ORIGINAL ARTICLE

Anti-reflective coatings prepared via layer-by-layer assembly of mesoporous silica nanoparticles and polyelectrolytes

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Mesoporous silica nanoparticles (NPs) with diameters of ~30 nm were fabricated using a dialysis process. The resulting NPs exhibit high colloidal stability and are applicable for the preparation of coating films on glass substrates via electrostatic layer-by-layer (LbL) assembly using cationic polyelectrolytes. The thickness and packing density of coating films can be controlled by layer number and mesoporous silica NP dispersion concentration. It was found that glass substrates that were coated with mesoporous silica NPs in an LbL process exhibited high anti-reflective (AR) performance. The highest AR effects (<1% in the wavelength region of 450–600 nm) were obtained with films prepared with six bilayers of cationic polyelectrolytes and mesoporous silica NPs at a concentration of 40 $\mu\text{g ml}^{-1}$.

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INTRODUCTION

Anti-reflective (AR) coatings are increasingly being studied because of the large demands for devices with glass substrates.^{1–12} These coatings are commonly applied to devices to prevent light reflection-associated problems, such as flares and ghost images in optic lenses and reduced visibility on display screens. To date, several strategies have been developed to prepare AR coatings.^{13,14} In particular, the introduction of low- n films has represented a very important breakthrough in the development of interference AR coatings.³ The basic principle of AR coatings using low- n films has been utilized for over two centuries.^{15–17} Optical elements based on glass and/or polymers have refractive index (n) values in the range of 1.4–1.7, and they reflect ~10% of normal incident light. This reflection could be suppressed at a given wavelength by a single AR coating layer with (a) $n_f = (n_s \times n_a)^{1/2}$ (with n_f , n_s and n_a representing the indices of film, substrate and air, respectively) and (b) an optical thickness that is one-fourth of the reference wavelength. Although condition (b) can be easily met, condition (a) requires an n_f of ~1.2–1.3 to achieve efficient AR performance. The lowest attainable n values of homogeneous dielectric materials are typically ~1.35.^{18,19} To overcome this issue, porous materials have been proposed for AR applications. Average n_f values can be drastically reduced with very-limited light scattering when the pore size is much smaller than the light wavelength. In recent years, great efforts have been put forth to develop porous inorganic coatings for AR applications. Yoldas and Partlow prepared low-refractive index (low- n) glasses by controlling the surface morphology of coating films.² Highly porous silica films were

obtained by etching silica films prepared from tetraethoxysilane by the sol-gel method with HF. Mukherjee and Lowdermilk prepared a low- n glass with 0.1–0.2% visible light reflectance by applying a phase-separable thin film with a composition of $84\text{SiO}_2 \cdot 12\text{B}_2\text{O}_3 \cdot 4\text{Na}_2\text{O}$ and subsequently leaching out the B_2O_3 -rich phase.⁴ Makita *et al.*⁵ prepared silica-based coatings with various surface morphologies, such as flat, porous and concave-convex structures, using a mixture of two sols derived from polymerized tetraethoxysilane and methyltriethoxysilane (MTES). Yamaguchi *et al.*^{7–10} prepared porous Al_2O_3 coatings with flowerlike structures via the sol-gel method and subsequent hot water treatment. Mesoporous silica nanoparticles (NPs) are one of the most versatile candidates for obtaining porous inorganic coatings with high AR performance. Imai and co-workers¹¹ prepared transparent thin films with an ultralow refractive index ($n = 1.07$ – 1.16) through a spin-coating technique using mesoporous silica NPs. Shimojima and Okubo reported on nanocomposite films with well-dispersed mesoporous silica NPs in a silica matrix prepared using a bar-coater.¹² Both of these mesoporous silica-based coatings exhibited excellent AR properties. However, these coating techniques are limited to use on planar substrates. AR coatings are currently required not only for flat panels but also for optical materials with complicated structures, such as microlens arrays.²⁰

In this study, we developed mesoporous silica NP-based coatings films via layer-by-layer (LbL) assembly using oppositely charged polyelectrolytes. LbL assembly has the important advantage of high control over thickness, which arises because of the linear growth of the films that occurs with increasing the number of bilayers. Ionic attraction

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between opposite charges is the driving force for the multilayer build-up in the LbL assemblies. Coating films with homogeneous thicknesses can be fabricated not only on planar surfaces but also on surfaces with complicated structures, such as concave–convex structures. Therefore, the LbL technique is appropriate for the fabrication of AR coatings on optical materials with complicated structures, such as microlens arrays. Here, we examine the LbL assembly of mesoporous silica NPs with cationic polyelectrolytes. To control the packing density of mesoporous silica NPs in the layer, mesoporous silica NP dispersions with various concentrations were examined. In addition, coating films with different thickness were prepared by changing the number of layers to optimize the AR performance.

EXPERIMENTAL PROCEDURE

Materials

Tetramethyl orthosilicate, hexadecyltrimethylammonium bromide (CTAB), triethanolamine, acetic acid and ammonia water (1 mol dm^{-3}) were purchased from Kishida Chemical Co., Ltd. (Osaka, Japan). Ethanol (EtOH) was obtained from Nacalai Tesque, Inc. (Kyoto, Japan). Poly(diallyldimethylammonium chloride) (PDDA; low molecular weight, 20% (w/w) in water) and 3-mercaptopropylpropanesulfonate (MPS) were purchased from Sigma-Aldrich. Co. LLC. (St Louis, MO, USA). Poly(sodium *p*-styrenesulfonate) (PSS, $M_w = 70\,000 \text{ g mol}^{-1}$) was obtained from Acros Organics (Geel, Belgium). All reagents were used as received without any further purification. The water used in all experiments was deionized by a Millipore Milli-Q system (Billerica, MA, USA). Quartz crystal microbalance resonators (9 MHz, gold electrode, AT-cut quartz) were purchased from USI Co., Ltd. (Fukuoka, Japan). QCM resonators and gold-coated glass substrates were cleaned via treatment with Piranha solution (70:30 (v/v), sulfuric acid:hydrogen peroxide). Owing to its high corrosiveness, Piranha solution was handled with extreme care and only prepared in small quantities.

Preparation of mesoporous silica nanoparticles (NPs)

Colloidal mesoporous silica NPs were prepared by using tetramethyl orthosilicate as a silica source, based on a previous report by Kuroda and co-workers.²¹ Triethanolamine (0.420 g) and CTAB (2.00 g) were dissolved in deionized water (240 ml). The solution was stirred at 80°C for 0.5 h. Then, tetramethyl orthosilicate (11 mmol) was added to the solution and stirred vigorously for 0°C for 2 h. Finally, the colloidal dispersion was filtered through filtering paper (No. 5). The molar ratio of tetramethyl orthosilicate:CTAB:triethanolamine: H_2O was 1:0.5:0.25:1200. The resulting colloidal dispersion (35 ml) was transferred into a cellulose dialysis membrane tube (molecular weight cut-off = $12\,000\text{--}14\,000 \text{ Da}$) and was dialyzed for 24 h against a mixture of 2 M acetic acid and ethanol (1:1 (v/v); 170 ml) to remove CTAB. This process was repeated three times. Then, the tube with the mesoporous silica NPs was immersed in ammonia water (pH 9.6) for 24 h to remove the acetic acid. This process was also repeated three times. The obtained dispersion of mesoporous silica NPs was filtered through a $0.45\text{-}\mu\text{m}$ regenerated cellulose syringe filter.

Layer-by-layer assembly of mesoporous silica nanoparticles and polyelectrolytes on substrates

To quantify the amount of polyelectrolyte deposited with each adsorption step, a QCM was employed. The QCM resonators were first coated with MPS to yield negatively charged surfaces. Precursor layers of (PDDA/PSS)₂ were adsorbed onto the resonators prior to LbL assembly of mesoporous silica NPs and PDDA. The resonators were then exposed to a PDDA solution to yield positively charged surfaces. Each resonator was then dried under a gentle N_2 stream, and the process was repeated, replacing PDDA with PSS. PDDA/mesoporous silica NP multilayered films were assembled on the substrates coated with precursor layers by sequential deposition of PDDA and mesoporous silica NPs using the same procedure as that used for the precursor layers. Film growth was monitored by changes in the QCM frequency, as measured by a frequency counter (SEIKO EG&G, Tokyo, Japan). Frequency changes were measured after the deposition of each layer. The QCM frequency (ΔF) decreases proportionally to increases in mass on the QCM surface. In our system, the following relationship was obtained between the adsorbed mass,

ΔM (g), and the frequency change, ΔF (Hz), taking into account the characteristics of the quartz resonator:

$$\Delta F = -1.83 \times 10^8 \times \Delta M/A \quad (1)$$

where A is the cross-sectional area of the QCM between the electrodes ($0.16 \pm 0.01 \text{ cm}^2$). All experiments were conducted at 25°C . LbL assembly of mesoporous silica NPs and polyelectrolytes was also performed on glass substrates. Glass substrates used for LbL assembly were cleaned by using the RCA protocol (that is, by immersing in a 5:1:1 $\text{H}_2\text{O}/\text{H}_2\text{O}_2 \text{ aq.}/\text{NH}_4\text{OH}$ (v/v/v) aq. mixture for 10 min at 70°C) and rinsed with deionized water. The multilayer films with the (PDDA/PSS)₂ precursor layer and (PDDA/mesoporous silica NPs)_{*n*} layer were assembled onto the glass substrates using the same procedure as that described for the QCM resonators.

Characterization

ζ -potentials and hydrodynamic diameters of mesoporous silica NPs were measured in deionized water with a light scatterer equipped with a laser Doppler system (Ohtsuka Electronics, Co., Ltd., Osaka, Japan, ELS-Z). The mesoporous silica NP morphology was observed using a transmission electron microscope (Hitachi High-Technologies Co., Tokyo, Japan, H-800, operated at 200 kV). Transmission electron microscope samples were prepared by depositing droplets of aqueous suspensions of the precipitates on Cu grids and allowing them to air dry overnight. The surfaces and cross-sections of the films were examined with a field emission scanning electron microscope (FE-SEM) (Hitachi High-Technologies Co. S-4800 operated at 2.0 kV). Optical transmission and reflection spectra (angle of incidence = 5°) were measured with air as the reference using a UV–visible spectrometer (JASCO Co., Tokyo, Japan, V-570). Fourier transform–infrared spectra were collected with a JASCO FT/IR-4200 spectrometer.

RESULTS AND DISCUSSION

A photograph of an aqueous dispersion of mesoporous silica NPs is shown in Figure 1a. The dispersion was almost transparent in the range of visible light and was stable for several months in water without precipitation, aggregation or gelation. The morphology and size of the mesoporous silica NPs were investigated by transmission electron microscope observation, as shown in Figure 1b. The micrograph demonstrates that the majority of the NPs have a diameter of $\sim 30 \text{ nm}$ and that a black and white contrast is present within each NP. The hydrodynamic diameter of the mesoporous silica NPs was estimated to be 29.6 nm (polydispersity index: 0.122) by dynamic light scattering, which corresponded well with transmission electron microscope observations. These results indicate that the mesoporous silica NPs dispersed in the media as primary particles without any aggregation. The ζ -potential of NPs before dialysis was +82.0 mV (pH

Figure 1 (a) Photograph of mesoporous silica nanoparticle dispersion and (b) transmission electron microscope image of mesoporous silica nanoparticles. A full color version of this figure is available at *Polymer Journal* online.

7.4). The positive surface charge is attributed to the presence of CTAB on the NP surface.²² After dialysis, the ζ -potential decreased to -37.3 mV (pH 9.4). This result indicates that the cationic surfactant, CTAB, was removed by dialysis, as silica colloids are typically negative above their isoelectric point at pH 2.7.²³ Previously, Kuroda and co-workers¹⁹ reported that mesoporous silica NPs obtained in a similar procedure were positively charged ($+3.1$ mV), even after dialysis. In their system, water was utilized to remove acetic acid and EtOH after dialysis against an acetic acid/EtOH mixture. Here, ammonia water (pH 9.6) was employed after dialysis against an acetic acid/EtOH mixture. It appears that the second dialysis step with ammonia water facilitated the complete removal of CTAB from mesoporous silica NPs. Fourier transform-infrared analyses also confirmed that the surfactant was completely removed (see Supplementary Figure S1).

Figure 2 Quartz crystal microbalance frequency shifts ($-\Delta F$) for layer-by-layer assembly on Au-quartz crystal microbalance resonators coated with a precursor layer (3-mercaptopropylsulfonate/(poly(diallyldimethylammonium chloride)/poly(sodium *p*-styrenesulfonate))₂). Open symbols: poly(diallyldimethylammonium chloride) (1.0 mg ml^{-1} in 0.5 mol dm^{-3} NaCl aq.); solid symbols: mesoporous silica nanoparticles. Circles: $4.0 \mu\text{g ml}^{-1}$; squares: $8.0 \mu\text{g ml}^{-1}$; diamonds: $40 \mu\text{g ml}^{-1}$; triangles: $400 \mu\text{g ml}^{-1}$.

To quantify the amount of polyelectrolytes and mesoporous silica NPs deposited in each adsorption step, a QCM was employed throughout the assembly process. The QCM frequency, $-\Delta F$, decreases proportionally to increased mass on the crystal surface, according to the Sauerbrey equation.²⁴ Prior to LbL assembly of mesoporous silica NPs and PDDA, a PDDA/PSS multilayer precursor film was prepared to stabilize the surface charge. QCM electrodes were alternately immersed for 15 min in aqueous PDDA and PSS solutions (in 0.5 mol dm^{-3} NaCl aq.) with intermediate washing and drying under an N_2 stream after deposition of each layer. This process was periodically interrupted to measure the QCM resonance frequency. From the $-\Delta F$ measured at each step of the assembly of PDDA/PSS, regular film growth was observed, and the average mass change from each monolayer adsorption step was $\sim 0.3 \mu\text{g cm}^{-2}$ for both PSS and PDDA layers (see Supplementary Figure S2). After the formation of the precursor film, LbL assembly of mesoporous silica NPs and PDDA was conducted in the same manner. Mesoporous silica NPs were not adsorbed onto the anionic PSS surface because mesoporous silica NPs are negatively charged at pH 9.4.²⁵ Figure 2 shows QCM frequency changes during the assembly of mesoporous silica NPs at pH 9.4 in alternation with cationic PDDA. One can observe a linear increase in film mass ($-\Delta F$ is proportional to mass, M) for all of the tested mesoporous silica NP concentrations. Larger and smaller steps correspond to adsorption of mesoporous silica NPs and PDDA, respectively. The magnitude of the growth step increases with mesoporous silica NP concentrations. The $-\Delta F$ values for single mesoporous silica NP adsorption steps are 88.3, 140.0, 416.3 and 598.7 Hz for NP concentrations of 4.0, 8.0, 40 and $400 \mu\text{g ml}^{-1}$, respectively. The deposited amount of mesoporous silica NPs on the substrate increased by approximately five times when the concentration of mesoporous silica NPs was increased from 4.0 to $40 \mu\text{g ml}^{-1}$. However, the deposition amount only increased by 1.5 times when the concentration of mesoporous silica NPs was increased from 40 to $400 \mu\text{g ml}^{-1}$. The concentration dependence of silica NP deposition cannot be explained by simple shifts of partition of silica NPs between bulk media and the surface. Kunitake and co-workers²⁵ presented two

Figure 3 Field emission scanning electron microscope images of layer-by-layer coating film surfaces prepared using mesoporous silica nanoparticle dispersions at (a) $4.0 \mu\text{g ml}^{-1}$, (b) $8.0 \mu\text{g ml}^{-1}$ and (c) $40 \mu\text{g ml}^{-1}$.

possibilities for the concentration effect. One explanation is based upon the increase in the ionic strength at high silica NP concentrations, which induces enhanced adsorption. Another explanation is related to the state of dispersion of silica NPs. Adsorption of silica NPs onto PDDA is saturated just within 15 s. These fast kinetics imply that adsorption is a nonequilibrium process. It is possible that large clusters of silica NPs are formed at high silica concentrations and are preferentially adsorbed.

To investigate the structure of the PDDA/mesoporous silica NPs assembly, the multilayer films were examined by FE-SEM. Figure 3 shows FE-SEM images of the surface of the mesoporous silica NPs/PDDA films formed on glass substrates. Mesoporous silica NPs were deposited onto (PDDA/PSS)₂/PDDA multilayer films (that is, single mesoporous silica NP layers were deposited). At low concentration of mesoporous silica NPs ($4.0 \mu\text{g ml}^{-1}$), sparse deposition and relatively low packing density (loose NP packing within layers) were observed. The packing density was improved with increased mesoporous silica NP concentrations. A high-quality film with a smooth surface was obtained with mesoporous silica NP dispersions at concentrations over $40 \mu\text{g ml}^{-1}$. Figure 3c shows well-packed NPs in the two-dimensional plane. These results indicate that the packing density of mesoporous silica NPs in this layer can be controlled by changing the concentration of dispersions. Figure 4 shows the optical reflection spectra of a

Figure 4 Optical reflection spectra of (a) soda-lime-silica glass substrate and glass substrates coated with layer-by-layer films prepared using mesoporous silica nanoparticle dispersions at (b) $4.0 \mu\text{g ml}^{-1}$, (c) $8.0 \mu\text{g ml}^{-1}$, (d) $40 \mu\text{g ml}^{-1}$ and (e) $400 \mu\text{g ml}^{-1}$.

Figure 5 Field emission scanning electron microscope images of cross-sections of layer-by-layer coating films of (poly(diallyldimethylammonium chloride)/poly(sodium *p*-styrenesulfonate))₂(poly(diallyldimethylammonium chloride)/mesoporous silica nanoparticles)₅. The mesoporous silica nanoparticle dispersion was employed at $40 \mu\text{g ml}^{-1}$ for the layer-by-layer process.

soda-lime-silica glass substrate ($n = 1.51$, (a)), and the corresponding substrates coated with mesoporous silica NPs/PDDA films prepared from mesoporous silica NPs dispersions with varied concentrations ($4.0 \mu\text{g ml}^{-1}$ (b), $8.0 \mu\text{g ml}^{-1}$ (c), $40 \mu\text{g ml}^{-1}$ (d) and $400 \mu\text{g ml}^{-1}$ (e)). The films were coated on only one side of the substrates. The data show that the reflectance of the coated substrate is decreased by the deposition of mesoporous silica NPs/PDDA films. In addition, the magnitude of the reflectance decrease was related to the concentration of mesoporous silica NPs. The LbL films prepared using dispersions at 40 and $400 \mu\text{g ml}^{-1}$ demonstrate similarly high AR performance. Based on the FE-SEM images and reflection spectra, the concentration of $40 \mu\text{g ml}^{-1}$ is adequate for obtaining a densely packed mesoporous silica NP layer with high AR performance. The light reflected from the

Figure 6 (a) Photographs of soda-lime-silica glass substrate and glass substrates coated with layer-by-layer films. (b) Optical reflection spectra of soda-lime-silica glass substrate and glass substrates coated with layer-by-layer films (one-sided coat and double-sided coat). (c) Optical transmission spectra of soda-lime-silica glass substrate and glass substrates coated with layer-by-layer films (one-sided coat and double-sided coat). The layer-by-layer film is (poly(diallyldimethylammonium chloride)/poly(sodium *p*-styrenesulfonate))₂(poly(diallyldimethylammonium chloride)/mesoporous silica nanoparticles)₆ prepared using a mesoporous silica nanoparticle dispersion at $40 \mu\text{g ml}^{-1}$.

air–film interface can be represented by the reflection coefficient $r = (n^2 - n^1)/(n^2 + n^1)$, where n^1 and n^2 are the refractive indices of the air and film, respectively.³ The reflection coefficient R is generally represented by the energy of reflected light as follows: $R = |r|^2$. Therefore, it is expected that LbL films prepared using mesoporous silica NPs should have a decreased R value. The AR properties of single-layer films depend upon the destructive interference of the reflected light under the following condition: $d = \lambda/4n_2$, where d is the film thickness, and λ is wavelength of visible light. Based on this equation, a suitable thickness for the film should be ~ 95 – 125 nm when the n_2 value is in the range of 1.45 – 1.10 , as human eyes are most sensitive to light in the wavelength of ~ 550 nm.²⁶ The reflection spectra for the LbL films have minimum values in the region of 400 – 600 nm. The minimal reflectivities for these films meet the requirement for AR coatings on glass substrates. In the LbL process, control of film thickness can be easily achieved by simply altering the number of layers. The thicknesses of the LbL films were examined by cross-sectional FE-SEM observations. A typical cross-sectional FE-SEM image of mesoporous silica NPs/PDDA films on the glass substrate is shown in Figure 5. In this case, five bilayers of PDDA/mesoporous silica NPs were deposited onto the glass substrate via LbL assembly, resulting in a film thickness of ~ 110 nm. Film thicknesses were also examined with other bilayer numbers. The film thicknesses of (PDDA/mesoporous silica NPs)₃, (PDDA/mesoporous silica NPs)₄ and (PDDA/mesoporous silica NPs)₆ were 35, 60 and 130 nm, respectively. These results suggest that the thicknesses of LbL films can be easily optimized to maximize the AR performance. Figure 6 shows photographs, reflection spectra and transmission spectra of glass substrates coated with the LbL mesoporous silica NPs/PDDA films that exhibit the best AR performance. The concentration of the mesoporous silica NP dispersion is $40 \mu\text{g ml}^{-1}$. Six bilayers of mesoporous silica NPs/PDDA films were deposited on the glass substrates. The LbL films were coated on one and two sides of the substrates. The double-sided-coated substrate shows a very-low reflectance of $<1\%$ and a high transmission of $>98\%$ in the wavelength region of 450 – 600 nm.

CONCLUSION

Mesoporous silica NPs (diameter of ~ 30 nm) were successfully prepared using triethanolamine and CTAB as a catalyst and a mesopore template, respectively. CTAB molecules were completely removed from mesoporous silica NPs by dialysis against an acetic acid/EtOH mixture and a subsequent dialysis against ammonia water. The obtained mesoporous silica NPs were well-dispersed in water without any aggregates and were negatively charged because of their genuine silica surface. Homogeneous films were formed with mesoporous silica NPs via LbL assembly with the cationic polyelectrolyte, PDDA. QCM results showed that regular deposition of mesoporous silica NPs can be achieved and that the packing density can be varied by altering the concentration of the mesoporous silica NP dispersion. In addition, film thickness can be controlled by simply changing the number of layers in the LbL process. Therefore, it is very easy to tune the characteristics of coating films by utilizing LbL process variables. These results suggest that LbL assembly is advantageous for obtaining consistent coating films with excellent AR properties. Currently, efforts are underway to further enhance the AR performance of the LbL coating film by precisely tuning the LbL conditions, such as the pH and ionic strength of the mesoporous silica NP dispersion as well as the size and porosity of mesoporous silica NPs.

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