a substantial $J_{ph}$ enhancement at 0 V$_{RHE}$ for the plasmonic device ($J_{ph} = -29 \pm 1 \mu A \ cm^{-2}$) as compared to the control ($J_{ph} = -9 \pm 1 \mu A \ cm^{-2}$). While both photocathodes displayed a linear $J_{ph}$ dependence with respect to incident light intensity, it is noted that the plasmonic device delivered superior $J_{ph}$ (~2 to 3 times) at any given power relative to the Cu$_2$O-only photocathode (Figure 5-10D).

Chronoamperometry [$J_{ph}(t)$] further demonstrated a reproducible 3-fold enhancement in $J_{ph}$ for the plasmonic photocathode upon exposure to periodic (2 s on/off) AM 1.5G irradiation at 1-sun intensity (Figure 5-10E and F).

Photocurrent action spectra [$J_{ph}(\lambda)$] were then acquired to correlate the photoelectrochemical response from the plasmonic and control photocathodes to their optical properties, as shown in Figure 5-10G. A set of band pass filters ($\lambda = 400–700$ nm, $\Delta \lambda = 20 \text{ nm} \pm 10 \text{ nm}$) were coupled with an AM 1.5G optical filter to assess the
incident photon-to-current conversion efficiency (IPCE) of these photocathodes across the solar spectrum. The IPCE of the control device qualitatively emulates the optical extinction of the Cu$_2$O nanowires, although there was a significant drop in IPCE for photon energies below 500 nm (Figure 5-10G, red points). We attribute this decline to the abrupt change in optical cross section for Cu$_2$O in this part of the visible spectrum (~2.5—2.0 eV). In contrast, the plasmonic device (Cu$_2$O/Au@SiO$_2$) displayed a more balanced absorption profile throughout the visible regime (Figure 5-10G, blue points). Notably, the largest improvements were engendered at wavelengths near the band edge of the Cu$_2$O nanowires ($\lambda = 500$ to 600 nm), where the weak optical response of the semiconductor inhibits the efficient absorption of incident light. This enhancement in IPCE at wavelengths coincident with the LSPR of the Au nanoparticles suggests a general strategy for incorporating plasmonic-metal nanostructures into light-harvesting devices to amplify the optical sensitivity of the semiconductor. Controlled potential electrolysis experiments ($E_{appl} = 0 \ V_{RHE}$) were further conducted over a 20 min period to confirm that these plasmonic photocathodes are also stable (Figure 5-12).

The incommensurate length scales required for simultaneously achieving sufficient light absorption ($\alpha^{-1} \sim 2—5 \ \mu m$) and efficient charge extraction ($l_d \sim 5—20 \ nm$) within a semiconductor-based device constitutes a challenging optimization problem commonly encountered in photoelectrochemical cell design. Although increasing the Cu$_2$O film thickness increases the optical density of the semiconductor film (Figure 5-13A and B), it also extends the diffusion distance for excited-state charge carriers within the device. Consequently, a $J_{ph}$ maximum is often observed with respect to semiconductor film thickness. This maximum occurs when the optimal balance between
light absorption and charge carrier extraction has been achieved. Figure 5-13C shows that a $J_{ph}$ maximum occurred for a Cu$_2$O film thickness of ca. 2.8 μm in the control device (filled red points), which is consistent with the reported optical absorption depth ($\alpha^{-1}$) for Cu$_2$O at the band edge ($\alpha^{-1}(600\ nm) = 2.2\ \mu m$).$^{148}$ The dramatic enhancement in light absorption provided by the Au@SiO$_2$ nanoparticles suggests the potential for alleviating this design constraint by harvesting light more efficiently while using less Cu$_2$O material. Indeed, the incorporation of Au@SiO$_2$ nanoparticles into the Cu$_2$O nanowire network substantially shifted the $J_{ph}$ maximum of the plasmonic device to lower Cu$_2$O loadings (~1.6 μm), eliminating the need for ca. 40% of the photoactive material in the plasmonic device (Figure 5-13C, blue points). Such a significant reduction in material requirements suggests the potential for supplementing semiconductor-based devices with plasmonic-metal nanostructures to boost the light harvesting capability of the photoactive layer while maintaining appropriate device dimensions to ensure efficient charge carrier collection.

Additional photoelectrochemical studies were then conducted to confirm that the device enhancement originates from improved light absorption by the Cu$_2$O nanowires. It has previously been shown that frontside illumination generates the majority of electron-hole (e-h) pairs farther away from the FTO back contact compared to backside illumination.$^{169,170}$ As a result, this condition increases the average diffusion distance for the majority carriers ($h^+$) and subsequently hinders the charge collection efficiency within the nanowire network. We therefore expected that the $J_{ph}$ obtained during frontside illumination would be diminished more significantly as the semiconductor film thickness was increased, because the thicker films would more effectively absorb
incident light. This phenomenon was quantified by comparing the $J_{ph}$ % difference between illumination directions, as plotted on the right ordinate axis in Figure 5-13C (open points). Indeed, the $J_{ph}$ % difference became more pronounced with increasing Cu$_2$O film thickness in the control device (Figure 5-13C, open red points). This phenomenon was further exacerbated by the incorporation of the Au@SiO$_2$ nanoparticles, as we observed a steeper increase in $J_{ph}$ % difference as a function of Cu$_2$O film thickness for the plasmonic device as compared to the control (Figure 5-13C, open blue points). These results strongly suggest that the device enhancements provided by the plasmonic nanoparticles originate from increased light-harvesting efficiency within the photoactive Cu$_2$O layer.

To correlate the device performance with the optical properties of the Au@SiO$_2$ nanoparticles, additional photoelectrochemical experiments were conducted under various excitation conditions (Figure 5-13D). In general, these data show that as the Cu$_2$O film becomes thicker, it absorbs all wavelengths of incident light more proficiently, increasing the overall $J_{ph}$ % difference for both plasmonic (filled points) and control (open points) devices. Since the light absorption depth ($\alpha^{-1}$) for Cu$_2$O varies as a function of wavelength ($\alpha^{-1}(620 \text{ nm}) = 5.2 \mu\text{m}; \alpha^{-1}(500 \text{ nm}) = 0.8 \mu\text{m}$), it is expected that these distinct wavelength ranges should show different dependencies on the Cu$_2$O film thickness. Indeed, by taking the slope of these curves to indicate the extent to which incident light is absorbed by the semiconductor film, a substantial discrepancy in light absorption is observed across different wavelengths (compare slope of open blue points to open green points in Figure 5-13D). In contrast, the slopes of the $\lambda > 435 \text{ nm}$ curve (Figure 5-13D, filled blue points) and $\lambda > 515 \text{ nm}$ curve (Figure 5-13D, filled green
points) for the plasmonic device are nearly identical. This increase represents a substantial improvement in the utilization of incident light with the plasmonic device as compared to the control. Interestingly, although the slope of the $\lambda > 435$ nm curves don’t significantly differ between plasmonic (Figure 5-13D, filled blue points) and control (Figure 5-13D, open blue points), the entire curve has been shifted upward with respect to Cu$_2$O film thickness. This shift in $J_{ph}$ % difference further indicates an overall improvement in light absorption at most visible-light wavelengths for the plasmonic device as compared to the control. It is also noted that even $\lambda > 610$ nm are attenuated within the plasmonic device with increasing Cu$_2$O film thickness, whereas the control device registers no difference in light absorption at these longer wavelengths regardless of the Cu$_2$O film thickness. Taken together, these photoelectrochemical studies strongly suggest that the device enhancements observed in the plasmonic photocathode originate from enhanced light absorption within the Cu$_2$O nanowires.

**Photoluminescence Studies of Cu$_2$O-Only and Cu$_2$O/Au@SiO$_2$ Devices**

To confirm that the $J_{ph}$ enhancements in the plasmonic device originate from increased light absorption due to the incorporation of Au@SiO$_2$ nanoparticles, the photoluminescence (PL) spectra of both control (Cu$_2$O-only) and plasmonic (Cu$_2$O/Au@SiO$_2$) devices were acquired and analyzed (see Experimental Methods section for details). Assuming the PL emission originates solely from radiative recombination of photogenerated electron-hole pairs within the semiconductor after optical excitation, examination of the PL spectrum provides a way to evaluate the light-harvesting efficiency of the device.$^{171-173}$ As the near-field EM mechanism is only operative at wavelengths where the optical absorption of the semiconductor and the LSPR of the plasmonic metal overlap,$^{57-61}$ a 532 nm laser ($\sim$2.3 eV) was used to ensure
simultaneous excitation of both constituents. A broad PL signal centered at ca. 2 eV was observed from the control device (Cu$_2$O-only) following irradiation with the 532 nm laser (Figure 5-14), indicating that PL emission occurs primarily via free-carrier recombination near the band edge. Significantly, the plasmonic device (Cu$_2$O/Au@SiO$_2$) displayed more than 3 times greater PL emission than the control device (Figure 5-14). It must be emphasized that this PL enhancement shows close agreement to the $J_{ph}$ enhancement (~3 times) observed via linear sweep voltammetry (Figure 5-10C) and chronoamperometry (Figure 5-10F). Such a direct correlation between the $J_{ph}$ and PL enhancements strongly suggests that the improved photoelectrochemical performance observed in the plasmonic device is attributable to increased light-harvesting efficiency.

**Elucidating the Enhancement Mechanism**

The three principle plasmonic enhancement mechanisms that have been commonly invoked in literature to explain the device enhancements observed experimentally include: (1) resonant photon scattering, (2) hot electron transfer, and/or (3) resonant energy transfer.\(^{57-61}\) In the Cu$_2$O/Au@SiO$_2$ system, the contribution from resonant photon scattering is negligible since the small size of the Au nanoparticles ($d = 10$ nm) substantially limits their scattering cross section.\(^{57,58}\) We also exclude increased photon scattering from the SiO$_2$ shell itself, as the integration of 12 nm SiO$_2$ nanoparticles into the Cu$_2$O device (Cu$_2$O/SiO$_2$-only) had no significant effect on the $J_{ph}$ of the photocathode (Figure 5-15A and B). Additionally, the use of a dielectric SiO$_2$ shell to encapsulate the Au nanoparticle also precludes the possibility of direct electron transfer between the Au nanoparticles and the Cu$_2$O nanowires. It is noted that the incorporation of 10 nm Au nanoparticles without SiO$_2$ coating into the Cu$_2$O device
(Cu₂O/Au-only) actually hindered the photoelectrochemical performance of the composite system (Figure 5-15C and D). Subsequent PL measurements indicated that these metal nanoparticles quench the excited-state of the Cu₂O nanowires if not coated by a SiO₂ shell (Figure 5-16). Therefore, the only likely plasmonic enhancement mechanism operative in the present system (Cu₂O/Au@SiO₂) must be associated with the presence of the enhanced EM fields generated by the Au nanoparticles.

Influence of SiO₂ Shell Thickness on Cu₂O/Au@SiO₂ Devices

The signature of a near-field EM enhancement mechanism involves the rapid decay of device performance with increased separation distance between the plasmonic-metal nanostructure and the adjacent semiconductor. To evaluate this proposed mechanism, the \( J_{\text{ph}} \) enhancements observed for the Au@SiO₂ nanoparticles containing the thinnest SiO₂ shell (5 ± 2 nm) were compared to that of devices composed of Au@SiO₂ nanoparticles with thicker SiO₂ shells of 9 ± 1 nm, 15 ± 1 nm, and 22 ± 2 nm (Figure 5-17). Indeed, Figure 5-18 (red points) shows that the \( J_{\text{ph}} \) enhancement factor [\( J_{\text{ph}} \) EF = \( J_{\text{ph}} \) (plasmonic)/\( J_{\text{ph}} \) (control)] was increasingly attenuated as the silica shell thickness increased. Such a rapid decline in device performance indicates that the plasmonic enhancement is highly sensitive to the spatial separation between the Au nanoparticles and the Cu₂O nanowires.

The light absorption properties of these devices were then further correlated with their \( J_{\text{ph}} \) enhancements by acquiring their PL spectra (Figure 5-19) and plotting their respective PL EFs as a function of SiO₂ shell thickness. As shown in Figure 5-18, a rapid decay in the PL EF was observed with increasing SiO₂ shell thickness (blue points) that was nearly identical to the trend observed for the \( J_{\text{ph}} \) EF obtained from photoelectrochemical measurements (red points). Such a striking similarity between the
$J_{\text{ph}}$ EF and the PL EF confirms that the improved photoelectrochemical performance of the plasmonic device is attributable to enhanced light absorption due to the incorporation of Au@SiO$_2$ nanoparticles into the Cu$_2$O nanowire network. We also emphasize that the trends observed in both PL and $J_{\text{ph}}$ enhancements are reminiscent of the well-known distance dependence of the EM field distribution around plasmonic-metal nanoparticles, implicating a near-field EM mechanism.

Optical simulations were then performed within the context of the discrete dipole approximation (DDA) to assess the influence of these local fields on the nearby Cu$_2$O nanowires (see Experimental Methods section for details). The Au@SiO$_2$ nanoparticles were modeled as concentric spheres immersed in a uniform dielectric medium (i.e. water) with physical dimensions congruent with those observed by HRTEM (Figure 5-6 and Figure 5-7). The spatial extent of the electric-field enhancement ($|E/E_0|^2$) around these Au@SiO$_2$ nanoparticles under the incidence of visible light ($\lambda = 525$ nm) is shown in Figure 5-20. As anticipated, the highest $|E/E_0|^2$ intensity was obtained for the Au@SiO$_2$ nanoparticles with the thinnest SiO$_2$ shell of 5 nm (Figure 5-20). The electric field enhancement ($|E/E_0|^2$) at a fixed distance of 1 nm from the SiO$_2$ surface was then plotted as a function of SiO$_2$ shell thickness with the $J_{\text{ph}}$ and PL enhancements to better correlate the theoretical trend with those of experiment (Figure 5-18, black points). There is a clear decrease in $|E/E_0|^2$ with increasing SiO$_2$ shell thickness, as the SiO$_2$ shell effectively modulates the distance between the enhanced EM fields from the Au nanoparticles and their surrounding environment. Notably, the distance dependence of this $|E/E_0|^2$ enhancement emulates the trends observed for both $J_{\text{ph}}$ and PL EFs as a function of SiO$_2$ shell thickness, confirming that the photoelectrochemical performance
is enhanced by this near-field mechanism. These spatially inhomogeneous EM near-fields increase the optical transition rate within the adjacent semiconductor, thereby enhancing the photocatalytic reaction rate of the plasmonic composite.

**Summary of Results**

We have unambiguously isolated the EM near-field contribution from plasmonic-metal nanoparticles on the light-harvesting efficiency of a p-type semiconductor via integration of Au@SiO$_2$ nanoparticles into Cu$_2$O-based photocathodes (Cu$_2$O/Au@SiO$_2$). The plasmon-enhanced photocathodes displayed increased IPCE at wavelengths commensurate with the LSPR of the Au nanoparticles to yield a 3-fold increase in $J_{ph}$ as compared to control photocathodes. PL studies were coupled with these photoelectrochemical measurements to demonstrate that this improved device performance was attributable to increased light absorption in the Cu$_2$O nanowire network due to the introduction of Au@SiO$_2$ nanoparticles. Systematic attenuation of this device enhancement via manipulation of the SiO$_2$ shell thickness (5—22 nm) provided conclusive evidence that the increased light absorption was directly attributable to the locally enhanced EM fields generated by the Au nanoparticles.

Experimental results were further correlated with electromagnetic field simulations to confirm that the device enhancements occur via this near-field mechanism. Notably, we discovered that this approach enabled substantial improvements in light absorption within the photoactive layer while alleviating the requirement for thicker semiconductor films that often adversely affect charge carrier collection.

This systematic study establishes general plasmonic design rules for augmenting semiconductor-based devices with plasmonic-metal nanostructures. Our results show that a plasmonic enhancement strategy based upon the exploitation of these enhanced
EM near-fields would be most successful at photon energies where the semiconductor exhibits a small optical cross section. It is noted that these plasmonic-metal nanostructures must be used sparingly, however, so as to minimize photonic competition between material components for incident photons (Figure 5-10B). Therefore, it is important to consider the unique optical properties of different material building blocks in order to most effectively harvest incident light within a composite system. The ability to reduce the semiconductor film thickness by ca. 40% while maintaining device performance represents a significant step towards decoupling the light absorption efficiency from the charge carrier mobility of a semiconductor-based device. This near-field enhancement strategy is therefore expected to be particularly advantageous for materials plagued by poor minority carrier diffusion lengths since the photocatalytic reaction rate can be increased without adversely affecting the overall carrier collection efficiency of the device. The wide variety of anisotropic architectures accessible by wet-chemical synthesis suggests that such an approach could be employed within a multitude of light-harvesting systems to amplify the absorption profile in regions of the solar spectrum otherwise untapped by the device. Taken together, these results demonstrate the potential opportunities provided by plasmonic-metal nanoparticles for improving the light-harvesting efficiency of semiconductor-based devices for photoelectrochemical applications. We anticipate that these insights will further the eventual establishment of a general set of design principles to guide the pursuit of plasmonic photocatalysts for efficient solar-to-fuel energy conversion.
Figure 5-1. Morphology and physical dimensions of Cu$_2$O nanowires. A) TEM image of Cu$_2$O nanowires. B) TEM image of Cu$_2$O nanowires. C) TEM image of Cu$_2$O nanowires. D) SEM image of Cu$_2$O nanowires on FTO glass substrates, forming Cu$_2$O-based photocathodes. E) SEM image of Cu$_2$O-based photocathodes. F) SEM image of Cu$_2$O-based photocathodes. Although some nanowires exhibit shorter lengths due to damage during sample preparation, a cursory inspection of the TEM images (A to C) reveals that the majority of these nanowires display diameters ($d$) of 80 ± 10 nm and typical lengths ($l$) of 10—25 μm. The tendency for these high-aspect ratio (~100—300) nanowires to form interwoven nanowire networks upon drying of the substrate is also apparent (B to C). This propensity for forming intertwined nanowire mats over a large area is more clearly shown by the SEM images (D to F). Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-2. Structural characterization of Cu$_2$O nanowires. A) XRD pattern of Cu$_2$O nanowires after deposition onto the FTO glass substrate. The peaks are indicative of the Cu$_2$O phase and labeled accordingly. No signs of metallic Cu or CuO phases were observed in the XRD pattern, indicating that these nanowires are composed of the Cu$_2$O phase. The peaks marked by an asterisk (*) denote those features from the underlying FTO substrate itself. B) Raman spectrum of Cu$_2$O nanowires. From group theory, a single Raman-active mode ($T_{2g}$) is predicted, although several other features were observed that correspond well with the Raman spectrum of Cu$_2$O from previous reports. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-3. Electron microscopy characterization of Cu$_2$O nanowires. A) HRTEM image of a single Cu$_2$O nanowire; black arrows highlight the amorphous layer along the length. B) High-magnification HRTEM image showing the amorphous layer coating the Cu$_2$O nanowire surface. C) High-magnification HRTEM image showing the crystal planes of the nanowire. Inset in (C) shows the FFT from the nanowire taken along the [101] zone axis with reflections indexed to the Cu$_2$O phase. D) ADF-STEM image of an individual Cu$_2$O nanowire showing the amorphous layer coating the Cu$_2$O surface (highlighted by white arrows). E) ADF-STEM image showing the lattice of the Cu$_2$O nanowire with crystal planes indexed to the Cu$_2$O phase. F) SAED pattern along the [101] zone axis from the nanowire shown in (E) with reflections indexed to those of the Cu$_2$O phase. Images courtesy of Dr. A. C. Johnston-Peck at the Center for Functional Nanomaterials, Brookhaven National Lab, Upton, NY. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-4. Electron energy loss spectroscopy (EELS) mapping of Cu$_2$O nanowires. Investigation of the chemical composition of these nanowires by A) ADF-STEM imaging with corresponding EELS mapping of the elemental distribution of B) convolution of all three copper (Cu, blue), oxygen (O, red), and carbon (C, green) signals, C) copper signals (Cu, blue), D) oxygen signals (O, red), D) and E) carbon signals (C, green) from a single Cu$_2$O nanowire. From these maps it is clear that a C/O layer persists along the length of the Cu$_2$O nanowires, which we assign to that of glucose present in the initial nanowire synthesis. The 20 nm scale bar at the bottom of the figure applies to all images (A to E). Images courtesy of Dr. A. C. Johnston-Peck at the Center for Functional Nanomaterials, Brookhaven National Lab, Upton, NY. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-5. X-ray photoelectron spectroscopy (XPS) of Cu$_2$O nanowires. A) Full scan XPS spectrum of Cu$_2$O nanowires with corresponding narrow scan XPS spectra of B) copper (Cu) 2p region, C) oxygen (O) 1s region, and D) carbon (C) 1s region. The Cu 2p region in (B) shows binding energies of 932.8 eV and 952.6 eV for the Cu 2p 3/2 and Cu 2p 1/2, respectively. The absence of any significant satellite peaks between 938-948 eV and 958-968 eV from possible CuO phase in our spectra further supports Cu$_2$O as the dominant phase. The O 1s region in (C) shows a broad feature centered at 531 eV with a discernible shoulder at lower binding energies. Deconvolution of this main feature suggests a contribution from the O atoms in the Cu$_2$O lattice itself (530.8 eV) and those O atoms bound to C (532.1 eV), likely from the glucose species. The C 1s region (D) shows a main peak from adventitious C at 284.8 eV, but also revealed the presence of a significant shoulder at higher binding energy. Deconvolution of this main peak into its components showed this shoulder could be fit by another peak centered around 288.4 eV, similar to that previously reported for C-coated Cu$_2$O nanowires. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-6. Au nanoparticles prior to deposition of SiO$_2$ shells. A) TEM image of Au nanoparticles showing size distribution. B) TEM image of Au nanoparticles. C) High-magnification TEM image showing a selected region of Au nanoparticles on the TEM grid. D) Size distribution histogram of Au nanoparticles showing an average diameter ($d$) of $d = 10 \pm 1$ nm. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-7. Physical dimensions and size distributions of Au@SiO$_2$ (core@shell) nanoparticles. TEM images and corresponding size-distribution histograms for 10 nm Au nanoparticles encapsulated by SiO$_2$ shells of various thicknesses: A to D) 5 ± 2 nm, E to H) 9 ± 1 nm, I to L) 15 ± 1 nm, and M to P) 22 ± 2 nm. Over 200 nanoparticles were counted for each of the four different Au@SiO$_2$ samples to construct the size distribution histograms. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-8. Optical properties of Au and Au@SiO$_2$ nanoparticles. A) UV-visible extinction spectra of Au@SiO$_2$ nanoparticles with a 10 nm Au nanoparticle core encapsulated by different thicknesses of SiO$_2$ shells: 5 ± 2 nm, 9 ± 1 nm, 15 ± 1 nm, and 22 ± 2 nm SiO$_2$ shells. B) A slight red shift in LSPR peak maximum ($\lambda_{\text{max}}$) was observed upon deposition of the SiO$_2$ shell, shifting from 521 nm for uncoated Au nanoparticles to 525 nm for Au@SiO$_2$ nanoparticles. However, after the initial change in $\lambda_{\text{max}}$, no significant shift was observed. We do note a slight increase in extinction occurring at shorter ($\lambda < 460$ nm) and longer ($\lambda > 600$ nm) wavelengths for the thickest SiO$_2$ shells (22 ± 2 nm). Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-9. Optical properties of materials used for plasmonic and control photocathodes. A) Extinction spectrum of Au nanoparticles (dashed blue curve) and Au@SiO$_2$ (solid blue curve) dispersed in H$_2$O. A modest red-shift in ($\lambda_{\text{max}}$) was observed upon deposition of the SiO$_2$ shell, shifting from 521 nm for uncoated Au nanoparticles to 525 nm for Au@SiO$_2$ nanoparticles. Inset shows a TEM image of a typical Au@SiO$_2$ nanoparticle used for construction of the plasmonic photocathodes. B) Absorbance spectra (Kubelka-Munk) of control (Cu$_2$O-only) photocathodes (red curve), plasmonic (Cu$_2$O/Au@SiO$_2$) photocathodes (blue curve) and FTO glass substrates (black curve) obtained by diffuse reflectance measurements. Inset shows a digital photograph of both control (i) and plasmonic (ii) devices. C) A Tauc plot of the control device used to extract the band gap ($E_G$) of the Cu$_2$O nanowires. From extrapolation of this curve we find that $E_G$ is ca. 2.1 eV. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-10. Photoelectrochemical properties of Cu$_2$O-only (red) and Cu$_2$O/Au@SiO$_2$ (blue) photocathodes. A) Controlled potential electrolysis of Cu$_2$O photocathode exposed to periodic ($t = 2$ s on/off) AM 1.5G irradiation at 3-sun intensity ($I_0 = 300$ mW cm$^{-2}$). Inset shows the period from 5—6 min to better show the periodic $J_{ph}$ response. B) Influence of Au@SiO$_2$ loading (wt.%) on the device photocurrent ($J_{ph}$). C) Influence of applied electrode potential ($E_{appl}$) on the device $J_{ph}$. D) Influence of incident light power ($I_0$) on device $J_{ph}$ under AM 1.5G irradiation. E) Controlled potential electrolysis ($E_{appl} = 0$ V RHE) of photoanodes under periodic ($t = 2$ s on/off) AM 1.5G irradiation at 1-sun intensity ($I_0 = 100$ mW cm$^{-2}$). F) Expanded view of (E) from $t = 120$—180 s showing that the plasmonic device produces ca. 3 times more photocurrent ($J_{ph} = -29 \pm 1$ μA cm$^{-2}$) than the control ($J_{ph} = -9 \pm 1$ μA cm$^{-2}$). G) Incident photon-to-charge conversion efficiency (IPCE) of plasmonic and control photoanodes. All error bars represent standard deviation. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-11. Extended photoelectrochemical stability of Cu$_2$O photocathodes. SEM images of control (Cu$_2$O-only) photocathodes A) before and B) after extended photoelectrochemical testing for 1 h, rather than the shorter 20 min period usually employed for evaluation of Cu$_2$O photocathodes. C) Controlled potential electrolysis of the control photocathode poised at 0 V$_{RHE}$ and irradiated with periodic (5 min on/off) AM 1.5G light at 300 ± 25 mW/cm$^2$ for 1 h. The stability of the photocathode was evaluated by comparing the $J_{ph}$ at 5 min ($J_5$) to that observed at 55 min ($J_{55}$), which showed that ca. 82% of the initial $J_{ph}$ was retained after the 1 h irradiation period. This value is very similar to that previously reported for Cu$_2$O photocathodes employing C-based coatings (80%). D) X-ray diffraction pattern of Cu$_2$O-based photocathode before (black curve) and after (red curve) 1 h of controlled potential electrolysis shown in (C). The peaks marked by an asterisk (*) denote those features from the underlying FTO substrate itself. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
The photoelectrochemical stability of the plasmonic photocathode was investigated in a similar manner to that employed for the control device. The plasmonic photocathode was first poised at 0 V\textsubscript{RHE} for 20 min in the dark (black curve) to determine the stability of these materials under the influence of the applied bias itself (\(E_{\text{appl}} = 0\) V\textsubscript{RHE}) while in the dark. The experiment was then repeated at the same potential (0 V\textsubscript{RHE}) under AM 1.5G irradiation at 100 ± 10 mW/cm\(^2\) for another 20 min (red curve). A steady-state \(J_{\text{ph}}\) was achieved after ~2 min and maintained over the 20 min irradiation period without any sign of electrochemical degradation. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-13. Influence of Cu$_2$O film thickness on optical properties and device performance of control and plasmonic photocathodes. A) Extinction spectra of Cu$_2$O-only photocathodes of varying semiconductor film thickness from 0.5 ± 0.2 μm to 3 ± 0.2 μm. B) Extinction at 465 nm from plot (A) showing a linear increase in extinction with increasing Cu$_2$O film thickness. C) Influence of Cu$_2$O film thickness on photocurrent ($J_{ph}$) produced from plasmonic (filled blue points) and control (filled red points) devices (left ordinate axis). The $J_{ph}$ % difference between frontside (through Cu$_2$O) and backside (through FTO) illumination for the plasmonic (open blue points) and the control (open red points) devices are plotted on the right ordinate axis. The $J_{ph}$ difference [$\Delta J_{ph} = J_{ph}$(backside) − $J_{ph}$(frontside)] was used to calculate the $J_{ph}$ % difference. D) The $J_{ph}$ % difference produced by the plasmonic device (filled points) and the control device (open points) as a function of Cu$_2$O film thickness under different irradiation wavelengths: λ > 435 nm (blue), λ > 515 nm (green), and λ > 610 nm (red). All error bars represent standard deviation. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-14. Average photoluminescence (PL) spectra of control and plasmonic photocathodes. A) SEM image of control (Cu$_2$O-only) photocathode. B) SEM image of plasmonic (Cu$_2$O/Au@SiO$_2$) photocathode involving 10 nm Au nanoparticles coated with SiO$_2$ shells of 5 ± 2 nm. C) PL spectra for the control (Cu$_2$O-only) photocathode (black curve) and the plasmonic photocathode (blue curve) under 532 nm laser excitation. These data represent average PL signals taken from at least 9 different spots to remove sampling variability caused by film irregularity. A 532 nm laser was chosen to ensure simultaneous excitation of both the Cu$_2$O nanowires and the Au@SiO$_2$ nanoparticles. A broad PL signal centered at ca. 2.1 eV was observed for all devices, indicating that recombination in these nanowires occurs primarily by radiative recombination via electron-hole pairs near the band edge of Cu$_2$O ($E_G$ ~2.0 eV). The incorporation of Au@SiO$_2$ nanoparticles into the device increases the PL emission of the Cu$_2$O nanowires by ca. 3 times compared to the control device. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-15. Photoelectrochemistry of control photocathodes (Cu$_2$O/Au-only and Cu$_2$O/SiO$_2$-only). Controlled potential electrolysis experiments were conducted under 1-sun AM 1.5G irradiation at 0 V$_{RHE}$ for Cu$_2$O-based photocathodes containing: A and B) SiO$_2$-only nanoparticles or C and D) Au-only nanoparticles. The incorporation of 12 nm SiO$_2$ nanoparticles into the Cu$_2$O-only device exerted little effect on device performance ($J_{ph} = -8 \pm 1$ μA cm$^{-2}$) compared to that of the control device ($J_{ph} = -9 \pm 1$ μA cm$^{-2}$). In contrast, the introduction of 10 nm Au nanoparticles into the Cu$_2$O-only device substantially reduced device performance ($J_{ph} = -4 \pm 1$ μA cm$^{-2}$) compared to the control ($J_{ph} = -9 \pm 1$ μA cm$^{-2}$). Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-16. Photoluminescence (PL) of photocathodes with uncoated Au nanoparticles. A) SEM image of Cu$_2$O/Au-only plasmonic photocathode. B) SEM image of Cu$_2$O/Au-only plasmonic photocathode showing distribution of Au nanoparticles along the Cu$_2$O nanowires. C) PL spectrum of the Cu$_2$O-only (red curve) and the Cu$_2$O/Au-only photocathode (blue curve). The introduction of uncoated Au nanoparticles without SiO$_2$ shells into the Cu$_2$O-based device almost completely quenched the PL signal from the Cu$_2$O nanowires (blue curve). This result confirms that the Au nanoparticles act as electron sinks to quench the excited state of the semiconductor within the nanowire network if not covered by an insulating SiO$_2$ shell. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-17. SEM images of plasmonic Cu2O/Au@SiO2 photocathodes. Plasmonic photocathode composed of Au@SiO2 nanoparticles with different SiO2 shell thicknesses: A and B) 5 ± 1 nm SiO2 shell, C and D) 9 ± 1 nm SiO2 shell, E and F) 15 ± 1 nm SiO2 shell, G and H) 22 ± 2 nm. These images show that the drop-casting methods used for plasmonic photocathode fabrication provide a roughly homogeneous distribution of Au@SiO2 nanoparticles embedded on and within the Cu2O nanowire network. It is also apparent from these images that the thickness of the SiO2 shell affects the distribution of these Au@SiO2 nanoparticles within the nanowire networks. The Au@SiO2 nanoparticles encapsulated by thicker SiO2 shells tend to spread out over a larger area compared to those covered with thinner SiO2 shells, as the thicker SiO2 coatings prevent the Au cores from ever becoming too close together. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-18. Correlating the device enhancements observed in plasmonic photocathodes with the plasmonic near-fields. Influence of Au-Cu$_2$O separation distance (modulated by SiO$_2$ shell thickness) on the photocurrent ($J_{ph}$, red), photoluminescence (PL, blue), and electromagnetic field ($|E/E_0|^2$, black) enhancement factors (EFs) for the plasmonic (Cu$_2$O/Au@SiO$_2$) photocathodes containing Au@SiO$_2$ nanoparticles of different SiO$_2$ shell thicknesses (5—22 nm). The direct relation between the improvements in device performance and the electromagnetic near-field EF indicates that the device enhancement originates solely from the near-field mechanism. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-19. SEM images and corresponding photoluminescence (PL) spectra of control and plasmonic photocathodes containing Au@SiO$_2$ nanoparticles coated with SiO$_2$ shells of various thickness: A) 5 ± 2 nm, B) 9 ± 1 nm, C) 15 ± 1 nm, and D) 22 ± 2 nm. Insets show TEM images of individual Au@SiO$_2$ nanoparticles. E) Corresponding PL spectra for control (Cu$_2$O-only) photocathodes (black curve) and plasmonic photocathodes (Cu$_2$O/Au@SiO$_2$) as a function of SiO$_2$ shell thickness under 532 nm laser excitation. These data represent average PL signals taken from at least 9 different spots to remove any variability caused by film irregularity. A 532 nm irradiation wavelength was chosen to ensure simultaneous excitation of both the Cu$_2$O nanowires and the Au@SiO$_2$ nanoparticles. A broad PL signal centered at ca. 2.1 eV was observed for all devices, indicating that recombination in these nanowires occurs primarily by radiative recombination via electron-hole pairs near the band edge of Cu$_2$O ($E_G$ ~2.0 eV). Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
Figure 5-20. Electric field distribution around Au@SiO$_2$ nanoparticles as a function of SiO$_2$ shell thickness. TEM images along with corresponding DDA simulation results showing the spatial distribution of the electric field enhancement ($|E/E_0|^2$) around Au@SiO$_2$ nanoparticles coated with SiO$_2$ shells of various thickness: A and B) 5 nm, C and D) 9 nm, E and F) 15 nm, and G and H) 22 nm. The Au@SiO$_2$ nanoparticles were modeled as concentric spheres with physical dimensions congruent with those observed by TEM (Figure 5-7). A cursory inspection of these plots shows that the highest $|E/E_0|^2$ intensity was obtained for the Au@SiO$_2$ nanoparticles with the thinnest SiO$_2$ shell of 5 nm. These plots further show that these fields extend away from the SiO$_2$ surface into the surrounding water medium. Cu$_2$O nanowires within close proximity to these Au@SiO$_2$ nanoparticles should encounter these enhanced electric fields and exhibit increased photon absorption rates. Adapted with permission from DuChene et al. Copyright 2015 Advanced Energy Materials.
CHAPTER 6
CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions

Using two completely separate photoelectrochemical systems, we have isolated two distinct plasmonic enhancement mechanisms and systematically studied the effects of these plasmonic processes on the photoelectrochemical performance of n-type photoanodes (TiO$_2$) and p-type photocathodes (Cu$_2$O). Systematic studies of plasmon-enhanced photoelectrochemistry have served to clarify specific design rules that should be considered when constructing plasmonic photocatalysts for solar-to-fuel energy conversion. In particular, we find that the construction of a Schottky barrier at plasmonic-metal/semiconductor (Au/TiO$_2$) heterojunctions is critical for providing a pathway to physically separate charges and prolong the lifetime of hot electrons within the semiconductor conduction band (CB) via plasmon-mediated electron transfer (PMET). We have further followed the fate of hot electrons within the semiconductor CB via \textit{in situ} electron paramagnetic resonance spectroscopy to identify the structural sites of the semiconductor support involved in the PMET process. These studies indicate that hot electrons preferentially populate the rutile phase of TiO$_2$ instead of the anatase phase, suggesting that the increased CB edge of anatase TiO$_2$ hinders hot electron transport across the Schottky barrier. Such an observation confirms the critical influence of interfacial barrier height in regulating hot carrier transmission across the plasmonic-metal/semiconductor heterojunction. Finally, systematic evaluation of the near-field enhancement from plasmonic-metal@dielectric (Au@SiO$_2$) nanoparticles embedded within Cu$_2$O nanowire-based photocathodes demonstrates the merits of augmenting the optical cross section of a semiconductor photodeode with plasmonic nanostructures.
for enhanced light absorption. Such a strategy enabled a significant reduction (ca. 40%) in semiconductor film thickness without sacrificing device performance. These results have significant implications for photoelectrochemical systems, as this approach alleviates traditional design constraints associated with simultaneously optimizing both light absorption and charge carrier collection within a photocatalytic device. Taken together, these studies demonstrate the merits of incorporating plasmonic-metal nanostructures into semiconductor-based photoelectrochemical architectures to amplify the absorption of visible light within the composite. More importantly, our systematic evaluation of these plasmonic enhancement mechanisms has established a general theoretical framework with which to implement these plasmonic principles into the design of more advanced artificial photosynthetic constructs for improved solar-to-fuel energy conversion.

**Future Directions**

Plasmonic photochemistry is quickly emerging as a promising direction for harnessing sunlight to perform chemical reactions.\(^{56-62}\) It must be emphasized that the role of plasmonic nanostructures as sources of hot carriers requires careful reconsideration of the traditional definition of a catalyst: an entity that influences the rate of a reaction but does not alter the outcome. As an active contributor of a reactant in a chemical process (hot electron or hot hole), plasmonic photocatalysts can potentially manifest a new set of reaction products, not just change the overall reaction rate.\(^{56}\) Plasmonic-metal nanostructures offer unique prospects for photocatalysis in this regard, as they couple catalytically-active surfaces of precious metals with similar photophysical properties as traditional semiconductors. There are, however, additional questions that
remain within the field that must be addressed before plasmonic photocatalysts can realize their full potential.

Despite numerous reports of plasmon-enhanced photochemistry for a variety of chemical reactions, little is known about the physical structure of the active sites on plasmonic photocatalysts.\textsuperscript{61} For instance, it is known that isolated reactive sites on metal nanocrystals exhibit markedly different plasmonic properties to sites where two particles are in close proximity to one another, forming plasmonic hot spots. The local electric field is substantially enhanced at such hot spots, and so it is likely that these fields locally enhance both photothermal and charge-transfer effects. It remains unclear, however, whether the photochemical processes occur mainly at these hot spots or across the entire nanostructure surface.\textsuperscript{61} To date, most studies have employed colloidal plasmonic photocatalysts synthesized by wet-chemical methods freely-dispersed in aqueous solution. While such systems are sufficient for establishing photocatalytic activity and establishing performance benchmarks, they are incapable of deciphering the underlying physicochemical processes responsible for chemical activity. Further refinements in our understanding of these photochemical processes require a platform for probing plasmonic photocatalysts at the single-particle level.\textsuperscript{175-179} Such studies would enable a greater understanding of the actual structure of the photocatalytically-active sites on plasmonic nanostructures. In general, the field of plasmonic photocatalysis must move towards well-defined plasmonic structures and surfaces that will enable the requisite level of quantification necessary for establishing true structure-function relationships.
While evidence of plasmonic photochemistry abounds, harvesting hot carriers from plasmonic-metal nanostructures remains a significant challenge. Very little is known about the ensuing energy distributions of hot electrons and hot holes established on the surface of a plasmonic-metal nanocrystal under optical excitation. Detailed photocatalytic studies are required to systematically chart the energy distributions of plasmonic nanostructures as a function of nanocrystal size, shape, and elemental composition. Knowledge of these hot carrier distributions are of paramount importance to photocatalysis: a determination of the energy distribution of these hot carriers allows for predicting which photocatalytic reactions can be performed and what interfacial Schottky barrier heights can be surmounted.

An improved understanding of the factors governing the efficiency of the PMET process across a plasmonic-metal/semiconductor heterojunction is also required to effectively harness hot carriers for photocatalysis. Elucidating key device parameters regulating photoelectrochemical performance is non-trivial, however, as numerous components collectively contribute to the efficiency of the PMET process obtained from the system. To that end, lithographically patterned plasmonic substrates would provide an experimental platform for probing the subtle interplay between the physical dimensions of the plasmonic nanostructure, the internal device architecture, and the interfacial electronic structure that modulates hot electron transfer across the metal-semiconductor heterojunction. It is further unknown how the crystal structure of the metal nanostructure affects the hot carrier production rate and subsequent energy distributions. Fundamental knowledge of these complex relationships is required to furnish plasmon-driven devices for photoelectrochemical applications.
It must be recognized that the eventual deployment of plasmonic technologies on a global scale requires plasmonic photocatalysts be composed of Earth-abundant elements. Although the majority of research on plasmonic photocatalysts to date has involved either Ag or Au-based nanostructures, the use of alternative plasmonic metals (e.g. Al or Cu) and highly-doped metal oxides (e.g. ZnO or ITO) deserve further study. In particular, the plasmonic metals Al and Cu have garnered immense scientific interest, as they offer similar plasmonic performance as the noble metals (Au, Ag, Pd) at a fraction of the cost. Unfortunately, simple strategies for the synthesis of nanostructures composed of these alternative plasmonic metals are lacking, exacerbated by difficulties associated with the chemical instability of metallic Al and Cu in ambient air. Nevertheless, the eventual implementation of plasmonic technologies will require a shift towards these more abundant elements to provide affordable plasmonic systems.

In what follows, several new avenues of both fundamental and applied plasmon-driven photocatalysis are proposed. A new approach based on electrochemical deposition is proposed to provide the level of control over nanoscale features required to perform detailed studies of plasmon-driven photocatalysis while simultaneously leveraging established methods to ultimately fabricate plasmonic photocatalysts using only Earth-abundant elements.

**Alternative Metals for Earth-Abundant Plasmonic Photocatalysts**

The vast majority of plasmonic photocatalysts employ either Ag or Au as the plasmonic metal. While these precious metals are suitable for scientific studies, the eventual implementation of plasmonic photocatalysts on a global scale requires the use of more Earth-abundant elements to ensure scalability. In light of such concerns, we
have begun to explore the use of Cu nanoparticles as visible-light-harvesting sensitizers in a strategy identical to that previously employed for Au/TiO$_2$ photoanodes (Chapter 3). The viability of these alternative plasmonic metals for photocatalysis has been demonstrated through the use of Cu/TiO$_2$ heterostructures, prepared via UV-light photodeposition of CuCl$_2$ salts onto TiO$_2$ nanowire arrays under inert Ar atmosphere. Removing O$_2$ (g) from the solution and reactor headspace gas is critical for obtaining the plasmonic Cu$^{(0)}$ phase as opposed to Cu$_2$O. The photodeposition of Cu nanoparticles onto TiO$_2$ nanowire arrays imparts a purple color to the plasmonic substrate, indicating these nanoparticles are predominantly metallic Cu$^{(0)}$ nanoparticles. Inspection of the device by SEM shows large Cu nanoparticles ca. 220 ± 50 nm in diameter uniformly dispersed across the entire substrate, but primarily located at the tips of the individual TiO$_2$ nanowires (Figure 6-1A). The Cu nanocrystals also present rough surfaces consistent with the presence of a thin Cu$_2$O shell (Figure 6-1B). X-ray diffraction of the Cu/TiO$_2$ heterostructures indicates that the Cu nanoparticles are primarily Cu$^{(0)}$ but do present some features indicative of the Cu$_2$O phase (Figure 6-2A). Analysis of the Cu oxidation state by X-ray photoelectron spectroscopy reveals these nanoparticles to be primarily composed of metallic Cu$^{(0)}$, though a slight degree of surface oxidation consistent with Cu$_2$O is apparent in the Cu 2p spectrum (Figure 6-2B). These data suggest that a surface oxide forms around the Cu nanoparticle upon exposure to ambient air but that the underlying nanocrystal is composed of metallic Cu.

The plasmonic Cu/TiO$_2$ photoanode is expected to exhibit PMET from Cu to TiO$_2$ upon optical excitation of the Cu surface plasmon resonance ($\lambda_{\text{max}} \sim 600$ nm), analogous to that observed for the Au/TiO$_2$ heterostructures. Cyclic voltammetry was first used to
study the electrochemical properties of the plasmonic photoanode in the dark while immersed in 0.1 M Na$_2$SO$_4$ solution (pH 6.7) at a scan rate of 20 mV s$^{-1}$ (Figure 6-3A). The presence of several redox waves attributable to Cu$^{(0)/(I)}$ and Cu$^{(I)/(II)}$ couples were observed upon the negative and positive scans,$^{141-148}$ indicating that these Cu nanoparticles are redox active and that the surface chemistry can be controlled by the applied electrochemical waveform. Controlled potential electrolysis ($E_{\text{appl}} = 1.0$ V$_{\text{RHE}}$) was then used to evaluate the potential for harvesting hot electrons from the Cu nanoparticles under visible-light excitation ($\lambda > 610$ nm). Indeed, Figure 6-3B shows that the Cu/TiO$_2$ photoanodes readily exhibit a prompt $J_{\text{ph}}$ response under periodic ($t = 10$ s on/off) visible-light excitation at an incident power of 1-sun ($I_0 = 100$ mW cm$^{-2}$).

Unfortunately, the chemical instability of Cu nanoparticles under anodic conditions leads to rapid oxidation of Cu$^{(0)}$ and the eventual inactivation of the plasmonic photocatalyst as the periodic $J_{\text{ph}}$ response quickly decays over the course of several minutes (Figure 6-3B). The plasmonic photoanode also changed color over the course of the experiment from purple to white as the Cu nanoparticles increasingly oxidized. Thus, while it is feasible to harvest hot electrons from the Cu nanoparticles, the poor chemical stability of Cu limits continued photoelectrochemical operation under these conditions.

As UV light was used to initially reduce Cu$^{(II)}$ salts in solution to form Cu$^{(0)}$ nanoparticles, it was anticipated that the application of UV light might enable recovering the plasmonic properties of the oxidized species. To investigate this possibility, colloidal TiO$_2$ nanorods were used instead of TiO$_2$ nanowire arrays, and Cu nanoparticles were UV photodeposited onto the surface to form Cu/TiO$_2$ heterostructures (Figure 6-4). These nanostructures exhibit similar optoelectronic properties as the Cu/TiO$_2$
photoanodes, but are much easier to produce in higher yields to enable extensive testing. To mimic photoelectrochemical oxidation, the heterostructures were exposed to ambient air at a known rate for a given period of time and the extinction of the Cu/TiO$_2$ heterostructures at the plasmon resonance ($\lambda_{\text{max}} \sim$600 nm) was monitored to follow the oxidation of the Cu nanoparticles. Over the course of $\sim$10 min, the purple colloid changed to a milky-white suspension and the plasmonic properties of the material is lost, as evidenced by the continued decline in extinction over time (Figure 6-5). Interestingly, however, the oxidized CuO$_x$ species on the TiO$_2$ surface can be recovered via the application of UV light (Figure 6-6). Optical excitation of the TiO$_2$ nanorods generates CB electrons within the TiO$_2$ support that are thermodynamically capable of reducing the CuO$_x$ species on the TiO$_2$ surface back to the original Cu$^{(0)}$ metal. This exceptional recoverability of these plasmonic photocatalysts was further demonstrated by periodically oxidizing and reducing these Cu nanoparticles upon periodic exposure to ambient air and UV light, respectively (Figure 6-6B). Photoelectrochemical cycling experiments are currently underway to assess the prolonged chemical stability of these heterostructures. It was further shown that this plasmonic state may be substantially prolonged under continued UV-light irradiation of the sample, exhibiting plasmonic properties ca. 40% longer under optical excitation as compared to in the dark (Figure 6-7). These results suggest the potential for optically switching between passive (CuO$_x$) and active (Cu metal) oxidation states of plasmonic-metal nanoparticles by controllably interfacing with a semiconductor support and cycling the incident light wavelength. Such a feature may open new avenues for optically controlling catalytic selectivity, as the active sites are manipulated via modulation of the incident light energy.
Energetics of Hot Carriers in Plasmonic Photocatalysts

Hot carriers from plasmonic photocatalysts have participated in photochemistry with a variety of adsorbed surface molecules, but the thermodynamic limits of these processes have yet to be established. In principle, the tunable optical response of plasmonic-metal nanostructures allows for panchromatic photocatalysts that can harvest the entire solar spectrum.\(^5\)\(^7\) For photochemistry to proceed, however, the redox potential of the photo-excited charge carriers on the plasmonic photocatalyst must be sufficient to initiate the reaction.\(^1\)\(^1\)\(^-\)\(^1\)\(^4\) Detailed knowledge of the hot carrier distributions is needed to establish the range of photochemical reactions that can be driven by plasmonic photocatalysts (Figure 6-8A). As the hot carrier distributions of plasmonic metals are governed by the energy of the plasmon resonance itself,\(^5\)\(^6\) the energy distribution of these carriers within the metal is continuously tunable via manipulation of nanostructure morphology (Figure 6-8B). The energetics of these hot carriers as a function of photon energy must be mapped onto the electrochemical energy scale to enable comparison with the redox potentials of various chemical reactions and inform the design of plasmonic photocatalysts for a given purpose. As such, greater fundamental insight into the yield and energy distributions of hot carriers is required to exploit these photophysics for new chemical reactions.

While the incident photon energy determines the extent to which the hot electron distribution is displaced relative to the metal Fermi level (\(\sim E_F \pm \hbar \omega\)), the band structure of the metal itself dictates how this energy is partitioned amongst the respective charge carriers.\(^8\)\(^5\)\(^-\)\(^8\)\(^7\) Recent theoretical studies suggest that the plasmonic metals Al and Ag possess roughly equivalent distributions of hot electrons and hot holes equidistant from the metal Fermi level, while Au and Cu exhibit an inequitable distribution of hot
electrons relative to hot holes.\textsuperscript{85-87} Such a result implies that plasmonic metals like Au and Cu are well suited to perform hot-hole-driven photochemistry but may fail to facilitate reduction reactions or struggle to surmount Schottky barriers when interfaced with n-type semiconductors. Elucidating the influence of intrinsic material properties on the hot carrier distributions would inform the selection of a particular plasmonic metal that could then be further tailored for a given application.

Knowledge of these hot carrier distributions, as a function of both photon and plasmon energy, is critical for the eventual use of plasmonic nanostructures as broadband solar photocatalysts. To date, there have been several reports of near-IR-driven photocatalysis via plasmon excitation of anisotropic Au nanorods.\textsuperscript{104,177,191} Plasmon-driven H\textsubscript{2} evolution has also been correlated with the plasmon-driven production of hot carriers in the metal, but these studies have typically employed sacrificial hole scavengers (i.e. methanol) to alleviate the kinetic hurdles associated with water oxidation. While such an approach is sufficient for isolating the hot electrons, the use of sacrificial reagents inherently restricts simultaneously probing the photocatalytic potential of both hot electrons and hot holes for overall water splitting. As the use of sacrificial reagents is incompatible with sustainable photocatalytic cycles, these initial studies illustrate the opportunities in harvesting hot carriers from plasmonic nanostructures, but fail to provide general principles for guiding the design of solar-driven plasmonic photocatalysts.

To systematically evaluate these hot carrier distributions, we employ a simple electrochemical synthesis strategy that exploits the pores of anodized aluminum oxide (AAO) as templates for the electrochemical deposition of plasmonic-metal nanorods
with continuously tunable physical dimensions (Figure 6-9). Such an approach is favorable over traditional wet-chemical synthesis, as the reproducibility and scalability is substantially improved, while offering additional versatility in photocatalyst design; electrochemical deposition enables the construction of plasmonic-metal/electrocatalyst heterojunctions to facilitate the formidable chemical reactions requisite for overall water splitting (Figure 6-10). Catalytic challenges associated with the sluggish kinetics of water oxidation and reduction requires OER and HER catalysts, respectively, to ensure an accurate evaluation of the hot carrier redox potential as function of plasmon energy. Furthermore, this approach enables the synthesis of nanorods composed of a variety of plasmonic metals (Au, Ag, Cu, Al, etc.) while maintaining comparable dimensions between plasmonic systems.

As a model system, Au nanorods will be used and the energy of the hot electrons and hot holes will be compared relative to the potentials for water reduction $E^0(\text{H}_2\text{O}/\text{H}_2)$ and oxidation $E^0(\text{O}_2/\text{H}_2\text{O})$, respectively. HER (i.e. Pt) and OER (i.e. IrO$_2$) electrocatalysts will be electrodeposited on opposite ends of the nanorod to engender the smallest possible overpotential for overall water splitting with the plasmonic photocatalyst. The construction of anisotropic nanorods endows the plasmonic nanostructure with two distinct plasmon modes: a transverse mode that will remain roughly constant at ca. 550—600 nm and a longitudinal mode that varies according to nanorod length throughout the visible and near-IR region (Figure 6-8B). By increasing the nanorod length for a fixed diameter, the LSPR maximum of the longitudinal plasmon mode can be continuously tuned throughout the visible and IR spectrum ($\lambda \sim$600—2000 nm). As the plasmon mode is red-shifted into the IR regime the energy of these hot
carriers will inevitably fall closer to the metal Fermi level (Figure 6-8A). Selectively exciting the longitudinal plasmon mode enables adjusting the energy distribution of the hot carriers until they eventually fall below the thermodynamic threshold for photochemical reaction to proceed. It is predicted that overall water splitting will occur for plasmon modes up to ~1000 nm (~1.23 eV), but at lower photon energies the hot carriers will be thermodynamically incapable of effecting overall water splitting. The stoichiometric evolution of both O₂ and H₂ can be quantified via gas chromatography along the course of the reaction to monitor the photocatalytic process over time. On the basis of theory, the limited reduction ability of hot electrons in Au nanostructures is anticipated to restrict H₂ evolution at lower photon energies, thereby halting the production of O₂ without the ability to compensate charge on the photocatalyst. In the presence of a sacrificial reagent such as methanol, the thermodynamic restrictions on overall water splitting are lifted and it is expected that plasmon-driven water reduction (sacrificial H₂ evolution) will continue farther into the IR regime (λ ~1600 nm).

After the energy distribution of hot carriers derived from Au nanorods has been mapped onto the electrochemical energy scale, Ag nanorods will be fashioned in a similar manner and used for comparison. The photocatalytic window for Ag is anticipated to constitute a broader range of chemical potentials than Au, as the plasmon resonance of Ag is known to lie substantially blue-shifted of Au. Furthermore, the position of the Ag Fermi level on the electrochemical energy scale, coupled with the lower plasmon-damping of Ag due to the higher onset energy for interband transitions, manifests a stronger plasmon resonance in Ag than Au. The different band structure of Ag is also predicted to provide a more equitable distribution of hot electron-hole pairs
relative to the Ag Fermi level.\textsuperscript{85,86} It is therefore expected that overall water splitting will proceed over a larger range of photon energies for Ag than for Au, and these hypotheses will be examined in an analogous fashion as that employed for the Au system. Finally, Al and Cu nanorods can also be constructed through the same approach to verify that these elements also follow the trends predicted from theory.

By carefully controlling the aspect ratio of the plasmonic nanorods, the hot carrier distributions can be mapped onto the electrochemical energy scale relative to the redox potentials for water splitting. This knowledge essentially provides an energy-level diagram similar to that used for predicting the photocatalytic reactions of semiconductor photocatalysts. Establishing the thermodynamic limits of these plasmon-driven photocatalytic processes will therefore assist with the \textit{a priori} design of advanced plasmonic photocatalysts to perform a given chemical reaction.

\textbf{Harvesting Hot Carriers from Plasmonic-Metal Nanostructures}

It is known that PMET from Au to TiO\textsubscript{2} occurs on an ultrafast timescale ($t < 240$ fs) with ca. 40\% quantum efficiency,\textsuperscript{91} and therefore effectively competes with hot carrier relaxation as long as the metal and semiconductor are in intimate physical contact. Theoretical models suggest that the charge-separated state is instantaneously generated within the semiconductor CB upon optical excitation of the plasmon resonance.\textsuperscript{90} Indeed, recent optical studies of the dynamics of hot carriers generated near plasmonic hot spots have shown that hot electron injection from Au to TiO\textsubscript{2} occurs on an ultrafast timescale ($t \sim 45$ fs).\textsuperscript{92} This plasmonic photosensitization mechanism constitutes a general photocatalytic strategy, as PMET has been observed in various plasmonic-metal/semiconductor systems (Au/ZnO, Au/SrTiO\textsubscript{3}, Au/WO\textsubscript{3}, Au/CeO\textsubscript{2}).\textsuperscript{56,57} The addition of anisotropic Au nanorods to TiO\textsubscript{2}-based photoanodes has also been
shown to endow the plasmonic composite with additional photoelectrochemical activity in the IR regime by selectively exciting the longitudinal plasmon mode of the Au nanorods, demonstrating the potential for broadband solar energy conversion. While promising, the physical device parameters that govern the transmission probability for these hot carriers across a metal-semiconductor heterojunction have not been experimentally determined in a systematic fashion. A greater understanding of the factors that regulate this process is therefore required to inform the design of more efficient plasmon-driven photocatalytic devices.

To systematically assess the fundamental material properties governing hot electron transmission across the Schottky barrier requires a well-defined plasmonic system that can reliably establish the quantum efficiency of hot electron transfer and correlate the PMET efficiency with the physical device structure. The following device parameters must be specifically investigated: plasmonic nanostructure size and shape, elemental composition, crystallinity, Schottky barrier height, interfacial contact area, and local near-field enhancement. For such a purpose, we propose to use a patterned plasmonic device to demarcate a known illumination area, comprised of a given number of plasmonic light-harvesting elements of known size, shape, and interfacial contact area with the underlying semiconductor substrate (Figure 6-11). An electronically-addressable architecture further enables modulating the band-bending at the metal-semiconductor heterojunction via the application of an external electrical bias and allows for quantifying the hot electron transfer process by monitoring device photocurrent at a given light wavelength and incident light power. A patterned substrate composed of anisotropic nanostructures further provides a platform to probe the
influence of incident light polarization and local field enhancement on hot electron
transmission across the heterojunction.

Large-scale (~mm\(^2\)) periodic arrays of anisotropic Au nanorods will be defined on
an n-type TiO\(_2\) single crystal substrate of either rutile or anatase phase using electron-
beam lithography to construct a photoactive area of known size and composition.\(^1\)\(\text{03,200-202}\) The physical dimensions and elemental composition of each plasmonic nanoantenna
element, the number density of nanoantennas on the surface, and their interfacial
contact area with the underlying semiconductor substrate can be carefully controlled
with only minimal structural variation across the array (Figure 6-11). The optical
response of the device will be characterized using diffuse reflectance spectroscopy. The
internal quantum efficiency of hot electron injection can be evaluated by assessing the
device photocurrent under a known power density based on a given set of device
parameters.

Theory suggests that the plasmon-driven production rate of hot carriers may be
dependent on both the nanocrystal size and shape.\(^\text{85-90}\) The confinement of electrons at
reduced dimensions allows photon-assisted electronic transitions with high excitation
energies, leading to a large number of energetic carriers.\(^\text{89,90,92}\) Linear momentum is not
conserved in a nanocrystal, which enables the potential for exciting hot electrons and
holes with very large energies relative to the metal Fermi level (\(\sim E_F \pm \hbar \omega\)).\(^\text{89,90,92}\) As the
total amount of optical energy dissipated by the nanocrystal via hot carrier production is
determined by the incident photon itself, hot carriers generated near the Fermi level
must be produced at higher rates. Thus, large nanoparticles generate a greater number
of hot carriers than small nanoparticles, but their energies remain close to the metal
Fermi level (i.e. they are not as hot). Consequently, the production of high-energy electrons and holes becomes possible in nanostructures smaller than the bulk mean free path ($l_{\text{mfp}} = 20 \text{ nm}$). A series of nanoantennas of variable size can be patterned on the semiconductor substrate to investigate the influence of nanocrystal dimensions on hot electron injection.

The momentum distribution of the hot carriers produced in the plasmonic metal will have important implications for the transmission rate for hot carriers across the metal-semiconductor interface. It is predicted that the hot carriers produced in Al nanocrystals are highly oriented spatially, relative to metals like Au or Cu, which exhibit more isotropically-oriented hot carrier distributions. As such, plasmonic nanoantennas composed of different elements may require different device architectures to effectively harvest hot carriers from a given metal. Such a prediction could potentially be verified by constructing plasmonic nanoantenna arrays composed of either Al or Au on a single-crystal TiO$_2$ substrate and irradiating the nanoantennas with s- or p-polarized visible light on resonance with the longitudinal plasmon mode of the nanoantennas. The Al-based nanoantennas are anticipated to show a substantial modulation of device photocurrent with incident light polarization. It has recently been shown that embedding plasmonic Au nanoantennas within a nearby semiconductor enables a substantial enhancement in the number of hot electrons that can be collected from the plasmonic-metal nanocrystal. Accordingly, a more detailed investigation of the influence of interfacial contact area on hot electron collection is needed. Such “3-D” Schottky barriers have the potential to harvest many more hot carriers than “1-D” Schottky
barriers, but require more systematic study to establish general design rules for efficiently collecting hot carriers from plasmonic-metal nanocrystals.

While the total number of hot carriers produced on the metal nanocrystal is dependent on the incident light intensity, it has been suggested that the energy distribution of these hot carriers is primarily governed by the plasmonic near-fields. It is predicted that the production rate of hot carriers with large energies ($\sim E_F \pm \hbar \omega$) is given by $\delta n \sim |E_n|^2/\omega^4$, where $E_n$ is the electric field normal to the nanostructure surface. The local amplitudes of surface charge density were found to exhibit a strong dependence on the local intensity of these plasmonic near-fields, as the field inhomogeneity produces significant matrix elements between pairs of electronic states with well-separated energies. As such, hot carriers with high energies are preferentially produced near plasmonic “hot spots,” where the local electric field strength is orders of magnitude larger than the incident optical field.

To evaluate the role of near-fields on hot carrier production, the substrate can be modified with the addition of a plasmonic thin-film underneath the semiconductor layer. A sandwich-type structure (metal/semiconductor/metal) confers additional field enhancements within the semiconductor layer by confining the incident optical energy at the heterojunctions. The photovoltage of the device can be monitored under open-circuit conditions to ascertain the number of hot carriers transferred to the semiconductor and compared to that observed in the absence of the plasmonic thin-film layer. Simulating the near-field distributions around the heterojunction and assessing the amplitude of the local field enhancements will provide further insight into the relationship between the plasmonic near-fields and hot carrier injection. Advanced
photocurrent mapping studies could also be conducted to elucidate the influence of the local plasmonic near-fields on the production and collection of hot carriers. Photocurrent mapping is ideally-suited to such a task, as this technique is capable of routinely resolving features on the nanometer scale, and would allow correlating the local structure of the plasmonic hot spot with the collection of hot carriers. Electric-field simulations of the local plasmonic hot spots would then be performed to assess the local field intensity and correlate the near-field enhancements with the photocurrent performance to confirm the role of plasmonic near-fields on hot carrier production.

Constructing plasmonic photoelectrochemical devices by e-beam lithography ensures a well-defined photoactive area of known illumination volume and interfacial surface area. While these devices will enable a quantitative determination of the internal and external quantum efficiency of the hot electron injection process, such a substrate fashioned by so-called “top-down” methods is intrinsically composed of polycrystalline metal nanostructures. Previous studies have shown a significant difference in the propagation lengths of surface plasmon polaritons along metal nanowires comprised of single-crystalline vs. polycrystalline structures. We propose to examine the role of crystal structure on hot carrier production by constructing plasmonic-metal/semiconductor heterojunctions via Langmuir-Blodgett (LB) assembly in parallel with e-beam lithography, as per previous reports. A mask will be used to define a photoactive area composed of a number of trenches with specified dimensions, such that only a given number of nanorods can fill a prescribed area, and a thin-film of nanoparticles will be dragged across the substrate to place a single Au nanowire within a single trench. This strategy again provides a known illumination volume by which to
quantify the internal and external quantum efficiency of hot electron transfer while using plasmonic nanostructures comprised of single-crystalline nanostructures synthesized by wet-chemistry methods. Such a device can be directly compared to that observed for the lithographically patterned plasmonic device to investigate the influence of crystal structure on the hot electron production and collection. Taken together, these systematic studies will elucidate the various device parameters regulating the plasmon-driven production of hot carriers within metal nanocrystals and their subsequent transmission across an interfacial Schottky barrier at the metal/semiconductor heterojunction.

The exceptional optoelectronic characteristics of plasmonic-metal nanostructures offer great promise for photocatalytic applications, with the potential for truly panchromatic photoelectrochemical devices that harvest the entire solar spectrum. The completion of these studies is expected to improve our fundamental understanding of the yield and energy distribution of hot carriers, as well as the device parameters governing their collection in plasmonic-metal/semiconductor heterostructures. It is hoped that these insights may further inform the design and construction of panchromatic plasmon-driven photoelectrochemical cells comprised of Earth-abundant elements for solar-to-fuel energy conversion.
Figure 6-1. SEM images of plasmonic Cu/TiO$_2$ photoanodes. A) Low-magnification SEM image showing the distribution of Cu nanoparticles on the TiO$_2$ nanowires. B) High-magnification SEM image showing the surface structure of the Cu nanoparticles.
Figure 6-2. Physicochemical characterization of Cu/TiO$_2$ photoanodes. A) X-ray diffraction pattern from Cu/TiO$_2$ photoanodes showing peaks from the underlying TiO$_2$ (open circles) and FTO substrate (open squares), but also peaks indicative of Cu$^{(0)}$ (filled squares) and Cu$_2$O phases (filled circles). B) XPS scan of the Cu 2p region, showing a clear indication of surface oxidation on the as-deposited Cu nanoparticles.
Figure 6-3. Photoelectrochemistry of plasmonic Cu/TiO$_2$ photoanodes. A) Cyclic voltammetry in the dark at a scan rate of 20 mV s$^{-1}$. The black arrows indicate the direction of the CV scan. B) Controlled potential electrolysis of Cu/TiO$_2$ photoanodes under periodic ($t =$ 10 s on/off) visible-light excitation. Despite a strong initial $J_{ph}$ response from the device, it quickly inactivates due to oxidation of the Cu nanoparticles under anodic conditions, as evidenced by the loss of $J_{ph}$ over time.
Figure 6-4. Plasmonic Cu/TiO$_2$ heterostructures. A) Extinction spectra of TiO$_2$-only (black curve) and Cu/TiO$_2$ heterostructures (red curve) showing the prominent LSPR peak at 603 nm. Inset shows a digital photograph of the Cu/TiO$_2$ heterostructures dispersed in solution under inert Ar atmosphere to preserve the optical properties of the Cu nanoparticles. B) TEM image of the Cu/TiO$_2$ heterostructures showing the loading of Cu nanoparticles on the TiO$_2$ surface.
Figure 6-5. Optical properties of Cu/TiO₂ heterostructures over time while exposed to ambient air. A) Extinction spectra of Cu/TiO₂ dispersed in aqueous solution taken every min over a 20 min period, showing the loss of LSPR from the Cu nanoparticles as they are oxidized to CuOₓ species. B) Expanded view of the extinction spectra from (A) showing only the first 10 min to better observe the loss of LSPR over time.
Figure 6-6. Photocatalytic cycling experiments demonstrating the recyclability of the Cu/TiO₂ heterostructures. A) Extinction spectra of Cu/TiO₂ heterostructures dispersed in aqueous solution and exposed to ambient air, showing a loss of the Cu LSPR peak at $\lambda_{\text{max}} = 603$ nm over the course of 10 min due to oxidation of the metallic Cu. B) Photocatalytic cycling experiments conducted on Cu/TiO₂ heterostructures. A cycle consists of exposing Cu/TiO₂ to ambient air for 20 min to ensure complete oxidation and then irradiating the sample for 10 min under UV light to reduce the CuOₓ species back to Cu metal. The absorbance ($A$) is then taken at $\lambda_{\text{max}}$ (603 nm) and compared to the initial absorbance obtained from the sample ($A_0$) prior to oxidation. The recoverable optical properties demonstrate that the Cu oxidation state can be cycled multiple times while anchored onto the TiO₂ support. Inset are digital photographs of the sample in the cuvette after each cycle showing the purple color of the photocatalysts.
Figure 6-7. Extinction spectra of Cu/TiO$_2$ heterostructures dispersed in aqueous solution and exposed to ambient air. A) Exposure to ambient air in the dark shows a loss of the Cu LSPR peak at 603 nm over the course of 10 min due to oxidation of the metallic Cu. B) Exposure to ambient air under UV light excitation of the TiO$_2$ support shows an extended period of prolonged plasmonic activity by the Cu nanoparticles, as it takes ~40% longer to oxidize under the presence of UV light.
Figure 6-8. Evaluating hot carrier distributions of plasmonic-metal nanostructures. A) Energy level diagram of plasmonic metals (violet shaded box) showing the Fermi level ($E_F$) of plasmonic metals relative to the absolute energy scale (vacuum level) and the electrochemical energy scale (V vs. SHE at pH 0). The potential energy levels of hot electrons and hot holes in the metal relative to the metal Fermi level is shown relative to the formal potentials for water reduction and oxidation, as well as a general redox acceptor (A/A$^-$) or donor (D/D$^+$). By manipulating the nanorod aspect ratio, the LSPR maximum can be shifted into the IR until the hot carrier energy falls below the thermodynamic threshold for photocatalytic reaction. B) Extinction spectra of Au nanorods of various aspect ratio, showing the changing optical response across the visible to near-IR region as a consequence of increasing the nanorod aspect ratio (as given by the ratio: length/width).
Figure 6-9. Template-based synthesis of anisotropic metal nanowires for electrochemical deposition of plasmonic photocatalysts. A silver backing is first evaporated onto the AAO template to provide Ohmic contact with the template (i). A sacrificial Ag layer is then electrodeposited to ensure a clean connection with the evaporated backing (ii). Multi-segmented nanowires are grown by electrochemical deposition within the AAO pores (iii). The Ag backing is dissolved (iv). The AAO template is dissolved either incompletely to leave residual AAO as a protective coating (v-1) or completely dissolved to release the nanowires from the templates and provide freely dispersed multi-segmented nanowires (v-2). Adapted with permission from Banholzer et al. Copyright 2009 Nature Protocols.
Figure 6-10. Autonomous plasmonic photocatalysts made by template-assisted electrochemical deposition of metal nanowires. A) Autonomous plasmonic photocatalyst composed of a plasmonic element (Au, Ag, Cu, Al, etc.) bound by a hydrogen evolution reaction (HER) catalyst and an oxygen evolution reaction (OER) catalyst to facilitate water-splitting photochemistry. The plasmonic element can be further encapsulated within a protective Al₂O₃ coating by incompletely dissolving the AAO template after photocatalyst synthesis. A Schottky junction contact (omitted for clarity) will be constructed between the plasmonic element and the HER. B) Energy level diagram showing scheme of plasmon-drive solar water splitting. Absorption of a photon by the plasmonic metal excites hot electron-hole pairs. The hot electrons transfer across the Schottky barrier and eventually diffuse to the HER catalyst where water reduction occurs while the hot holes diffuse to the OER to oxidize water. The electron-selective contact (e.g. TiO₂, SrTiO₃) is used to ensure that the hot carriers are sufficiently separated across the plasmonic photocatalyst to reach their respective catalytic sites.
Figure 6-11. Photoelectrochemical device used for evaluating the efficiency of hot electron injection from a plasmonic metal to an n-type semiconductor. A) Proposed device architecture fashioned by electron-beam lithography to define plasmonic nanoantennas on top of n-type semiconductor substrates. Lithography enables demarcation of known illumination volumes with control over nanoantenna size (length, $l$, diameter, $d$), shape, and elemental composition, all of which can be continuously tuned across the periodic array along a single-crystal semiconductor substrate of thickness, $h$ on top of an Ohmic back contact. B) Optical excitation of the plasmonic-metal nanoantennas with visible light ($\hbar \omega$) creates hot electron-hole pairs within the metal. The hot carriers with enough energy to surmount the Schottky barrier ($\varphi_B$) will transfer to the semiconductor and be collected by the back contact while those without will be reflected at the metal-semiconductor interface. Similarly, free carriers generated via interband transitions (d-band to sp-band) will not possess enough energy to surmount the Schottky barrier at these photon energies and will not be collected.
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BIOGRAPHICAL SKETCH

Joseph DuChene is the son of Steve and Teresa DuChene and the brother of Kimberly DuChene. He grew up in Lutz, Florida and attended Vivian Gaither High School. His love of the environment began at an early age, spending a lot of time outdoors throughout his youth. Joseph initially enrolled at the University of South Florida to obtain a bachelor’s degree in Environmental Science, but eventually transferred to the University of Florida (UF) to pursue an undergraduate degree majoring in Natural Resource Conservation. He graduated with honors in 2007 with a B.S. in Forest Resources & Conservation. It was during his time at UF as an undergraduate student that his passion for scientific discovery was cultivated. After spending numerous years in several different labs his desire to continue doing research led him to enroll at UF in 2010 to pursue a Ph.D. in Chemistry. Working under the direction of Dr. W. David Wei, his research involves the synthesis of plasmonic-metal nanostructures and their applications in photoelectrochemical systems for solar-to-fuel energy conversion. After graduation, Joseph intends to continue studying solar photochemistry as a postdoctoral scientist and pursue a career in renewable energy research.