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Antifogging antireflective coatings on Fresnel lenses by integrating solid and mesoporous silica nanoparticles

Gang Zhou [a,b], Junhui He [a,*], Ligang Xu [a,b]

[a] Functional Nanomaterials Laboratory and Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Zhongguancundonglu 29, Haidian District, Beijing 100190, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Antifogging antireflective coatings were fabricated on Fresnel lenses by integrating solid silica nanoparticles (SSNs) and mesoporous silica nanoparticles (MSNs) via spin-coating assembly without any high temperature post-treatments. Superhydrophilicity and a maximum transmittance of 96.4% was achieved in the visible spectral range for the $(MSNs)_4$ coating deposited on Fresnel lens. The maximum transmittance even reached as high as 98.5% in the visible spectral range for the $(SSNs)_1/(MSNs)_2$ (i.e., 1 layer of SSNs and 2 layers of MSNs) coating by using the $(SSNs)_1$ coated Fresnel lens instead of uncoated Fresnel lens as the substrate, while superhydrophilicity was well retained. Transmission electron microscopy (TEM) was used to observe the morphology and structure of nanoparticles. Optical properties were characterized by a UV–vis–NIR spectrophotometer. Surface wettability was studied by a contact angle/interface system. Surface morphologies and structures of coatings were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The influences of surface morphology and structure on the optical and wetting properties of coatings were also discussed. The coverage of MSNs was considered to significantly influence both the light transmission and hydrophilicity of coated Fresnel lenses.

1. Introduction

Lenses are widely used in optics [1,2]. However, when the size of lenses is large, conventional spherical lenses suffer from cumbersomeness and spherical aberration [1,3]. The advent of Fresnel lenses, which are made of thin pieces with equidistant concentric circular patterns on one surface of them, has made it possible to solve the problem of conventional spherical lenses. Compared to spherical lenses, Fresnel lenses are plane and could be very thin and light, and they could correct most of the spherical aberration [3]. Because of these advantages, Fresnel lenses are more attractive than convex lenses in many cases such as solar cells and projectors.

Recently, antireflection and antifogging have attracted more and more attention due to their wide range of applications in mirrors, glasses, goggles, face masks, windows for vehicles and solar cells [4–6]. Antireflective and antifogging coatings were reported in previous works of ours [7–14] and other researchers [15,16], and superhydrophilic AR coatings had been successfully fabricated on glasses. In general, Fresnel lenses are made of poly(methyl methacrylate) (PMMA), which is easier to be processed, and has higher transmittance and flexibility than glass. However, as PMMA has low glass transition temperature, high temperature treatments, such as calcination, are not applicable to Fresnel lenses [12,17,18]. Hence, the previous preparation methods of antireflective and antifogging coatings, mostly including the step of high temperature treatments such as calcination, could not be used for Fresnel lenses. Therefore, new approaches to coating fabrication need to be explored to avoid high temperature treatments. Very recently, highly antireflective coatings were also successfully prepared on Fresnel lenses by spin-coating solid silica nanoparticles (SSNs) [17], where nearly zero reflection was achieved and the maximum transmittance reached as high as 99.8%. Unfortunately, the wettability of the coating could not reach superhydrophilicity.

Inspired by previous works [8–12,19–25], mesoporous silica nanoparticles (MSNs) were preliminarily used as building block for fabrication of AR and superhydrophilic silica coatings on Fresnel lenses by spin-coating in the current work. The $(MSNs)_4$ coating on Fresnel lens has excellent superhydrophilicity, but the maximum transmittance of coated Fresnel lens is only 96.4% (an enhancement of 2.1% from uncoated Fresnel lens). On the other hand, our previous work [17] indicated that the $(SSNs)_1$ coating renders Fresnel lens excellent AR property, and the maximum transmittance can reach as high as 99.8%. Therefore, the fabrication of rationally designed coating structures using both SSNs and

* Corresponding author. Tel./fax: +86 10 82543535.
E-mail address: jhhe@mail.ipc.ac.cn (J. He).

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MSNs as building blocks is expected to produce coatings of both superior antireflective and superhydrophilic properties on Fresnel lenses. It is in fact the case. The fabrication of highly antireflective and antifogging coatings on Fresnel lenses was realized by spin-coating SSNs and MSNs on both surfaces of Fresnel lenses without any high temperature treatments. To the best of our knowledge, Fresnel lenses simultaneously with both antifogging (superhydrophilic) and antireflective properties have never been reported before.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS, 99+%) was obtained from Alfa Aesar. 3-Mercaptopropyltrimethoxysilane (MPTS, 95%) was purchased from Aldrich. Ammonia (25%), concentrated hydrochloric acid (37%), cetyltrimethylammonium chloride (CTAC, 25 wt.% in water), diethanolamine (DEA, 98%) and absolute ethanol (99.5%) were purchased from Beihua Fine Chemicals. All chemicals were used as received. 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). PMMA Fresnel lenses (diameter: 28 mm, thickness: 1.5 mm and focal length: 15 mm) were purchased from Shenzhen Haiwang Sensors & Controls Co.

2.2. Preparation of silica nanoparticles

SSNs of ca. 16 nm in size were synthesized as follows [26]. 150 mL absolute ethanol (99.5%) and 7.5 mL aqueous ammonia (25%) were mixed with stirring in a round-bottomed flask. After the mixture was heated to 60 °C in a water bath, 4.5 mL TEOS was added to the mixture with stirring. The mixture was then stirred for additional 12 h, and finally the ethanolic suspension of SSNs of ca. 16 nm in size was obtained.

MSNs of ca. 41 nm in size were synthesized as follows [12,27]. 64 mL of water, 11.25 mL of ethanol, 10.4 mL of a 25 wt.% CTAC aqueous solution, and 0.2 g of DEA were mixed, and stirred in a water bath at 40 °C for 30 min. Then 7.0 mL of TEOS and 0.6 mL of MPTS were added into the mixture within 2 min under stirring. The resulting mixture was stirred at 40 °C for additional 2 h. The as-prepared precipitate was extracted three times in ethanolic HCl (15 mL of conc. HCl in 120 mL of absolute ethanol) at 40 °C for 2 h [28]. The surface of MSNs was then modified with sulfonate groups [12,29], which would make the MSNs more hydrophilic. Finally, the MSNs were centrifuged, washed with absolute ethanol, and dispersed in absolute ethanol.

2.3. Surface treatment of Fresnel lens and preparation of nanoparticle films

The Fresnel lenses were pre-cleaned with deionized water, and dried at 60 °C. Then they were treated with oxygen plasma (0.84 W) for 5 min to remove any organic contaminants on their surfaces [30] and render their surfaces a significant amount of surface hydroxyl groups. The suspension of SSNs (1.0 wt.%) or MSNs (1.0 wt.%) was spin-coated on the pre-treated Fresnel lenses first at 50 rpm for 15 s and then at 2000 rpm for 40 s to prepare $(SSNs)_1$ coatings or $(MSNs)_n$ coatings [17]. To fabricate $(SSNs)_1/(MSNs)_n$ coatings on Fresnel lenses, the Fresnel lenses with $(SSNs)_1$ coatings were used as substrate, and the suspension of MSNs (1.0 wt.%) was spin-coated on the $(SSNs)_1$ substrates likewise.

2.4. Methods of characterization

To examine the morphologies of as-prepared SSNs and MSNs, the ethanolic suspension of SSNs and MSNs were added onto carbon-coated copper grids. After drying at 60 °C overnight, they were examined by high-resolution transmission electron microscopy (HRTEM) on a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 150 kV. The surface morphologies of as-prepared coatings were examined by atomic force microscopy (AFM) on an MM8-SYS scanning probe microscope (Bruker AXR) and scanning electron microscopy (SEM) on a Hitachi S-4300 scanning electron microscope operated at 5 kV. The specimens were coated with a layer of gold by ion sputtering before SEM observations. Transmission spectra in the range of 350–800 nm were recorded using a Varian Cary 5000 UV–vis–NIR spectrophotometer. Water contact angles (WCAs) of surfaces were measured at ambient temperature on a JC2000C contact angle/interface system (Shanghai Zhongchen Digital Technique Apparatus Co.), the angle precision of which is ±0.5°. Water droplets of an appropriate volume (ca. 2 μL) were dropped carefully onto the sample surfaces. The Brunauer–Emmett–Teller (BET) specific surface areas were calculated by using adsorption data in P/P_0 = 0.04–0.25 (six points collected). Pore-size distributions were estimated from adsorption branches of the isotherms by using the Barrett–Joyner–Halenda (BJH) method. Pore volumes were determined from the amounts of N_2 adsorbed at a single point of P/P_0 = 0.98. For examination of antifogging property, a Fresnel lens with nanoparticle coatings and an uncoated Fresnel lens (as control) were cooled at ca. −15 °C for 3 h in a refrigerator, and then exposed to humid laboratory air (room temperature: 20–30 °C, relative humidity: 20–40%).

3. Results and discussion

3.1. Morphology and structure of silica nanoparticles

SSNs can be synthesized by the Stöber method, and the size of SSNs can be regulated by changing the temperature of reaction [26]. In the current work, we prepared SSNs by controlling the temperature at 60 °C. The TEM image of obtained SSNs is shown in Fig. 1a. It could be seen that they are basically monodisperse. Some particles are connected together, producing SSNs of peculiar shapes, which are attractive for construction of rough and stable surfaces [10]. Fifty particles in Fig. 1a were measured and the mean size of SSNs was estimated to be ca. 16 nm.

There are varied approaches to the synthesis of MSNs [27,31,32]. In this work, a facile synthetic route was used to produce monodisperse MSNs in high yields. The particle size could be controlled by adding suitable additives (e.g., inorganic bases, alcohols), which would affect the hydrolysis and condensation of silica species [27]. Fig. 1b shows the morphology and structure of as-prepared MSNs. Clearly, the obtained nanoparticles are monodisperse and well dispersed. Again, fifty particles in Fig. 1b were measured and the average diameter of the nanoparticles was estimated to be ca. 41 nm. The BET surface area, pore volume and BJH pore diameter of MSNs were estimated to be 751.3 $m^2 g^{-1}$, 1.3 $cm^3 g^{-1}$ and 3.8 nm, respectively.

3.2. Spin-assembly of $(MSNs)_n$ coatings on Fresnel lenses and their optical and wetting properties

Fresnel lens has two surfaces, i.e., the smooth surface and the patterned surface. As Fresnel lens with coatings on both patterned and smooth surfaces is more antireflective than that with a coating on a single surface [17], all Fresnel lenses were coated on both surfaces in the current work. Coatings spin-assembled are named as