ELECTROSTATICALLY DRIVEN SELF-ASSEMBLED NANOPARTICLES ANTIREFLECTION COATINGS

By

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To my Mom, who always support me

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TABLE OF CONTENTS

page

ACKNOWLEDGMENTS 4

ABSTRACT 7

CHAPTER

1 INSTRUCTION 8

2 EXPERIMENTAL SECTION 10

Materials and Substrates 10
Procedure 10

3 RESULTS AND DISCUSSION 13

Formation of a Monolayer of APS on the Surface of Glass 13
Effect of Solvent of Silica Suspension 13
Effect of Silica Particle Suspension Concentration 14
Effect of Shaking the Suspension 15
Effect of Coating Time 15
Coating Larger Glass Substrate 18
Coating Multiple Glass Substrates at the Same Time 18
Coating Flask-curved Glass 19

4 CONCLUSIONS 26

LIST OF REFERENCES 27

BIOGRAPHICAL SKETCH 29

LIST OF FIGURES

Figure page

1-1 Photograph comparing the antiglare properties between the coated and the uncoated glass slide 11

1-2 Optical measurement 12

2-1 Mechanism of APT reaction with glass. 19

2-2 Optical spectrum comparing coatings resulting from different mass fractions of silica nanoparticles in ethanol and water mixture. 19

2-3 Optical spectrum comparing the effect of varying the coatings times. 20

2-4 Comparison of the uniformity of the coatings generated by different coating times. 21

2-5 Summary of the uniformity test for different coating times. 21

2-6 Average particle surface area coverage for different coating times. 22

2-7 Top-view SEM images showing surface area coverage achieved by 100 nm silica particles for different coating times. 22

2-8 5 inch X 5 inch glass substrate coated with 100 nm showing good antireflection properties. 23

2-9 Experimental setup for checking the feasibility of coating multiple substrates simultaneously without affecting the quality of the coating. 23

2-10 Optical data of the three simultaneously coated glass substrates. 24

2-11 Flask coated with 100 nm showing good antireflection properties. 24

2-12 Top-view SEM images showing coating of different locations of flask achieved by 100 nm silica particles 25

Abstract of Thesis Presented to the Graduate School
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We report a simple and scalable method for antireflection monolayer coating on both sides of glass substrates. Organosilane 3-aminopropyltriethoxysilane (APS) was applied to glass surface, and adjust the glass surface charge to positive, electrostatically attract the negatively charged silica. The effect of coating time was investigated. Electrostatically controlled adsorption results in uniform and high density coverage of silica. Also this method can coat large size glass or curved surface, and can be scaled up to coat multiple glass substrate and curved surface.

CHAPTER 1
INSTRUCTION

Glass normally has a refractive index around 1.5 and reflects approximately 4% of light on each surface. Reflected light off of glass surface, such as window windshield, instrument could pose safety hazards. Glass used for solar cell and green house will lower down the light efficiency. Therefore quarter-wavelength antireflection coating was widely used to minimize the reflection light and increase optical transmission.[1] Optical reflection can be efficiently suppressed if the refractive index of the coating is equal to the geometric mean of the refractive indices of the two media at the interface and the thickness of the coating is a quarter of the wavelength of light.[2] When light propagates from air to glass, the effective refractive index of quarter wavelength AR coating should equal to 1.22. However, there is no material can meet the low requirement. Thus, AR coating with 2- or 3- dimensional porous, moth eye and nanoparticles structures are commonly used to achieve the low refractive index.[3-6]

Nanoparticle self-assembly is a simple and inexpensive method to create antireflection coatings. Spin coating enables good control of film thickness by adjusting the spin rate.[7] Layer-by-layer (LBL) assembly of nanoparticles and electrolytes enables high performance antiglare coatings on nonplanar substrates. Langmuir-Blodgett dip coating method is also widely used to form uniform close packed monolayers on different substrates.

Unfortunately many of the bottom-up technologies involve several steps, limited to single-sided coatings on planar substrates, difficult to control experimental parameters, take too long to coat, or not very reproducible.[8]

In this experiment, we introduce a novel, scalable self-assembly method that can generate a monolayer of negatively charged silica nanoparticles on functionalized glass substrates.

CHAPTER 2
EXPERIMENTAL SECTION

Materials and Substrates

Mono-dispersed 100 nm silica microspheres synthesized by the standard Stöber method were obtained from Particle Solutions LLC. 3-Aminopropyltriethoxysilane(APS,99%) was obtained from ACROS ORGANICS. Toluene anhydrous, 99.8% was obtained from SIGMA-ALDRICH. Sulfuric acid (Certified ACS Plus), Hydrogen peroxide, 30% (Certified ACS) were both purchased from Fisher Chemical. Microscope slides (25*75*1.0mm) was obtained from Fisher brand. All water was used in our experiment is deionized water.

Procedure

The glass substrates were cleaned with Piranha solution (H_2SO_4: H_2O_2=4:1 by volume) at 70˚C for 90min to remove any organic residue off the substrates. The substrates were rinsed with deionized water and ethanol several times followed by air dry. Guarantee the glass substrates were anhydrous, because APS can react with water instead of being adsorbed on the surface of slides. The cleaned substrates were immediately placed into APS solution in toluene (APS 1ml+toluene 125ml) for 2h. After functionalization step, they were rigorously rinsed in pure toluene to remove non-covalently adsorbed APS compound on the surface, dry with air and use them immediately.

The as-synthesized silica colloids are purified by using multiple cycle centrifugation/redispersion in 200-proof ethanol several times and dispersed in ethanol-water mixture (90% ethanol by volume). The APS functionalized glass substrates were immersed vertically into silica suspension, varying the mass fraction of silica suspension and coating time to obtain the optimum coating condition. During coating, keep shaking the suspension to make it uniform preventing any the sedimentation effects. Following the coating, the coated glass slides were rinsed by ethanol-water mixture with the same composition, followed by pure ethanol and air dry.

The 100nm coated glass slides showed a shiny blue color caused by light diffraction. The coatings were uniform on both sides of the glass without the visible defects. Figure 1-1 shows a photograph comparing the antiglare properties of the coated and uncoated glass slide. It is apparent that the coated glass slide has suppressed reflection since no glare can be seen from its surface.

Optical measurements were performed on coated glass slides to measure the antireflection properties of the coating on the surface. The visible light shines directly normal to the substrate surface and a light detector to measure the amount of light reflected and transmitted.

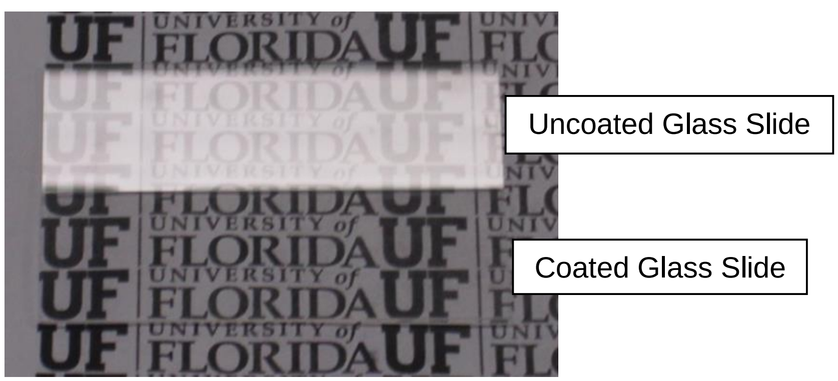

Figure 1-1. Photograph comparing the antiglare properties between the coated and the uncoated glass slide

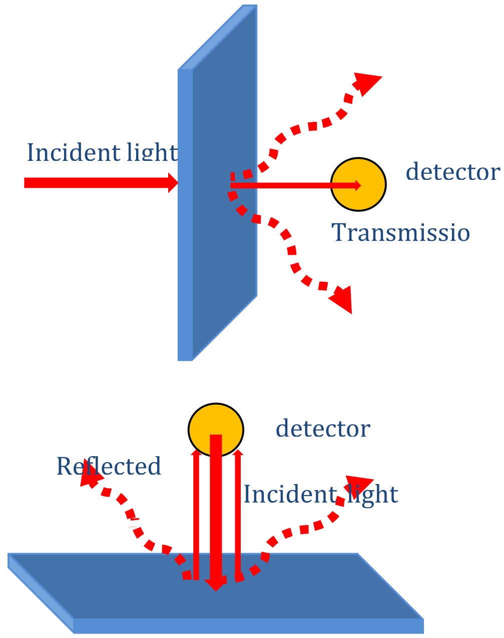

Figure 1-2. Optical measurement

CHAPTER 3
RESULTS AND DISCUSSION

Formation of a Monolayer of APS on the Surface of Glass

The piranha solution was used to cleaned the glass slides and hydroxylate the surface, creating more OH groups to allow for the APS to readily adsorb onto.[9] The bi-functional APS molecule react with OH group on glass surface forming siloxane (Si-O-Si) linkages. Hydrogen bonding between amino groups and OH groups contribute to the protonated amino groups protruding to the air-side.[10] Figure 2-1 clearly represents the mechanism used to functionalize the glass surface. This monolayer of APS contributes in adjusting the surface charge of glass surface from negative to positive. The APS-modified glass slides were immediately used for coating, otherwise it can adsorb any impurities or dust particles.

In experiments, we use 100nm silica particles and particles carry negative charge to provide stability in the colloid suspension. The surface of functionalized glass is positive charged, which can electrostatically adsorb the nanoparticles. We will further discuss effects of other forces such as repulsive force and capillary force to forming the monolayer of nanoparticle.

Effect of Solvent of Silica Suspension

The nanoparticles were dispersed in the mixture of water and ethanol (90% ethanol by volume). Zeta-potential was introduced here to describe the stability of colloid suspension. The suspension is mostly made out of ethanol to cause a decrease in the dielectric constant of the suspending medium thus lowering the conductivity of the suspension and increasing the zeta potential. Increasing the zeta potential can help in preventing agglomeration in the silica particle suspension. However, increasing the zeta potential further could result in increasing the repulsion between the silica particles thus high surface coverage can't be achieved. The surface coverage of the silica particles on the glass substrate depends on both the inter particle interactions and on the particle-substrate interaction. Therefore using 90% ethanol in the silica particle suspension plays a major role in achieving high surface coverage.

Effect of Silica Particle Suspension Concentration

Experiments used 100nm particles and conducted the effects of silica concentration of 1.6wt.%, 4.2wt.% and 16.7wt.%. In Figure 2-2, minimum point in reflection and maximum point in transmission correspond to a wavelength of 600nm. From Figure 2-2, the optimal mass fraction of silica particles is around wt.1.6% in the water ethanol mixture solvent. As the concentration of silica particles increase in suspension, the probability of particles adsorbing onto the surface of functionalized glass substrates also increase, thus improving the overall surface area coverage. There exists a peak at which further increase the concentration of silica particles would result in the formation of multilayers on glass surface which can worsen the antireflection properties. With 16.7wt.% silica particle concentration in suspension, the coated glass adsorb extra layers in some regions. These defects can be observed from thee shiny yellowish color on the surface of the glass slide, the same results shown in Figure 2-2, this multilayer cause yielding higher reflection and lower transmission as detected by the optical measurement. In addition, as shown in spectra the transmittance is not exact equal to 100%-reflection. This is potentially due to diffuse scattering of light happens in the voids between the randomly self-assembled particles.[11]

Effect of Shaking the Suspension

During coating process, constant shaking the nanoparticle suspension to prevent the any precipitation effects and allow for continuous movement. The silica particles exhibit Brownian motion under shaking operation, which ensure the silica move randomly around suspension. Besides, the constant motion exert silica particles electrostatically adsorbed onto the void space on glass surface, thereby improving the coverage of slides, reducing the defects.

Effect of Coating Time

Initially when the glass slides were immersed into silica suspension, the particles closed the glass substrate were adsorbed by electrostatic attraction quickly, creating a region where silica particles per volume is decreased. Since the particles are exhibiting Brownian motion and are moving in a random motion constantly colliding with each other, the particles in higher concentration region would diffuse, refill lower concentration region. The rate of particles adsorbed onto glass surface is much faster than the diffusion rate, forming a constant influx of particles flow from suspension to the glass surface, producing a more uniform coating. Additionally, shaking the silica particle suspension can improve the diffusion process, allowing faster coating and more particles depositing on the surface.

In experiments, we vary the coating time from instant to 90min and optical measurements were performed to measure the antireflection properties. From Figure 2-3, it is apparent that the antireflection properties improve as the coating time increases.

On the other hand, the uniformity of the coatings were test by choosing three samples, one with coating time 15sec, another with coating time 30min, the third one with coating time 90min. For each sample, ten random spots on the surface were conducted an optical measurement to test whether there are any differences in optical readings between different regions on the same coated glass. Figure 2-4 represents the results of the uniformity test operated on the three coated substrates. With increasing the coating time, the uniformity of the coating also improve. The summary of test conducted on several samples coated at different time was shown in Figure 2-5.

The coated samples were characterized by the use of an SEM to analyze the particle surface area coverage of the coating. Figure 2-6 shows SEM images of samples coated for 15 seconds, 5 minutes, 30 minutes and 90 minutes, which indicates that coating for longer times yields higher particle surface area coverage of the coating.

Moreover, From SEM images of 15sec and 5min, particles adhere existing islands of particles rather than the bare substrate surface, the same case also happen in Xue Li's work.[7] Increasing coating time, SEM images of coating time from 30min to 90min, particles randomly disperse forming uniform monolayer. Capillary attractive force stimulated from the menisci of solvent formed around the particles play a major role in this arrangement.[12]

Initially, negatively charged particles were attract to the functionalized surface until the available surface were fully occupied, then the capillary forces occur in all particle self-assembly processes once the evaporating solvent layer is thinner than the particle diameter, rearrangement of adsorbed particles started to occur. When the solvent was completely dried, all samples resulted in the irreversible 2-D particle aggregates.[13] But with longer coating time, much more particles were adsorbed on glass surface, the bond between substrate and particle become stronger without evident rearrangement. Further increase coating time, defects such as stacking effects also arise. In order to minimize the amount of defects present in the coating, longer rinsing in ethanol and water is essential. Since water has a high surface tension, rinsing the coated samples in a mixture of ethanol and water could remove any loosely adhered particles on top of the electrostatically adhered monolayer of particles. The particles directly adsorbed onto the substrate won't be affected by the longer rinse since the electrostatic interaction between the particles and the substrate is much stronger than the intermolecular interaction between the particles.

The SEM images were used along with an image processing program called ImageJ, to analyze the SEM pictures and estimate the particle surface area coverage obtained from the coatings. Multiple SEM pictures were taken for each sample from different regions of the coated glass slide. The pictures were inputted into the computer program to be analyzed. The image processing program can distinguish the particles from the blank background in the image from their colors. ImageJ will then separate the particles and the background and calculate the particle surface area coverage for every SEM image. Figure 2-7 summarizes the results obtained from ImageJ, which shows the average particle surface area coverage achieved for different coating times. For coating times up to 5 minutes, it can be seen that the particle surface area coverage remains almost constant around 32%. Coating times between 5 minutes and 60 minutes shows a linear increase in surface area coverage trend that goes from 32% to about 60%. Further increasing the coating time from 60min to 90 min coating almost have the same surface area coverage, plateau indicates maximum surface coverage of substrates, but as SEM pictures shown there are many voids between particles which are larger than the diameter of particle, as at this time, the repulsive force exerted by adsorbed particles on surface is dominant and hinder the subsequent adsorption of nanoparticles from suspension.

Coating Larger Glass Substrate

Upon experimenting on all different parameters that affect the coating, we can conclude the most optimum coating conditions to obtain high quality and uniform coatings should be by utilizing silica particle suspension dispersed in mixer made up with 90% ethanol by volume and 10% water, with silica particle 1.6wt% and coating time 90min. The ability of silica colloid to self assembly make it possible to cover large glass substrates. In Figure 2-8, it demonstrated that a 5 inch X 5inch glass substrate was easily coated with 100nm silica particles under the optimum conditions and illustrated the difference in the antiglare properties between the coated glass and bare glass.

Coating Multiple Glass Substrates at the Same Time

An excellent advantage of this coating technology is that you are not limited to coating one substrate at a time, instead you could coat several glass slides all at once. The experimental setup utilized to coat multiple slides of glass substrates was shown in Figure 2-9. Sample 1 was placed in the left, sample 2 was in the center and sample 3 was place in right. The optical results were analyzed to determine if the coating on each glass slide would be the same. In Figure 2-10, the results of experiments prove glass slides coated simultaneously all exhibited almost identical antireflection properties. Hence, this new coating technique could potentially be scaled up and used in industry to form uniform monolayer coatings on multiple glass slides at the same time.

Coating Flask-curved Glass

This innovative technique can be applied to nonplanar surface. Figure 2-11 compare the antireflection properties of coated flask and bare flask. SEM characterization was adopted to measure different six locations of coated flask.

Area 3 is the inner face on neck of flask, the silica particle suspension in the neck part was hardly shaken during coating, The particles surface average is lower than other places. The SEM image of area 5 shows multilayers of coating signify that gravitational force draw much more particles on the surface.

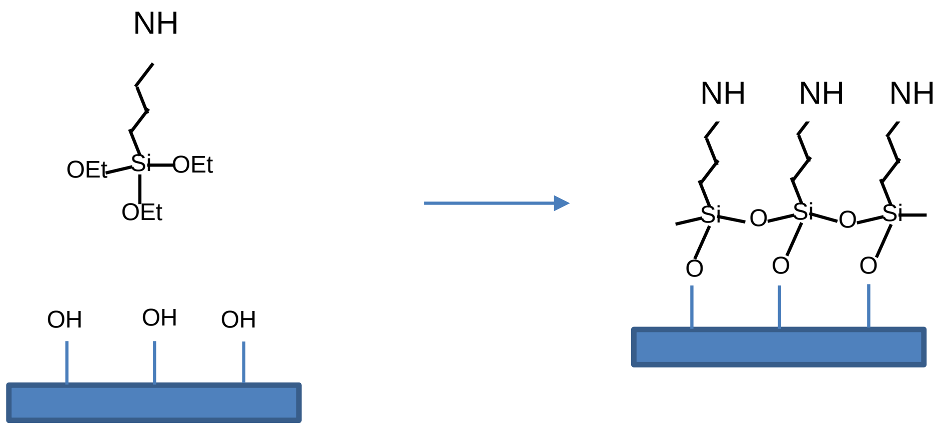

Figure 2-1. Mechanism of APT reaction with glass.

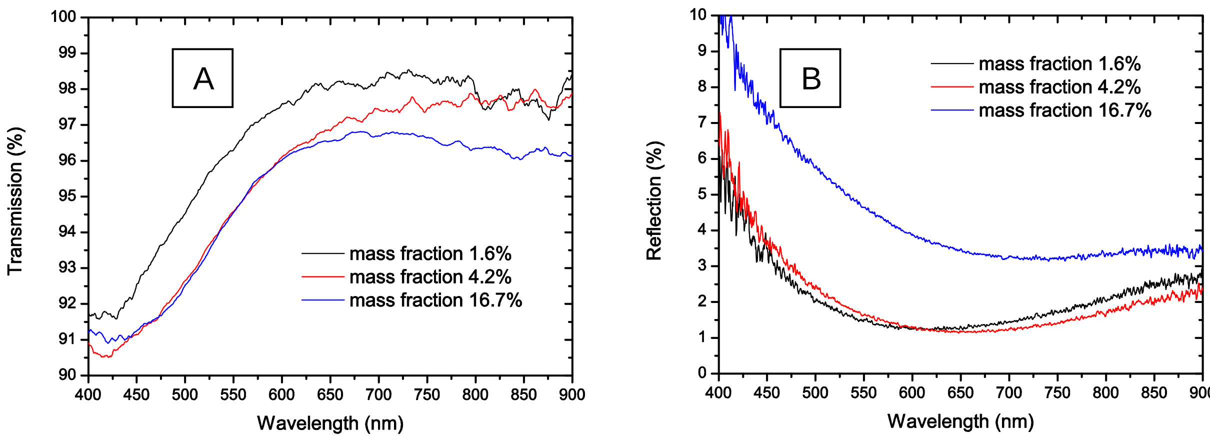

Figure 2-2. Optical spectrum A) reflection and B) transmission comparing coatings resulting from different mass fractions of silica nanoparticles in ethanol and water mixture.

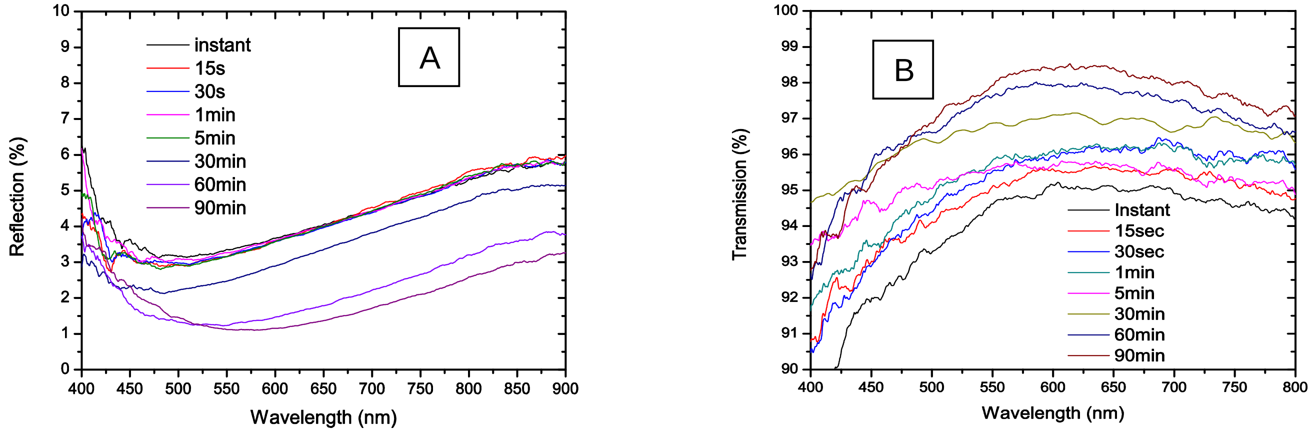

Figure 2-3. Optical spectrum A) reflection and B) transmission comparing the effect of varying the coatings times.

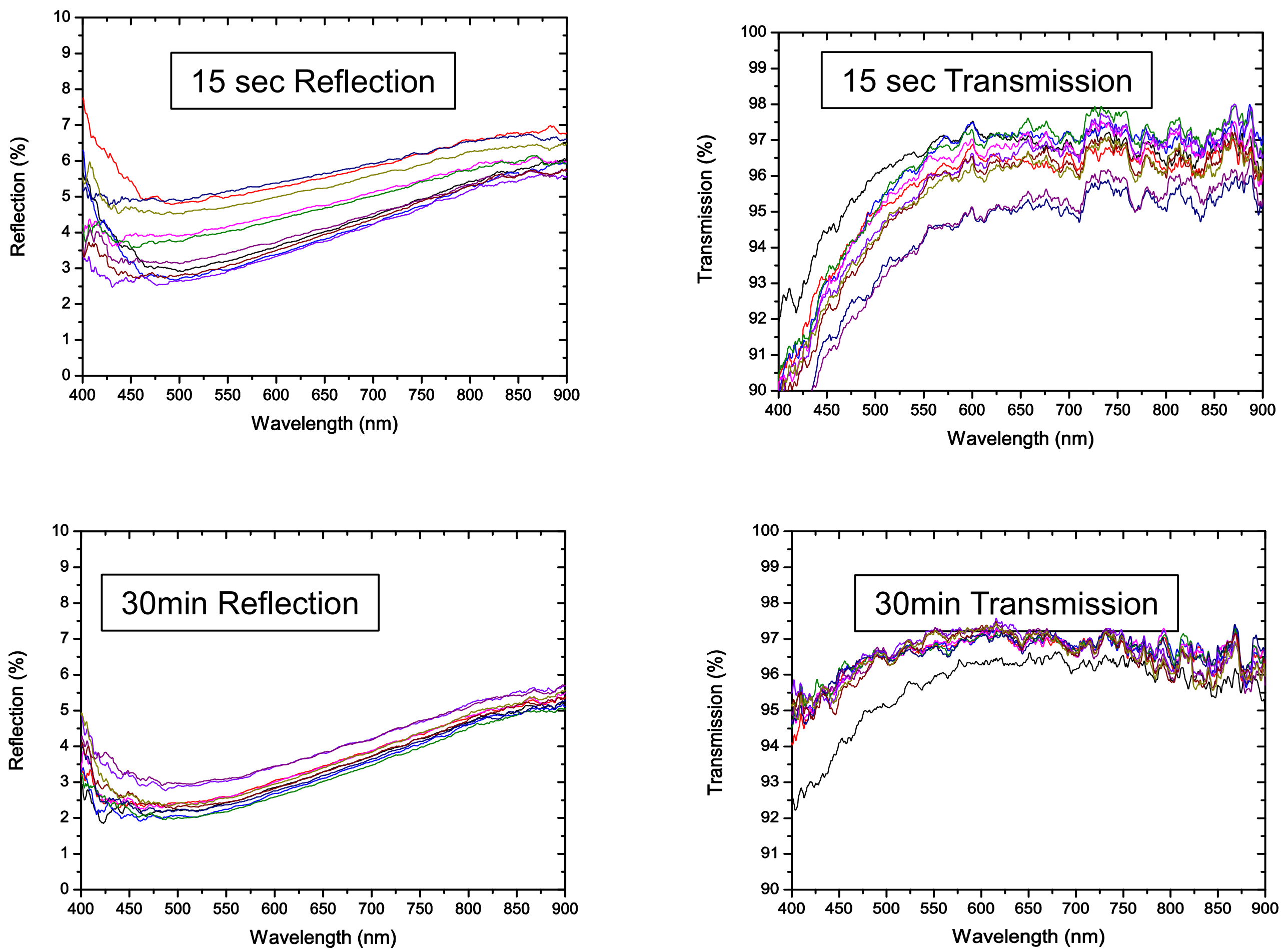

Figure 2-4. Comparison of the uniformity of the coatings generated by different coating times.

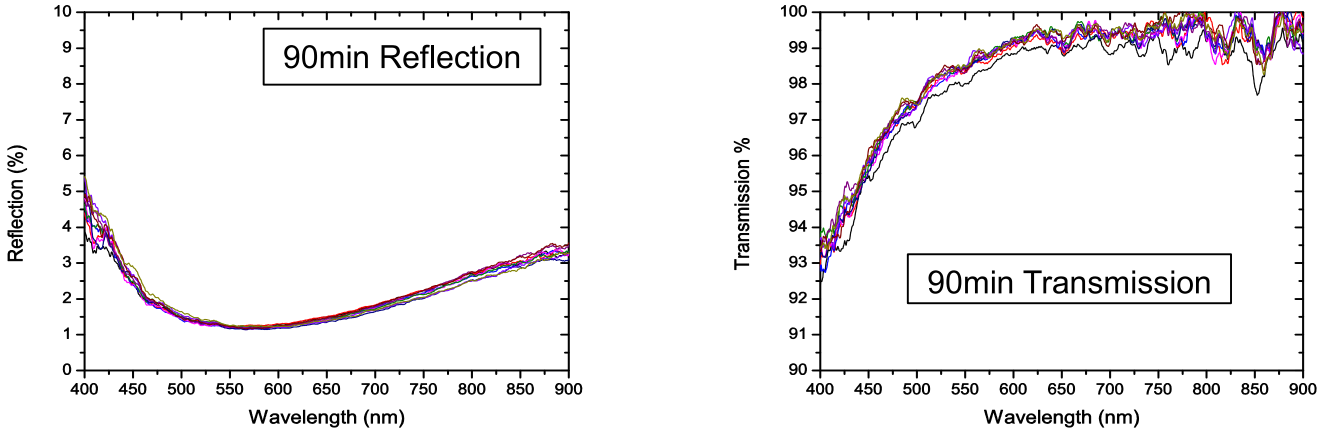

Figure 2-4. Continued

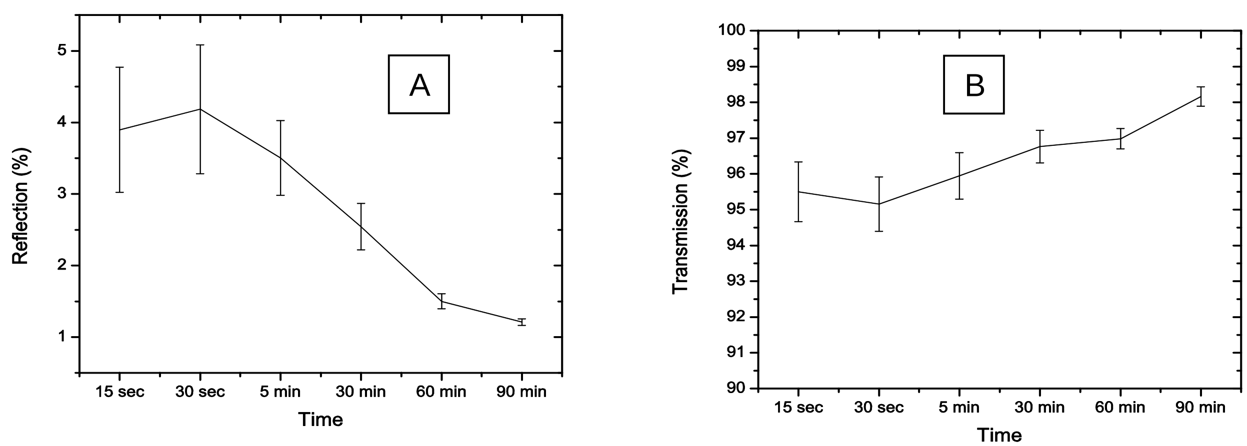

Figure 2-5. Summary of the uniformity test A) reflection and B) transmission for different coating times.

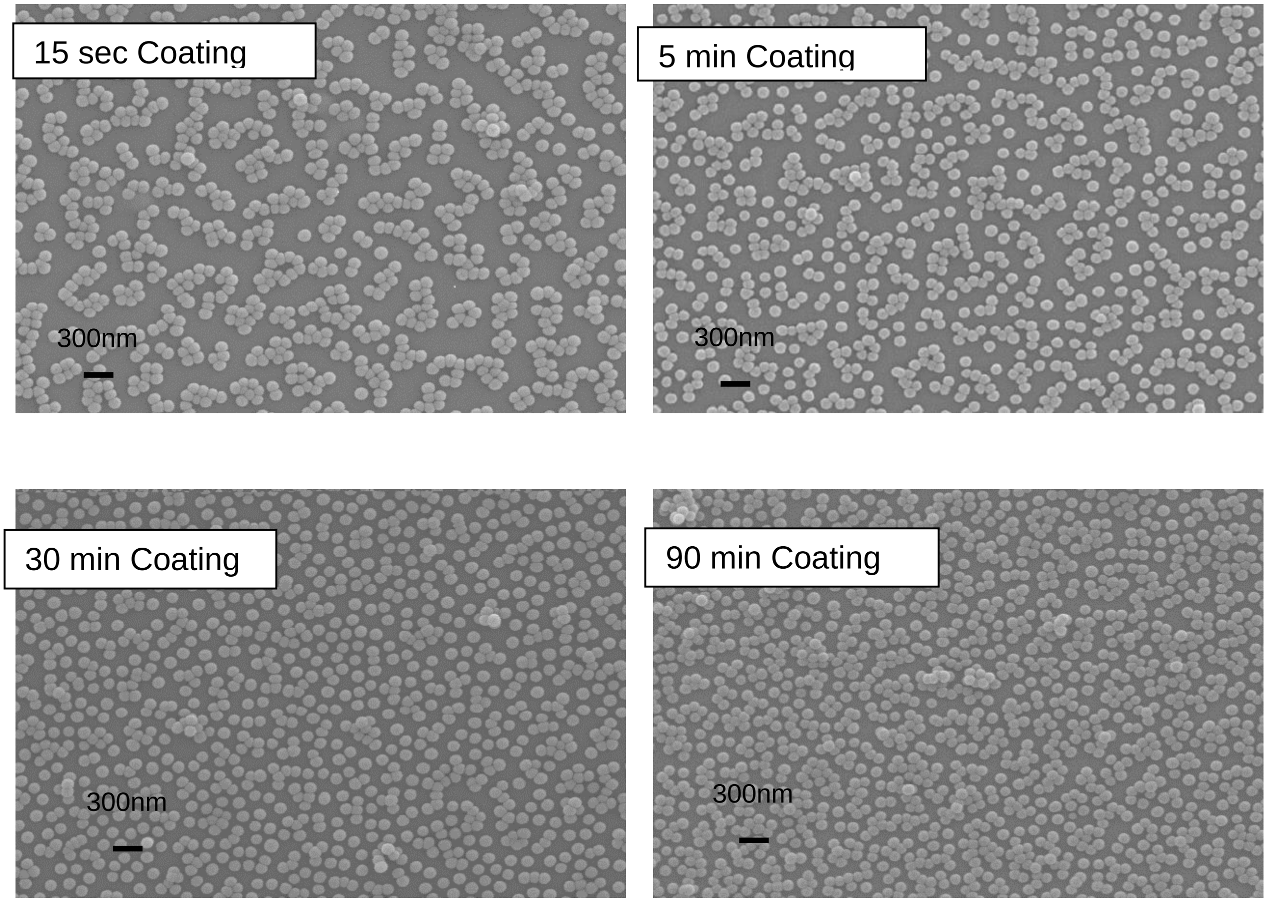

Figure 2-6. Top-view SEM images showing surface area coverage achieved by 100 nm silica particles for different coating times.

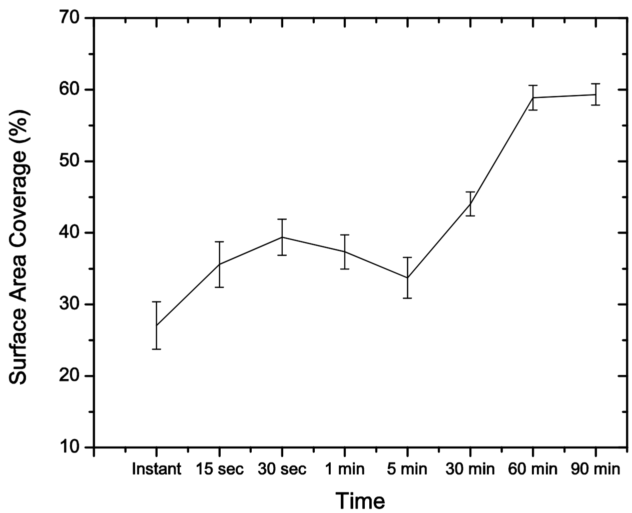

Figure 2-7. Average particle surface area coverage for different coating times.

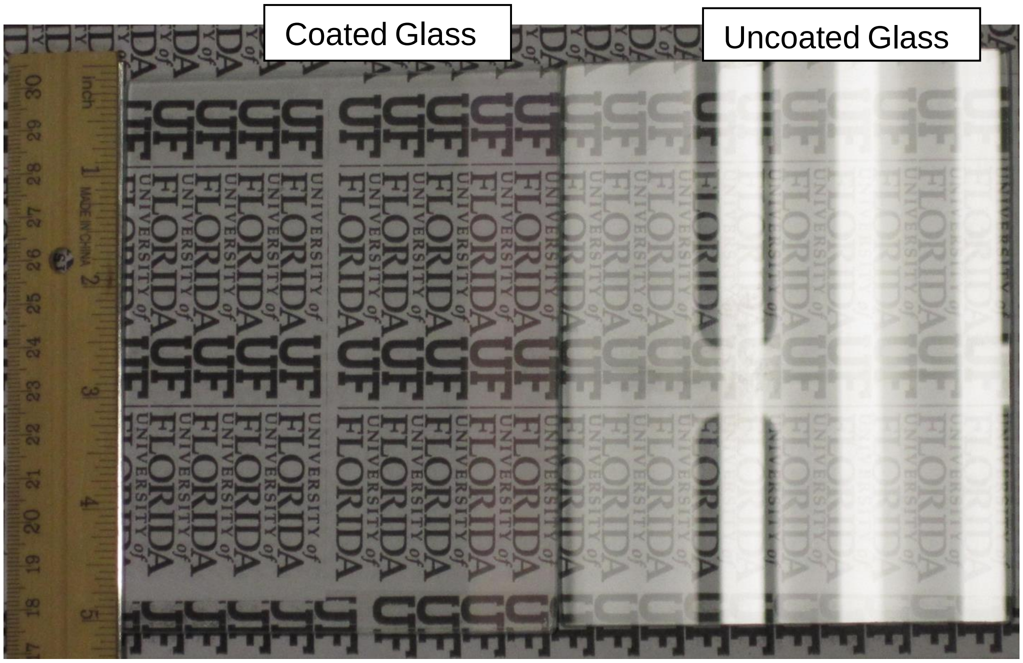

Figure 2-8. 5 inch X 5 inch glass substrate coated with 100 nm showing good antireflection properties.

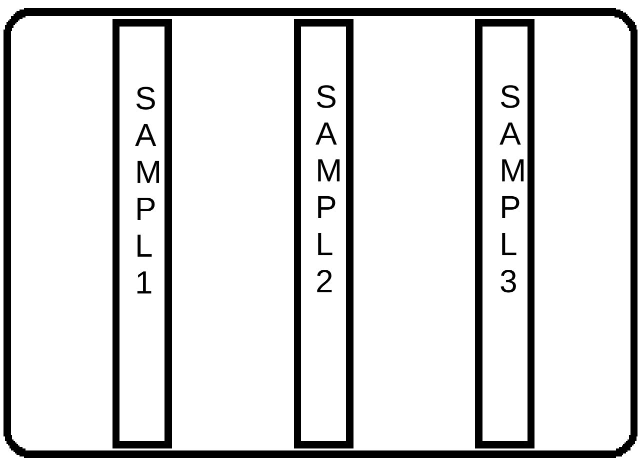

Figure 2-9. Experimental setup for checking the feasibility of coating multiple substrates simultaneously without affecting the quality of the coating.

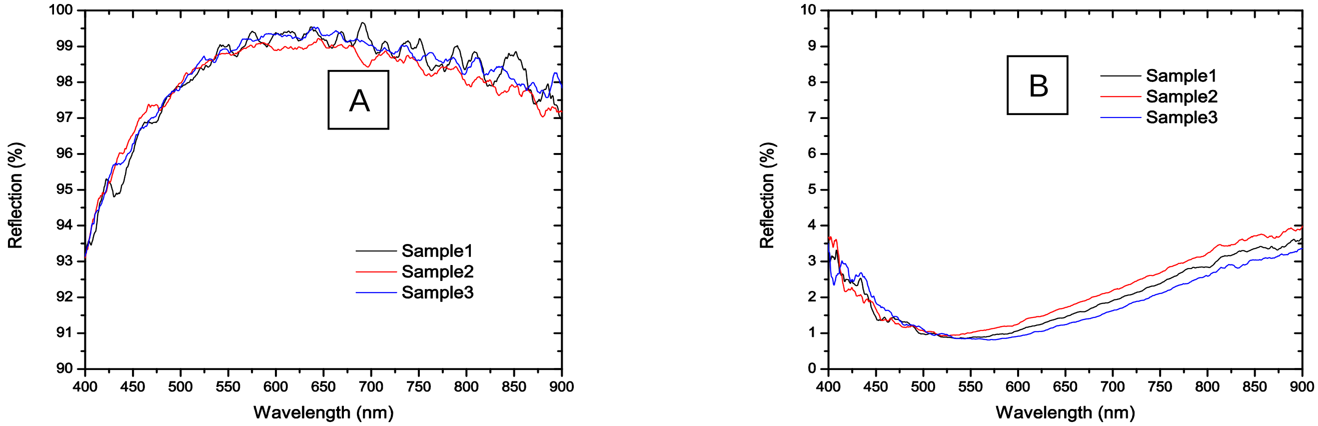

Figure 2-10. Optical data A) reflection and B) transmission of the three simultaneously coated glass substrates.

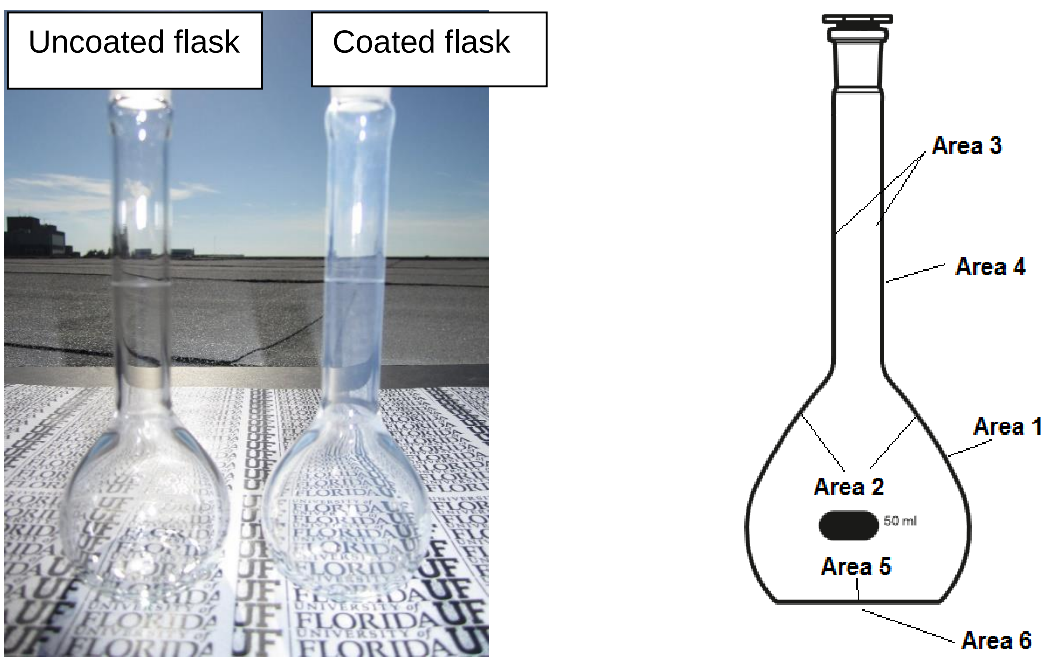

Figure 2-11. Flask coated with 100 nm showing good antireflection properties.

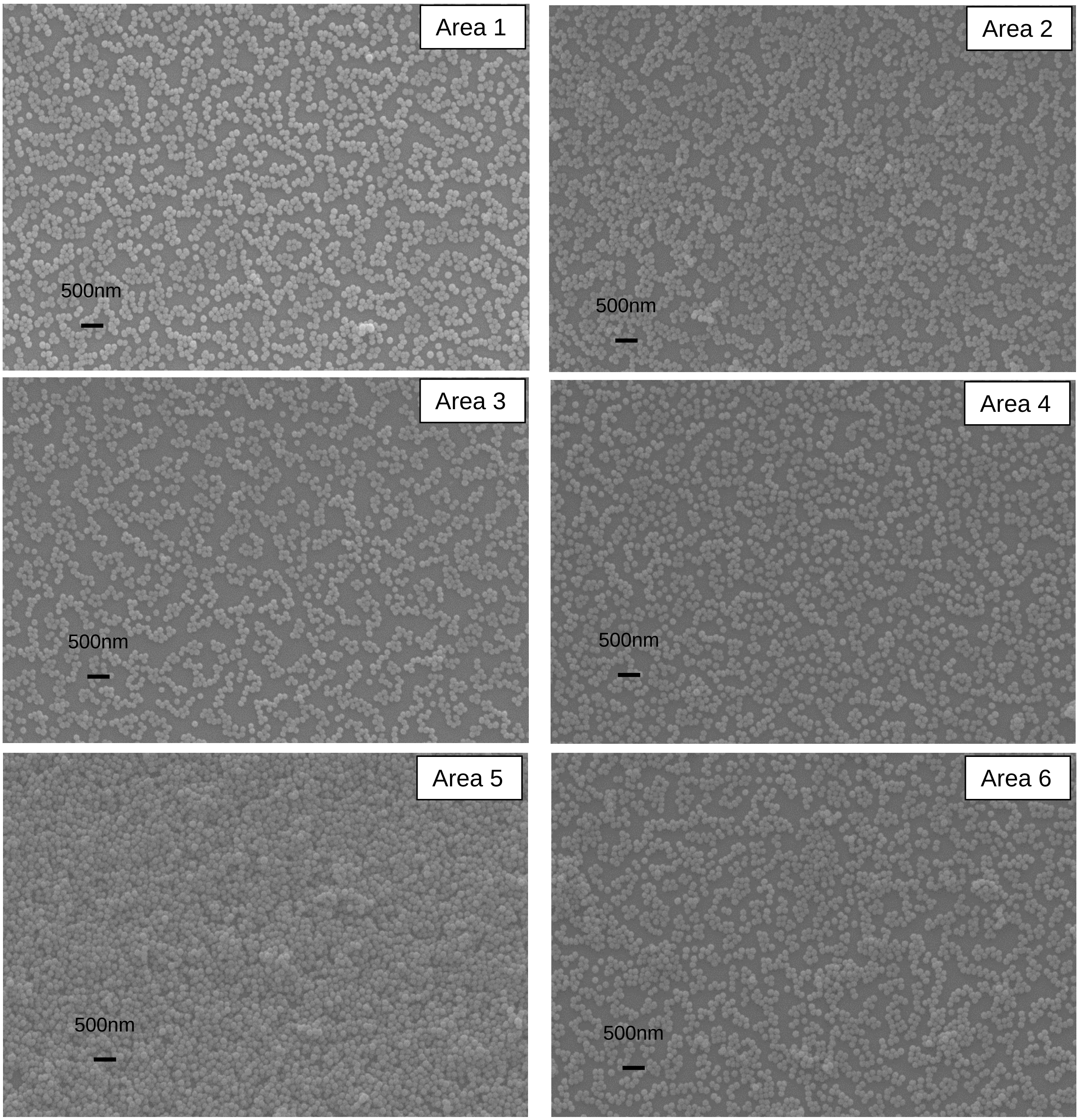

Figure 2-12. Top-view SEM images showing coating of different areas of flask achieved by 100 nm silica particles.

CHAPTER 4
CONCLUSIONS

In conclusion, we develop inexpensive scalable and simple method for simultaneously coating both sides of glass substrate with self-assembly SiO_2 particles on functionalized glass substrate by electrostatically controlled adsorption. The hydroxylated glass carrying negative charge can be adjusted to positive, which electrostatically attract the nanoparticles. Shaking the colloidal solution during coating prevent precipitation effects and improve the coverage. We also found duration time of coating have effects on the nanoparticle monolayer coverage. By post treatment of coated glass with two steps of washing, we successfully remove the excess layers of SiO_2 particles. Interestingly, nanoparticles easily form cluster by short time coating, with increasing coating time they disperse randomly forming uniform monolayer. Electrostatically controlled adsorption can be applied in coating large areas, multilayers of glass or curved surface with non-packed uniform surface coverage, by simple adjustment of surface charge. This method can also be chosen for depositing other kinds of nanoparticles.

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BIOGRAPHICAL SKETCH

Jiamin Wang grew up in Shandong, China. She received her bachelor’s degree at Hebei University of Technology in 2012. She began her graduate studies at the University of Florida in August 2012 and joined Professor Peng Jiang’s group in fall 2012. She received her MS degree from the University of Florida in the spring of 2014.