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Sol-gel based antireflective coatings with superhydrophobicity and exceptionally low refractive indices built from trimethylsilanized hollow silica nanoparticles

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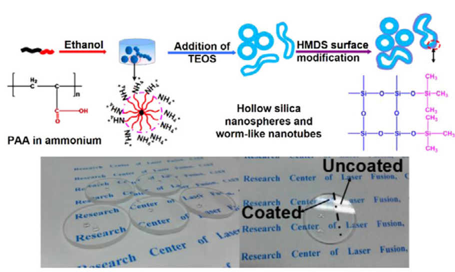
HIGHLIGHTS

- Antireflective coatings with ultralow refractive indices (as low as 1.08) were prepared via a sol-gel process.
- The prepared coatings are superhydrophobic without requiring any post-treatment.
- The coated substrate surface showed water contact angle value as high as 156°.
- The coating produced a fair antireflection effect consisting of more than a 4% increase in optical transmittance.

GRAPHICAL ABSTRACT



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ABSTRACT

We reported the preparation of antireflective (AR) coatings with superhydrophobicity and ultralow refractive indices (as low as 1.08) at room temperature from sols containing hexamethyldisilazane (HMDS)-functionalized hollow silica nanoparticles (HSNs) via a sol-gel process. The prepared sols were suitable for large area processing with ease of coating and being directly applicable without requiring any post-treatment. The water contact angles (WCAs) of the resulted coatings increased from 15° to 156° with the increase of HMDS content, which afforded the coatings superior water repellency properties. Besides this, HMDS-functionalized HSNs-based layer produced a fair antireflection effect consisting of more than a 4% increase in optical transmittance. These multifunctional coatings may find potential applications in fields of electronics, and optical devices.

1. Introduction

In optical sciences, the refractive index of a medium is considered as the most fundamental quantity because it determines not only the phase velocity of light, but also refraction, reflection and diffraction occurring at the interface of the medium [1]. It is well known that reflections will inevitably appear when light propagates across an interface of two media with different refractive indices. Thus, achieving a way to reduce the reflection loss would be of interest for Si-based solar cell and optoelectronic device applications. The simplest way should be designed with a single-layer material for destructive interference. To eliminate the reflection at the interface between air and the substrate, two requirements should be satisfied. First, $n_f = (n_s n_a)^{1/2}$, where n_f, n_s, and n_a are the

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refractive indices of coating, substrate, and air, respectively. Second, the coating thickness must be one-quarter of the incidence wavelength in the optical medium. The refractive index of a typical optical substrate such as glass is approximately 1.5. Therefore, the refractive index of the coating must be controlled to be smaller than 1.22. However, dense optical materials with very low refractive indices that closely match the refractive index of air (n = 1.0) do not exist in nature. Magnesium fluoride and silica materials have bulk refractive indices of 1.39 and 1.46, respectively, which are among the lowest [1]. One prominent way to achieve a lower refractive index is to introduce porosity into the materials [2] because of the relationship between refractive index and porosity. Therefore, highly porous silica-based coatings are highly desirable materials that can be used for preparing AR coatings as a result of their high accessible surface area, low dielectric constant, and adjustable refractive index.

Numerous investigations have been carried out to develop materials with an ultralow refractive index. Physical vapor deposition and chemical etching were two of the earliest techniques and are now among the most commonly used methods. Xi and co-workers [1,3] reported two silica nano-rod array films with refractive indices as low as 1.08 and 1.05. These coatings from oblique-angle deposition, an expensive process that is inconvenient to tune the refractive index and film thickness is unsuitable for large substrates. Yamaguchi [4] obtained highly porous coatings having ultralow refractive index (n = 1.07) and good transparency using mesoporous silica nanoparticles. But the use of environmentally hazardous solvents or high calcination temperatures is undesirable for certain polymer substrates. Our group [5] demonstrated the lowest refractive index of 1.03 through nanoetching of mesoporous silica films in hydrofluoric acid solution. However, the use of highly hazardous etchants is a disadvantage in large-scale applications. Thus, new fabrication methods under mild conditions for nanoporous materials are strongly desired.

It is well known that the sol-gel process is a potential method for the preparation of nanoporous materials because of its low process temperature, low cost, the high purity of the resulting materials and the availability of substrates with various shapes and sizes. As we can know from previous papers [6–14], the refractive indices of the coatings can be tuned by simply changing the ratio of starting materials bearing nonpolar groups, such as methyl, trimethylsilyl (–$Si(CH_3)_3$). Once these nonpolar groups incorporated into the coating materials coatings, they can prevent the collapsing of pores during solvent evaporation, and lower the surface energy of the coatings, thus providing extra-functionalities such as high surface area, good AR properties and intrinsic hydrophobicity. Unfortunately, to the best of our knowledge, the refractive index of 1.10 was the lowest one that this mild method can achieve [7,11,14]. How to further lower the refractive index (<1.10) of a coating and endow it with excellent AR and superhydrophobic properties simultaneously under mild conditions is still a big challenge.

In the current work, HMDS-modified HSNs were applied to fabricate porous silica films with ultralow refractive index, superhydrophobicity and AR properties via dip-coating process. The refractive indices of these coatings were in the range 1.13–1.08. The surface modification of HSNs significantly increased the hydrophobicity of silica thin film and the WCA of the film increased from 15° to 156°, increasing the durability of the pore structure in atmospheric conditions. These coatings also exhibited relatively excellent AR properties, and a maximum transmission value of 96.95% could be achieved. The main advantage of this strategy is the production, by eliminating the harsh template removal steps, of thin films with ultralow refractive index, excellent AR properties, and superhydrophobicity at room temperature.

2. Experimental section

2.1. Materials

Tetraethylorthosilicate (TEOS, 98 + %), hexamethyldisilazane (HMDS, 98%) were obtained from Alfa Aesar. Aqueous ammonia (25%), absolute ethanol (99.5%) were purchased from Tianjin Kemiou Chemical Reagents Co., Ltd. (Tianjin, China). Poly(acrylic acid) (PAA, Mw ≈ 3000) was obtained from Aladdin Chemistry. The water was deionized. All chemicals were used without further purification.

2.2. Preparation of HSNs and HMDS-modified HSNs

In a typical procedure [15,16], 0.06 g of PAA dissolved in 7 mL of aqueous ammonia was mixed with 180 mL of absolute ethanol, followed by the injection of 5 aliquots of TEOS totaling 1.0 mL over a time interval of 1 h under vigorous magnetic stirring at room temperature. After 48 h, HSNs were formed. HMDS was added into the HSNs sols and aged at 25 °C for more than 20 days to guarantee the surface modification of HSNs being carried out conveniently. The weight ratio of HMDS to TEOS (HMDS/TEOS) was varied from 0 to 10. The sols are denoted as "S-X", in which X means the HMDS/TEOS. That is, the sols prepared from various HMDS/TEOS (from 0 to 10) are abbreviated as S-0, S-2, S-4, S-6, S-8, and S-10, respectively.

2.3. Film preparation

The procedure for preparation of HMDS-treated HSNs coatings was divided into three steps. First, K9 glass or silicon substrates were cleaned with Piranha solution (98 wt% H_2SO_4/30 wt% H_2O_2; 7:3 v/v), and then washed with pure water (caution: the Piranha solution is highly dangerous and must be used with great care). Second, the substrates were modified by exposing all substrates to a saturated HMDS vapor for 24 h at room temperature to increase the hydrophobicity of the substrates. This was done by allowing substrates to stand near a bottle of HMDS in a sealed chamber. Finally, a dip-coating method was used for thin film production. The suspension was dip-coated on substrates at a fixed withdrawal speed (1000 mm min^{-1}). The procedure for preparation of the pure HSNs coatings were performed according to the first and third steps. The films prepared from S-X were denoted as "F-X".

2.4. Characterization

Transmission spectra in the wavelength range of 400–1200 nm were recorded using an UV–vis-NIR (Mapada, UV-3100PC, transmittance error ≤0.2%, wavelength ≤0.1 nm). Scanning electron microscopy (SEM) images of the as-prepared coatings were taken using a Zeiss Supra55 field-emission scanning electron microscope. The specimens were coated with a layer of gold by ion sputtering before the SEM observations. For transmission electron microscopy (TEM) observations, the sols were put onto carbon-coated copper grids. After drying, they were observed using a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV. WCAs of the coating surfaces were measured at ambient temperature on a JC2000C contact angle/interface system (Shanghai Zhongchen Digital Technique Apparatus Co.). Water droplets of 4 μL were dropped carefully onto the coating surfaces. The roughness and morphology of the coating surfaces were characterized by atomic force microscopy (AFM) on a SPA-300HV Scanning Probe Microscope. The thickness and refractive indices of the films deposited on silicon substrates were measured by a spectroscopic Ellipsiometer (SENTECH SE850 UV, error limits ≤2%), using the Cauchy model ($n(\lambda) = A + B/\lambda^2 + C/\lambda^4$) in the experimental range