Scalable Parallel Self-Assembly of Nanoparticle Anti-reflection Coatings

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Abstract

Here we report a simple, inherently parallel, and scalable bottom-up approach for fabricating nanoparticle anti-reflection coatings on large glass substrates. Negatively charged silica nanoparticles are electrostatically adsorbed onto a surface-functionalized glass substrate with positive surface charges to form a disordered monolayer nanoparticle coating. Systematic experiments have been conducted to optimize the critical process parameters, including the dispersing dielectric media, nanoparticle concentration of the colloidal suspensions, and the coating time, that significantly affect the uniformity and the anti-reflection properties of the final coatings. Specular reflection and transmission measurements demonstrate that good anti-reflection performance (with $< 1\%$ two-sided reflection) and high optical transmission ($> 99\%$) can be achieved by the self-assembled nanoparticle coatings. This innovative technology also enables the simultaneous coating of multiple 5-in.-sized glass substrates with high and reproducible qualities. Importantly, we combine experiments with theoretical calculations to address a fundamental question faced by the fabrication of monolayer nanoparticle-based anti-reflection coatings – what is the optimal nanoparticle surface area coverage for best anti-reflection performance? Our optical simulations based on a rigorous coupled-wave analysis model indicate that the optimal nanoparticle coverage is $\sim 60\%$ which is readily achievable by this electrostatics-assisted bottom-up technology.

Keywords: anti-reflection coating, colloidal self-assembly, electrostatics, surface modification, bottom-up, nanoparticles

1. Introduction

Anti-reflection coatings on transparent substrates (e.g., glass) are important components for a large number of optical and optoelectronic devices, such as displays, lenses, and photovoltaic (PV) panels[1-11].For instance, the unwanted optical reflection from the encapsulation glass layer of a PV panel could reduce the overall conversion efficiency of the solar device [12-14]. Anti-reflection coatings are therefore widely applied on optical glass surfaces to reduce the reflection loss and increase the light transmission of the optical components [1,15].Traditional quarter-wavelength anti-reflection coatings can effectively suppress optical reflection by satisfying the destructive interference conditions for the reflected light from the air/coating and the coating/substrate interfaces, thus decreasing the reflection and increasing the transmission of the substrate[15]. To satisfy the destructive interference conditions, the coating thickness needs to be close to one-fourth of the operating wavelength, while the refractive index of the coating (n_c)needs to meet $n_c = \sqrt{n_{air} \times n_s}$, where n_{air} is the refractive index of air (1.0) and n_s is the refractive index of the substrate[6,15].For a typical glass substrate with a refractive index of 1.5, the anti-reflection coating material needs to have a refractive index of ~ 1.225 . Low-refractive-index materials, such as MgF_2 (with a refractive index of ~ 1.37), are usually deposited on glass substrates by vacuum-based physical vapor deposition (PVD) technologies (e.g., sputtering) to achieve a precise control over the coating thickness [15,16]. Unfortunately, conventional PVD techniques suffer from high operating and equipment costs, limited material selection, low throughput, and small coating areas. These drawbacks particularly affect the applications where inexpensive anti-reflection coatings on large-area glass substrates are needed, such as in solar industry.

To address the high costs and the low throughput issues of the vacuum-deposited anti-reflection coatings, various simple solution processing technologies have been developed[1,6,17-

27]. In many of these methods, nanoporous coatings with a large fraction of entrapped air and thus a low effective refractive index, which could satisfy the aforementioned ideal quarter-wavelength refractive index requirement, were extensively explored[1,6,17,22,28]. For example, nanoporous polymer coatings created by phase separation of spin-coated polymer blends, followed by selective removal of one component, have been demonstrated to show good anti-reflection performance on glass substrates[1]. Multilayer silica nanoparticle coatings on glass substrates applied through common spin, dip, or roller coating techniques have already been commercialized for improving the efficiencies of PV panels (e.g., Honeywell's SOLARC R^{PV} products) [29-31]. Electrostatics-assisted layer-by-layer (LBL) deposition of nanoparticles and polyelectrolyte multilayers is another popular approach in assembling anti-reflection coatings on a variety of substrates[22,32,33]. Monolayers of colloidal nanoparticles created by convective self-assembly[34,35], spin-coating[19,31,36-38], or Langmuir-Blodgett deposition[21,39,40] have also been widely utilized as anti-reflection coatings on silicon and glass substrates. However, many of these existing wet-processing technologies involve multiple steps (e.g., LBL assembly)[20], are limited to single-sided coatings on planar substrates (approaches involving spin coating)[19], are not very reproducible over large areas[21], and/or are not inherently parallel for industry-scale manufacturing[34].

Here we report an electrostatics-assisted colloidal self-assembly technology for fabricating monolayer nanoparticle anti-reflection coatings over large areas. This approach is based on electrostatic adsorption of negatively charged silica nanoparticles on surface-functionalized glass substrates with positive surface charges[37,38,41]. This simple technology could enable simultaneous coating of both sides of glass substrates with complex geometries, and most importantly, is inherently parallel for potential large-scale fabrication of inexpensive anti-reflection coatings with high coating quality and reproducibility. Although some studies have

been conducted to investigate the electrostatic self-assembly of negative silica particles on positive glass substrates[42-48], the anti-reflection properties of the final coatings, especially the effects of the nanoparticle surface area coverage, have not been systematically investigated[37,38,41,49]. By combining experiments with theoretical simulations, herein we systematically examined the critical parameters that significantly affect the anti-reflection performance of the self-assembled nanoparticle coatings. We found that the theoretical optimal nanoparticle surface area coverage (~60%) was readily achievable by this electrostatics-assisted bottom-up technology.

2. Experimental

2.1. Materials and Substrates

Monodispersed 110 nm silica nanospheres synthesized by the standard Stöber method [50] were obtained from Particle Solutions LLC. 3-Aminopropyltriethoxysilane (APS, 99%) was purchased from Acros Organics. Anhydrous toluene (99.8%) was obtained from Sigma-Aldrich. Sulfuric acid (certified ACS plus grade), 200-proof ethanol, and hydrogen peroxide (30%, certified ACS grade) were purchased from Fisher Chemical. Glass microslides (75 × 25 mm) were provided by Fisher Scientific. Larger glass substrates (5 × 5 inch, typical soda-lime glass) was cut by a local glass company. Deionized (DI) water (18.2 MΩ cm) was used directly from a Millipore A-10 water purification system.

2.2. Instrumentation

Scanning electron microscopy (SEM) was performed on a JEOL 6335F FEG-SEM. A thin layer of gold was sputtered onto the samples prior to imaging. Normal-incidence specular reflection and transmission spectra were obtained by using an Ocean Optics HR4000 High Resolution Fiber Optic Vis-NIR spectrometer.

2.3. Surface Functionalization of Glass Substrates

The glass substrates were cleaned using a piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 4:1$ by volume) at 70°C for 90 min to remove organic residue on the surface of the substrates. The substrates were then rinsed with deionized water and ethanol several times followed by drying in air. The cleaned substrates were immediately placed into an APS solution in toluene (2.5 vol.%) for 2 hours[51]. After the glass substrates were functionalized, they were rigorously rinsed in pure toluene to remove non-covalently bonded APS molecules on the glass surface, followed by drying in air.

2.4. Electrostatics-Assisted Assembly of Silica Nanoparticles on Surface-Functionalized Glass Substrates

The as-synthesized silica nanoparticles were purified by using multiple (at least 3 times) centrifugation/re-dispersion cycles in 200-proof ethanol and finally dispersed in an ethanol-water mixture (90% ethanol by volume). The APS-functionalized glass substrates were immersed vertically into the silica/ethanol-water suspension. The mass fraction of the silica nanospheres in the suspension and the coating time were systematically varied to obtain the optimal coating conditions. During coating, the silica suspension was constantly shaken to allow for the nanoparticles to move freely in the suspension thus preventing possible sedimentation effects. Following the coating process, the coated glass substrates were rinsed with an ethanol-water mixture with the same concentration as shown above, followed by a pure ethanol rinse, and then the coated glass substrates were air-dried.

2.5. Optical Characterization of Electrostatics-Assembled Nanoparticle Anti-reflection Coatings

The anti-reflection performance of the electrostatics-assembled nanoparticle coatings was evaluated by measuring their specular transmission and reflection spectra using an Ocean Optics Vis-NIR spectrometer with a reflection probe. A calibrated halogen light source was used to

illuminate the sample. The beam spot size was about 3 millimeters on the sample surface. Measurements were performed at normal incidence and the cone angle of collection was less than 5° . Absolute reflectivity was obtained as the ratio of the sample spectrum and a reference spectrum. The reference spectrum was the optical density obtained from an aluminum-sputtered (1000 nm thickness) silicon wafer.

2.6. Numerical Simulation of Nanoparticle Anti-reflection Coatings

A multilayer rigorous coupled-wave analysis (RCWA) model [52,53] was set up to simulate the normal-incidence reflection spectra of the monolayer nanoparticle anti-reflection coatings when the nanoparticle surface area coverage (f_{sa}) was varied in the range from 10% to 90%. Each nanoparticle had a radius r and height $h = 2r$. A coordinate system was set up with z -axis perpendicular to the substrate surface ($z = 0$). The RCWA model was set up as follows. Firstly, we divided the whole nanosphere into $N = 100$ horizontal circular layers with thickness $\frac{h}{N}$. The z -coordinate z^* and the radius r^* of each circular layer satisfy $r^* = \sqrt{r^2 - (z^* - r)^2}$, where $0 \leq z^* \leq h$. Therefore, the horizontal layer at level z^* contained a fraction $f(z^*)$ of glass material with refractive index $n_{glass} = 1.5$, and a fraction $1 - f(z^*)$ of air with refractive index $n_{air} = 1$, where $f(z^*) = \frac{(r^*)^2}{r^2} f_{sa}$. Therefore, the effective refractive index $n(z^*)$ of the layer at height z^* could be approximated by $n(z^*) = [f(z^*) n_{glass}^q + (1 - f(z^*)) n_{air}^q]^{\frac{1}{q}}$ with $q = \frac{2}{3}$ based on the effective medium theory [54]. Secondly, we calculated the normal-incidence reflection of the whole system by solving the Maxwell equation to express the electromagnetic (EM) field in each layer and then matching EM boundary conditions between neighboring layers for determining the reflection and transmission of the system.

3. Results and Discussion

In this paper, we explored to use strong electrostatic adsorption of negatively charged silica nanospheres onto positively charged surfaces of an APS-functionalized glass substrate as a simple, inherently parallel, and scalable bottom-up approach for assembling monolayer nanoparticle anti-reflection coatings. Using the piranha solution we were able to clean the glass substrates from organic residues present on the surface of the substrates. The piranha solution also facilitates the hydroxylation of the glass surface to allow for APS molecules to readily react with the surface hydroxyl groups[55]. As shown by the scheme in Fig. 1, the well-established silane coupling reaction can form siloxane linkages on the surfaces of the glass substrates with the amino groups present in the APS molecules protruding outwards[55]. This functionalization step contributes in changing the surface charge of the glass substrate from negative to positive when the amino groups are protonated[56]. The functionalized glass substrates were immediately used for coating to prevent impurities or dust particles to get adsorbed onto the fresh surface. Although we only used 110 nm silica nanoparticles with a typical zeta potential of ~ -45 mV (in DI water) to assemble anti-reflection coatings on glass substrates in the current work, this electrostatics-assisted colloidal assembly approach can be readily applied to much larger silica particles (up to 8 μm in diameter tested so far) and many other substrates (e.g., silicon wafers).

As the surface adsorption of negative silica nanoparticles by the positively charged glass substrate is significantly affected by the electrostatic interaction between them[42], the dispersing dielectric medium plays a critical role in determining the final properties of the assembled nanoparticle coatings. In this work, silica nanoparticles were dispersed in the mixture of water and ethanol (90% ethanol by volume). The dielectric medium is mostly made out of ethanol with a dielectric constant of 24.3 at 20°C to cause a decrease in the dielectric constant of the suspending medium (compared to pure water with a dielectric constant of 80.4). This will

enhance the electrostatic attraction between the oppositely charged silica nanoparticles and the surface-functionalized glass substrate as the electrostatic force is inversely proportional to the dielectric constant of the dielectric medium[48]. Simultaneously, the stronger electrostatic repulsion between silica nanoparticles induced by the decrease in the dielectric constant of the dispersing medium can help in preventing particle agglomeration in the colloidal suspension[57]. However, the increase in electrostatic repulsion between neighboring silica nanospheres could result in lower nanoparticle surface area coverage which will affect the anti-reflection properties of the final coatings (see the optical simulation results in Fig. 9). The nanoparticle surface area coverage on the glass substrate depends on both the inter-particle electrostatic interactions and on the particle-substrate interaction. Our extensive experiments showed that an ethanol-water mixture (90 vol.% ethanol) is a good dielectric medium to disperse silica nanospheres to achieve high and tunable nanoparticle surface area coverage on surface-functionalized glass substrates.

In addition to the dispersing dielectric medium, the concentration of silica nanoparticles in the colloidal suspension also plays an important role in determining the anti-reflection properties of the self-assembled nanoparticle coatings. Systematic experiments were conducted to examine the effects of this critical experimental parameter. The silica nanoparticle concentrations tested were 1.6, 4.2, and 16.7 wt.%. The anti-reflection properties of the resulting nanoparticle coatings were evaluated by measuring their corresponding specular transmission and reflection spectra. Fig. 2 compares the optical reflection and transmission spectra obtained from the coatings prepared by using colloidal suspensions with the above three nanoparticle concentrations. The normal-incidence reflection from both sides of a glass substrate was reduced from ~8% (not shown here) [21] to ~2% for the coatings prepared by using 1.6 wt.% and 4.2 wt.% concentrations. The good anti-reflection performance of these two samples led to the high optical transmission (~98%) as shown in Fig. 2B. However, the coating assembled by using 16.7

wt.% silica suspension exhibited poor anti-reflection performance as illustrated by the high reflection and low transmission in its corresponding spectra. As show in Fig. 2, the minimum point in reflection and the maximum point in transmission for the two good anti-reflection coatings correspond to a wavelength of ~ 600 nm. This agrees with the prediction using the traditional quarter-wavelength condition: $\lambda_0 = 4n_c h_c$ [15], where λ_0 is the minimum reflection wavelength at which destructive interference occurs, n_c is the effective refractive index of the nanoparticle coating, and h_c is the coating thickness (110 nm). Here, the effective refractive index of the monolayer nanoparticle coating ($n_c \sim 1.278$) can be evaluated as: $n_c = f \times n_{\text{silica}} + (1-f) \times n_{\text{air}}$, where f is the volume fraction of silica nanoparticles in the self-assembled colloidal monolayer (~ 0.605 for a close-packed monolayer colloidal crystal), n_{silica} is 1.46, and n_{air} is 1.0. As the absorption of visible light by silica nanoparticles is quite small, the effects of the extinction coefficients of the self-assembled nanoparticle coatings on their final anti-reflection performance are neglected in the above calculations and the later optical modeling (see Fig. 9). From Fig. 2, it is apparent that the silica nanoparticle concentration of 1.6 wt.% yields the lowest reflection and the highest transmission. The coated glass substrate showed a very uniform bluish color on its surfaces. Therefore, we used this optimal mass fraction of silica nanoparticles to prepare anti-reflection coatings in the following parts of the paper.

The effect of the nanoparticle concentration on the anti-reflection properties of the self-assembled nanoparticle coatings could be qualitatively explained by considering the details of the electrostatic adsorption process. As the concentration of silica nanoparticles increases in the suspension, the probability of nanoparticles adsorbing onto the surface of the functionalized glass substrate also increases, thus improving the overall surface area coverage by the nanospheres. When the silica nanoparticles adsorb onto the surface of the glass substrate via strong electrostatic interaction, the particles will be held in place and will not have sufficient

energy to reassemble once again[42]. Therefore, the nanoparticles will self-assemble onto the surface of the glass substrate in a random arrangement which is confirmed by SEM images (see Fig. 7). There exists a point at which increasing the concentration of silica particles in the suspension further could result in the formation of a multilayer coating on the surface of the glass substrate. At 16.7 wt.% silica nanoparticle concentration in the suspension, our SEM examination showed that the coated glass substrate no longer had a colloidal monolayer, instead in some regions there were more than one monolayer that had adsorbed on the surface of the glass substrate. The colloidal multilayer could be easily distinguished from the shiny yellowish color on the surface of the glass slide. The self-assembled colloidal multilayer also resulted in yielding higher reflection and lower transmission as confirmed by the above optical measurements.

The uniformity and the overall surface area coverage of the nanoparticle anti-reflection coatings can be further improved by constantly shaking the silica nanoparticle suspension during the self-assembly process. The shaking allows for continuous movement of the particles in the suspension and prevents possible sedimentation effects. Constant shaking also facilitates the nanoparticles to be electrostatically adsorbed onto empty voids on the functionalized glass substrate, thus improving the nanoparticle surface area coverage on the glass surface. In addition, our experiments show that the mechanical shaking will increase the suspension temperature from 21.0 °C (1 min shaking) to 24.5 °C (30 min) to 27.0 °C (60 min) to 31.0 °C (90 min). This temperature change will increase the kinetic energy of the silica nanoparticles, facilitating to further improve the adsorption dynamics and the uniformity of the final samples. Fig. 3 shows photographs comparing samples prepared with (Fig. 3A) and without (Fig. 3B) shaking during the nanoparticle adsorption process. It is evident that the constant shaking can significantly improve the overall uniformity of the self-assembled nanoparticle anti-reflection coatings.

The coating time is also a major factor in controlling the uniformity of the self-assembled anti-reflection coatings. Initially when the glass substrate is immersed into the shaking silica nanoparticle suspension, the silica nanoparticles closest to the glass substrate will be adsorbed quickly onto the surface due to the strong electrostatic interaction between them, thus creating a depletion region where the silica nanoparticle concentration is decreased[48]. Silica nanoparticles will then diffuse from the regions of higher concentration to the adjacency of the glass substrate surface. This will create an influx of nanoparticles near the surface of the glass substrate which will constantly fill the voids between the immobilized nanoparticles on the glass surface, thus improving the uniformity of the final coatings. In addition, shaking the colloidal suspension can enhance the nanoparticle diffusion rate, allowing for faster coating formation and also improving the particle surface area coverage.

The coating time also significantly affects the anti-reflection performance of the final nanoparticle coatings. To optimize this important experimental parameter, eight glass substrates were coated at different coating times (ranging from instant immersion/withdrawal to 90 min), followed by optical measurements to characterize their anti-reflection properties. From Fig. 4, it is apparent that the anti-reflection (Fig. 4A) and the optical transmission (Fig. 4B) properties improve as the coating time increases. The sample with a coating time of 90 min exhibits a two-sided reflection of $\sim 1\%$ and an optical transmission of $> 98\%$ around 600 nm wavelength. On the other hand, the uniformity of the coatings were tested by selecting three samples with short (15 s), medium (30 min), and long (90 min) coating time. On each sample, ten random spots on the surface of the coating were chosen to conduct optical reflection and transmission measurements to evaluate its uniformity. Fig. 5 represents the results of the uniformity test conducted on the three coated glass substrates with different coating times. As the coating time increases, the uniformity of the coating also increases. Fig. 6 summarizes the results of the uniformity tests

conducted on six samples prepared with different coating times ranging from 15 s to 90 min. It is evident that the 90-min sample shows the lowest reflection and the highest transmission (at 600 nm wavelength), as well as the smallest variation in both reflection and transmission values.

To better understand the anti-reflection properties of the electrostatics-assembled nanoparticle coatings, we characterized the samples prepared with different coating times by SEM to determine the corresponding nanoparticle surface area coverage. Fig. 7 shows typical top-view SEM images of the samples coated for 15 s, 5 min, 30 min, and 90 min. These images illustrate that a longer coating time results in higher nanoparticle surface area coverage of the final coating. The adsorbed silica nanoparticles form a monolayer that is randomly assembled on the surface of the glass substrate without any particular arrangement. Some defects such as stacked particle aggregates also arise as the coating time increases. These defects could be attributed to the capillary interaction between the nanoparticles that caused the particles to get drawn to each other as the ethanol/water solvent in between them dried[48]. In order to minimize the amount of the "aggregate" defects present in the coating, longer rinsing in ethanol and water is essential. Since water has a high surface tension (72.75 mN/m at 20°C) than that of ethanol (22.27 mN/m at 20°C), rinsing the coated samples in a mixture of ethanol and water could remove loosely adhered nanoparticles on top of the electrostatically adsorbed colloidal monolayer. The silica nanoparticles directly adsorbed onto the glass substrate are not affected by the longer rinse due to the strong electrostatic interaction between the oppositely charged nanoparticles and the substrate.

The SEM images were analyzed by using an image processing software called ImageJ to evaluate the nanoparticle surface area coverage of the coatings. Multiple SEM pictures were taken of each sample from different regions of the coated glass substrate to get the average surface area coverage results versus different coating times as shown in Fig. 8. For coating time

up to ~5 min, it can be seen that the nanoparticle surface area coverage first increases to ~39% (at 0.5 min) and then slightly reduces to ~32% (at 5 min). We speculate that the initial rapid increase of the nanoparticle coverage is caused by the strong electrostatic attraction of the negatively charged silica nanoparticles onto the positively charged glass substrate. This will quickly deplete the silica particles in the vicinities of the oppositely charged glass surfaces, affecting the subsequent adsorption dynamics of the particle deposition process. We believe the slight reduction of the particle surface coverage from 0.5 to 5 min is due to the partial detachment of loosely attached silica nanoparticles from the glass surfaces. The electrostatically attracted silica nanoparticles may not adhere strongly on the glass substrates at the beginning of the deposition process. The electrostatic repulsion between neighboring silica nanoparticles and the friction between the fluid and the attached particles caused by the continuous shaking of the suspension may detach some loose nanoparticles. This is partially confirmed by the SEM images in Fig. 7. The silica nanoparticles transit from a clustered geometry at the early deposition stage (see Fig. 7A) to a more random distribution at later stages (Fig. 7C and 7D), indicating a dynamic detachment/attachment process. A longer coating time between 5 and 60 min leads to a nearly linear increase in the surface area coverage that goes from ~32% to about 60%. We attribute this linear increase to the reach of dynamic steady-state adsorption caused by balanced electrostatic attraction and repulsion of the influx silica nanoparticles by the oppositely charged glass substrate and the randomly immobilized silica nanospheres. Further increase in the coating time to 90 min barely changes the nanoparticle surface area coverage.

The above experimental measurements were complemented by numerical simulations based on the RCWA model [52] to gain better understanding of the anti-reflection properties of the self-assembled monolayer nanoparticle coatings, especially the effects of the nanoparticle surface area coverage on the final coating performance. Fig. 9A shows the simulated reflection

spectra from a glass substrate with different nanoparticle surface area coverage values (from 0% to 90%). The single-sided reflection from a flat glass substrate (4%) decreases when the nanoparticle surface area coverage increases until ~60%. The reflection then becomes higher with increasing nanoparticle coverage. In addition, the minimum point in reflection shifts to a longer wavelength when the nanoparticle coverage increases. This is reasonable as a larger nanoparticle coverage leads to a higher effective refractive index of the coating (n_e) in the aforementioned quarter-wavelength condition, thus resulting in a larger λ_0 . The effects of the nanoparticle surface area coverage on the anti-reflection and the reflection minimum are summarized in Fig. 9B. By comparing the simulated reflection spectrum (for 60% surface coverage) in Fig. 9A with the experimental spectra in Fig. 5E, it is clear that the experimental and theoretical spectra match with each other in regards with the shape and λ_0 of the spectra, although the experimental reflection is apparently higher than the simulated results. This mismatch could be attributed to the unwanted diffusive reflection caused by the large particle aggregates seen in the SEM images(Fig. 7)[58].

Above we have shown that by optimizing the important parameters (e.g., dispersing dielectric medium, nanoparticle concentration, and coating time) of the electrostatics-assisted colloidal self-assembly process, we can experimentally achieve monolayer anti-reflection coatings with the optimal nanoparticle surface area coverage predicted by numerical simulations. In addition, this new bottom-up technology enables the scalable fabrication of nanoparticle anti-reflection coatings on very large substrates. In all above experiments, only small glass microslides(75 × 25 mm) were used as the coating substrates to optimize the critical experimental parameters. Later it was demonstrated that coating larger glass substrates using the optimal conditions proved to be just as simple. It can be seen from Fig. 10 that a 5 × 5 inch glass substrate was coated with 110 nm silica nanoparticles. The coatings were uniform on both sides

of the glass substrate with no visible defects. The photograph in Fig. 10 compares the anti-reflection properties of the coated and an uncoated glass substrate. It is apparent that the nanoparticle coating can significantly suppressed optical reflection since no glare can be seen from the coated glass surface.

Unlike many other existing coating technologies (e.g., spin-coating and LB-assisted assembly)[19,21], a major advantage of this electrostatics-assisted methodology is that we are not limited to coat one substrate at a time. Instead, many glass substrates can be coated all at once. The experimental setup used to simultaneously coat multiple glass samples (5×5 inch) is shown in Fig. 11A. A proof-of-concept experiment was conducted to parallelly coat three glass substrates with 110 nm silica nanoparticles for 90 min. All three coated samples were very uniform and no distinguishable difference was noticed among them. Fig. 11B and Fig. 11C compare the typical specular reflection and transmission spectra obtained from these samples. They all exhibited almost identical anti-reflection and optical transmission properties. Therefore, this new coating technique could potentially be scaled up and used in industry to parallelly fabricate high-quality nanoparticle anti-reflection coatings on large glass substrates.

4. Conclusions

In conclusion, we have developed a simple, inexpensive, and scalable bottom-up technology for simultaneously coating both sides of glass substrates with self-assembled silica nanoparticles by electrostatically controlled adsorption. The hydroxylated glass substrates carrying negative surface charges can be adjusted to positive, which attract the negative nanoparticles via electrostatic attraction. We found that the coating time plays a major role on the nanoparticle monolayer surface coverage, which is a critical parameter in determining the anti-reflection performance of the self-assembled coatings as demonstrated by both experiments and RCWA simulations. Importantly, the optimal nanoparticle surface area coverage was determined by

theoretical calculations to be ~60% which can be readily achieved by the electrostatics-assisted self-assembly technology. We have also demonstrated that this technology can be applied in parallellycoating multiplelarge-area glass substrates with uniform coatings, promising for industry-scale fabrication of inexpensive anti-reflection coatings for a wide spectrum of applications (e.g., efficient photovoltaic panels).

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Figure Captions

Fig. 1. Schematic illustration showing the surface functionalization of a glass substrate by APS.

Fig. 2. Two-sided specular reflection (A) and transmission (B) spectra comparing anti-reflection coatings resulting from different mass fractions of silica nanoparticles in ethanol and water mixture.

Fig. 3. Photographs comparing nanoparticle anti-reflection coatings prepared with (A) and without (B) shaking during the electrostatics-assisted deposition process.

Fig. 4. Two-sided specular reflection (A) and transmission (B) spectra comparing the effect of varying the coating times.

Fig. 5. Two-sided specular reflection (A, C, E) and transmission (B, D, F) spectra comparing the uniformity of the coatings prepared with different coating times. (A and B) 15 s. (C and D) 30 min. (E and F) 90 min.

Fig. 6. Summary of the average two-sided reflection (A) and transmission (B) values at 600 nm wavelength for nanoparticle coatings prepared with different coating times.

Fig. 7. Typical top-view SEM images showing surface area coverage achieved by 110 nm silica nanoparticles for different coating times. (A) 15 s. (B) 5 min. (C) 30 min. (D) 90 min.

Fig. 8. Average nanoparticle surface area coverage for coatings prepared with different coating times.

Fig. 9. (A) Simulated single-sided reflection spectra from a glass substrate with different nanoparticle surface area coverage values. (B) Minimal reflection and the corresponding wavelength vs. nanoparticle surface area coverage.

Fig. 10. Photograph comparing the anti-reflection properties of an uncoated (top) and a nanoparticle-coated (bottom) glass substrate (5×5 inch in size).

Fig. 11. (A) Schematic illustration of the experimental setup used to parallelly coat multiple glass samples. (B and C) Specular reflection and transmission spectra obtained from 3 simultaneously coated samples.

Figures

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