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Broadband antireflective superhydrophilic antifogging nano-coatings based on three-layer system

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ABSTRACT

The multifunctional nano-coatings with super-wettability, unique optical property, and excellent mechanical strength and weatherability are highly desirable due to their wide applications. However, up to now, it is still very difficult to balance the relationships among these properties due to structural confliction. In this work, the broadband antireflective superhydrophilic antifogging nano-coatings are successfully constructed based on three-layer system by a sequential dip-coating method. The coating of dendrimer-like mesoporous silica nanoparticles (DMSNs) as top-layer not only increases the roughness of coating surface to enhance the wettability, but also keep high transmittance of the coated glass slides. Simple chemical vapor deposition is performed to improve the mechanical stability of nano-coatings. The finally obtained glass slide with the optimal nano-coating has high transmittance (97.7% at the wavelength of 494 nm, and ca. 5.0% increase of mean transmittance in the visible wavelength range of 390 −780 nm), superhydrophilic (WCAs after 0.5 s of spreading: 4.3°) anti-fogging behavior, and good mechanical strength. This work provides an exploration way about how to balance the structural parameters to obtain the multifunctional nano-coatings for optical devices and energy harvesting.

1. Introduction

Recently, the design and fabrication of nano-coatings with combined property of antireflection (i.e., enhanced transmittance) and super-wettability (such as superhydrophilicity (water contact angle (WCA) less than 5° within 0.5 s or less) for antifogging or superhydrophobicity (WCA larger than 150° and extremely low WCA hysteresis) for self-cleaning) have attracted significant attention due to their wide range of applications in mirrors, glasses, goggles, face masks, showcases, windshields windows for vehicles, solar cells and everyday items [1–5]. The wettability of nano-coatings is enhanced with increase of the roughness of coating surfaces, while the reflection of nano-coatings usually increases with increasing the surface roughness due to diffuse scattering [1–5]. Although high transmittance and super-wettability have contradictory structure requirements (smooth surface *vs.* micro- or/and nanostructured rough surface), significant advances in constructing antireflective nano-coatings with super-wettability on glass surface have been made in recent years by balancing both structural conflict [6–15]. However, the big problem of weak mechanical stability still exists for most these nano-coatings.

Good mechanical strength and weatherability are prerequisite for a nano-coating in a wide range of practical applications [16–19]. Generally, compact nano-coatings or porous nano-coatings with high crosslinking/adhesion degree among building blocks own high mechanical abrasion robustness and long-term durability. However, the surface textures with micro- or/and nanostructured roughness are highly susceptible to mechanical wear from rain,

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snow, wind, sand and scrubbing, and such abrasion may also alter surface chemistry (i.e., surface energy) of nano-coatings. Both results can lead to the loss of surface wettability, which makes mechanical durability become a crucial concern [16–19]. Because a majority of rough surfaces have limited mechanical abrasion robustness and long-term weather durability, this problem has restricted their commercial or industrial applicability, thus prompting scientists to do extensive research efforts on improving resistance against various types of wear damage. For the nano-coatings composed of nanoparticles (NPs), several strategies, such as TEOS CVD treatment, ammonia or HCl vapor treatment, acid-catalyzed silica sol as binder or polymer as adhesive, fluoroalkyl- or organo-silane modification [20–27], have been developed to improve the adhesion degree among NPs, thus achieving higher mechanical strength and weatherability. However, these developed methods also affect the porosity and roughness, resulting in the change of the wettability and optical properties. Up to now, it is still very difficult to balance the relationship among wettability, optical property, and mechanical strength and weatherability by regulating and optimizing the structure and morphology of nano-coating (Fig. 1a). Therefore, it is very significant to explore the promising avenues to construct ideal multifunctional nano-coatings.

Herein, we use the facile dip-coating method to prepare the broadband antireflective superhydrophilic antifogging nano-coatings based on three-layer system by using acid-catalyzed silica sol (ACSS), small solid silica nanoparticles (SSNs) and dendrimer-like mesoporous silica nanoparticles (DMSNs) as building blocks, as shown in Fig. 1b. The coatings comprise the ACSS base-layer for binding/adhesion with substrate, the nanoporous SSNs middle-layer for antireflection and the DMSNs top-layer for superhydrophilicity. The cycle numbers of dip-coating procedure was regulated for the optimal balance of optical property and wettability. The appropriate post-treatments of calcination and simple chemical vapor deposition (CVD) were performed to enhance the mechanical strength of nano-coatings, but unobviously affect the transmittance and hydrophilicity.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS, $\geq$ 99%), cetyltrimethylammonium tosylate (CTA·Tos, $\geq$ 98%) and triethanolamine (TEA, $\geq$ 99%) were purchased from Sigma Aldrich. Aqueous ammonia (NH_3, 25%), absolute ethanol (99.5%) and concentrated hydrochloric acid (HCl, 37%) were purchased from Beihua Fine Chemicals. Ultrapure water with a resistivity higher than 18.2 MΩ cm was used in all experiments and was obtained from a three-stage Millipore Mill-Q Plus 185 purification system (Academic).

2.2. Synthesis of ACSS

ACSS was fabricated according to a reference [27]. TEOS (6.5 g) was mixed with ethanol (53.25 g) and water (2.25 g) that contained the concentrated HCl (0.0125 g). The solution was left in a closed glass container, stirred for 4 h, and aged for at least 4 days at room temperature. ACSS (20 mL) was mixed with ethanol (80 mL) for dip-coating.

2.3. Preparation of SSNs

ca. 20 nm of SSNs were synthesized according to the stöber method [13]. Typically, absolute ethanol (100 mL) and aqueous ammonia (5 mL) were added into a flask. Then, the flask was placed in a 60 °C water bath with magnetic stirring. TEOS (3 mL) was added in the mixture with stirring after the temperature became stable. After stirring for additional 12 h, the ethanolic suspension of SSNs of ca. 20 nm in size (particle concentration: 1.0 wt %) was obtained. Aqueous NH_3 was removed by placing the suspension in a ventilating cabinet for overnight. The obtained SSNs suspension is very stable, which is directly used in the dip-coating.

2.4. Synthesis of DMSNs

Monodispersed DMSNs were synthesized using CTA·Tos as a surfactant, TEA as a mineralizing agent, water as a solvent and TEOS as a silica source [28]. A typical synthesis was performed as follows: a mixture of CTA·Tos (0.96 g), TEA (0.1735 g) and water (50 mL) was stirred at 80 °C for 1 h, and then TEOS (7.8 mL) was quickly added into the surfactant solution. The mixture was stirred with a speed of 1000 rpm at 80 °C for another 2 h. The formed DMSNs were filtered, washed, and dried in an oven at 60 °C. The CTA·Tos was removed from particles by template extraction. The as-prepared DMSNs (1.0 g) were added into ethanolic HCl (concentrated HCl (15 mL) in ethanol (100 mL)), and sonicated for 2 h. The suspension was stirred at 70 °C for 24 h. The extraction procedure was repeated three times to efficiently remove the surfactant. Finally, the precipitates were centrifuged, washed with pure water, and dispersed in ethanol or dried in air at 60 °C. The extracted DMSNs were suspended in ethanol (particle concentration: ca. 0.4 wt %). for the use of dip-coating The calcined DMSNs were obtained by heating at 550 °C for 6 h with a ramp rate of 1 °C/min in air.

2.5. Fabrication of silica particulate coatings

All the silica particulate coatings were prepared by dip-coating method on both surface of glass slides as substrate. The glass substrates were cleaned in ultrapure water by sonication for 10 min and then treated by oxygen plasma for 5 min. The schematic illustration of the dip-coating process in Fig. 1b exhibits that the glass substrate was immersed vertically into different species (ACSS, SSNs and DMSNs suspensions) with a withdrawal speed of 100 mm/min, maintained in the suspension for 20 s, and then kept in the room for 10 min (ACSS) or 30 s (SSNs and DMSNs suspensions) for dry. The dip-coating procedure was repeated for varied times to obtain optimal transmittance and wettability. Then, the as-prepared nano-coatings were calcined at 550 °C for 3 h to remove the organic species and enhance the mechanical durability.

In order to reinforce the mechanical strength of coatings, simple TEOS CVD was used to deposit silica on the coatings [14]. The nano-coatings were placed in an exsiccator together with 2 vessels containing 0.5 mL of TEOS and 0.5 mL of ammonia, respectively. TEOS CVD was performed for 1 h to maintain the high transmittance. Finally, the nano-coatings were calcined at 500 °C for 1 h to further promote hydrolysis and condensation reaction of TEOS for superhydrophilicity.

2.6. Characterization

For transmission electron microscopy (TEM) observations, powder samples were added on carbon-coated copper grids and observed on a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) observations were carried out on a Hitachi S-4800 scanning electron microscope operated at 10 kV. Specimens were coated with a layer of gold with a size of 5 nm by ion sputtering before SEM observations. Transmission spectra in the wavelength range of