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Preparation of super-hydrophobic antireflective films by rod-like MgF_2 and SiO_2 mixed sol

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ABSTRACT

Antireflective films with self-cleaning and abrasion-resistance properties show good performance in outdoor contaminated environments. In this paper, hollow rod-like MgF_2 sol was synthesized using the solvothermal method and 50 nm SiO_2 particle sol was prepared using the Stöber method. The SiO_2-MgF_2 mixed sol was prepared by adjusting the zeta potential of the two sols, and then the SiO_2-MgF_2 mixed films were coated on the glass using the dip-coating method. The maximum transmittance was 99.4% and the average transmittance was 97.5% in 400–800 nm wavelength regions. After the films were modified by n-hexadecyltrimethoxysilane (HDTMOS), the contact angle reached 150.2°, and the pencil hardness reached 4–5 H. In this way, the multi-functional antireflective films were endowed with significant practical value.

1. Introduction

Antireflective films with super-hydrophobic self-cleaning properties are important to the long-term use of solar photovoltaic and photothermal components used in the outdoor contaminated environments. Currently, super-hydrophobic surfaces are usually produced through the combination of micro-nanostructure and low surface energy [1]. However, the surface roughness of the micro-nanostructure can cause the scattering of incident light on the surface and reduce the transmittance of the films [2]. It is not easy to maintain a balance between high transmittance and superhydrophobicity.

It is possible to increase the hydrophobicity of films by adding organic group or plating hydrophobic materials onto the film surface. Cai et al. prepared antireflective films with the maximum contact angle of 108.7° through the copolycondensation of tetraethylorthosilicate and methyltriethoxysilane [3]. Ding et al. synthesized hollow nano-spherical MgF_2 films with a minimum refractive index of 1.2 and a Rq value of 3.34 nm on the surface [4]. The irregular protrusions of rod nanocrystals on the surface are greater than those of spherical nanocrystals. Moreover, the antireflective films with maximum transmittance of 91% and the maximum contact angle of 163° at 450 nm were produced by coating with polydimethylsiloxane and silica nanoparticle suspension [5]. In fact, the antireflective properties require lower surface roughness, which is incompatible with the pronounced roughness required by superhydrophobicity. Thus, the surface roughness needs to be optimized by balancing the optical and self-cleaning properties.

In this research, we report a novel modification of the widely-used MgF_2 suitable for use as an antireflective material. The SiO_2-MgF_2 mixed sol was synthesized by mixing hollow rod-like MgF_2 particles sol and 50 nm SiO_2 nanoparticles sol. The antireflective films were plated to the glass using the dip-coating method. The optical properties, hydrophobicity and mechanical properties of the mixed films were researched at 400–800 nm.

2. Experimental

2.1. Preparation of hollow rod-like MgF_2 and SiO_2 nanoparticles sol

The hollow-structure MgF_2 particles were obtained by the template-free synthesis method, which was different from other templates [6]. A mixture of magnesium acetate tetrahydrate ($Mg(CH_3COO)_2{\cdot}4H_2O$) and abs. methanol ($CH_3OH$, 99.9%) was stirred until the solids dissolved completely. Hydrofluoric acid (HF, 40 wt%) diluted with CH_3OH was added dropwise to give a solution of $Mg(CH_3COO)_2$: HF: CH_3OH = 1: 1.6: 250 (molar ratio). The solution was placed in 100 mL autoclave lined with polytetrafluoroethylene and heated at 240 °C for 24 h. After rapid cooling, the transparent rod-like MgF_2 sol with concentration of 0.1 mol/L was obtained.

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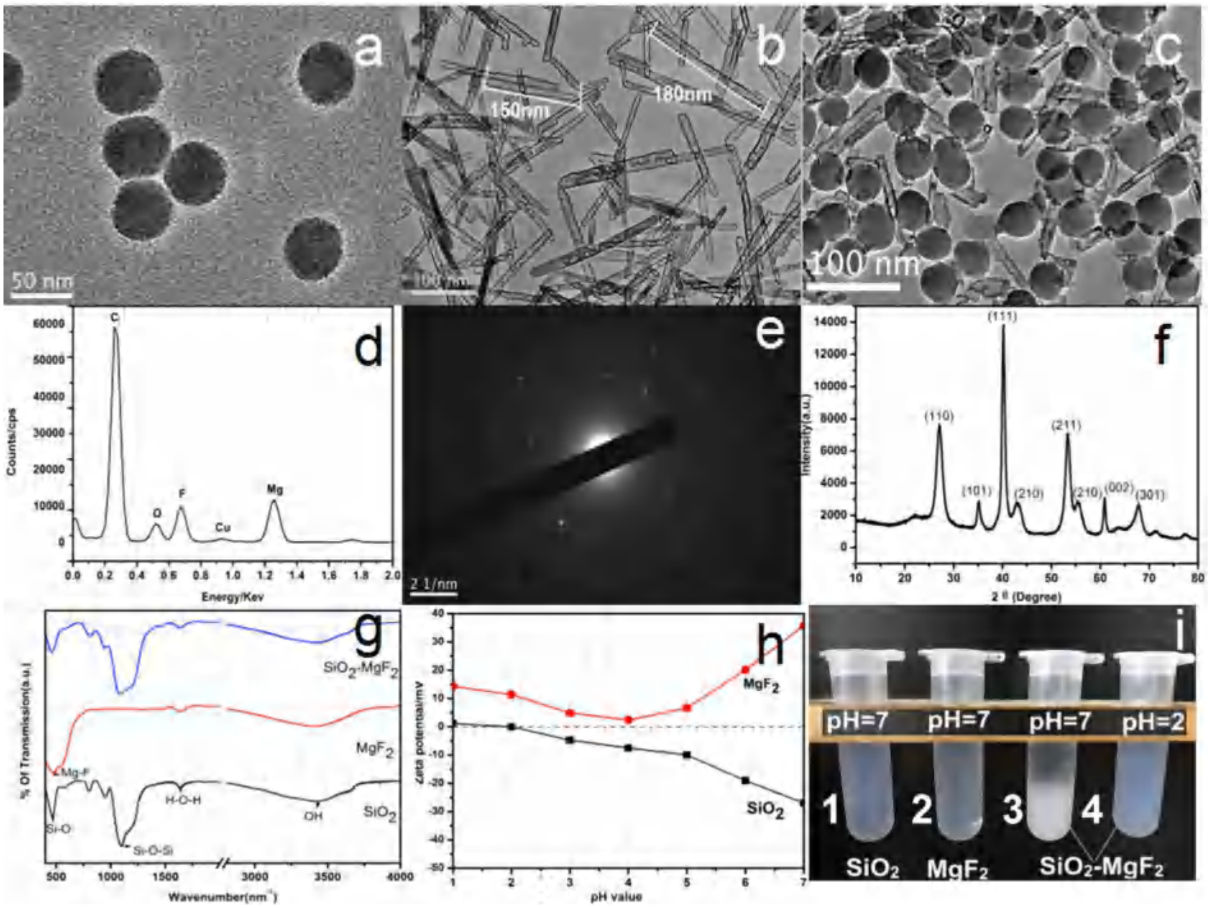

Fig. 1. (a–c) TEM images of SiO_2, MgF_2, and SiO_2-MgF_2 mixed sol. (d) EDS pattern of MgF_2. (e) Electron diffraction pattern of SiO_2-MgF_2 mixed film. (f) XRD pattern of MgF_2. (g) IR spectra of SiO_2, MgF_2, and SiO_2-MgF_2 mixed film. (h) pH-zeta potential of SiO_2 and MgF_2 sol. (i) Experimental image of different sols.

SiO_2 sol was prepared by the Stöber method [7]. The sol was heated at 100 °C for 2 h to remove ammonia to obtain the 0.3 mol/L 50 nm SiO_2 sol and the pH was about 7. All drugs and reagents were purchased from Sinopharm Group Chemical Reagent with the concentration of analytical grade.

2.2. Preparation of SiO_2-MgF_2 hydrophobic self-cleaning antireflective films

The SiO_2 sol was adjusted by 0.1 mol/L HCl solution and pH was 1.5–2.5 under stirred at room temperature for 6 h. Then, a certain amount of MgF_2 sol was added to the sol to prepare the SiO_2-MgF_2 sols with different molar ratios and stirred for 2 h. Borosilicate glass slides were cleaned [8]. The mixed SiO_2-MgF_2 sol was deposited on the glass by dip-coating method. Subsequently, the films were modified with HDTMOS (aladdin, 85%) [9], followed by drying at room temperature to obtain hydrophobic self-cleaning antireflective films.

2.3. Characterization

The structures of sol were observed by TEM (JEM-2100, JEOL). The surface micromorphology and microstructure of films were observed by FESEM (SUPRA55, Zeiss) and AFM (Nano Man VS, Veeco), respectively. The transmittance spectrum, refractive index and hydrophobic angle of the films were measured by UV–Vis spectrophotometer (UV-1700, Shimadzu), spectroscopic ellipsometer (E03, ELLITOP Scientific) and contact angle measuring instrument with HARKE-SPCA standard, respectively. The abrasion resistance was evaluated by pencil hardness tester (291-type, Erichsen). The adhesion strength between the films and the substrate was tested by scratch tester (WS-92). Apparent Zeta-potential was measured by Zeta potential analyzer (Malvern, ZEN3600).

3. Results and discussion

3.1. Preparation and stability of SiO_2-MgF_2 sol

TEM images of the spherical SiO_2 and hollow rod-like MgF_2 sol are shown in Fig. 1a and b. The average diameter of the SiO_2 nanoparticles is about 50 nm (Fig. 1a). MgF_2 sol exhibits a well-formed hollow rod-like structure with a length of 100–150 nm and a diameter of about 15 nm (Fig. 1b). Unlike the hollow spherical MgF_2 synthesized in previous work [4], the starting material ratio of Mg: F < 1: 2 (molar ratio) was adopted to produce $Mg(OH)_{2-X}F_X$ intermediate product. In the crystallization process, Mg^{2+} and F^- were dissolved to produce MgF_2 with hollow rod-like structures.

It is demonstrated that the MgF_2 sol contained only Mg and F elements through EDS analysis (Fig. 1d). The SAED pattern of SiO_2-MgF_2 mixed film is displayed in Fig. 1e. This consists of eight concentric rings per crystal plane. The indices of crystal face were determined by comparing the calculated value of crystalline interplanar spacing with that of standard PDF card (PDF: 41-1443). The results were closely consistent with those of XRD (Fig. 1f). The FTIR spectra of the mixed film were compared with the SiO_2 and MgF_2 films, and no new absorption peaks were found. It is indicated that no new chemical bonds formed between SiO_2 and MgF_2 particles,

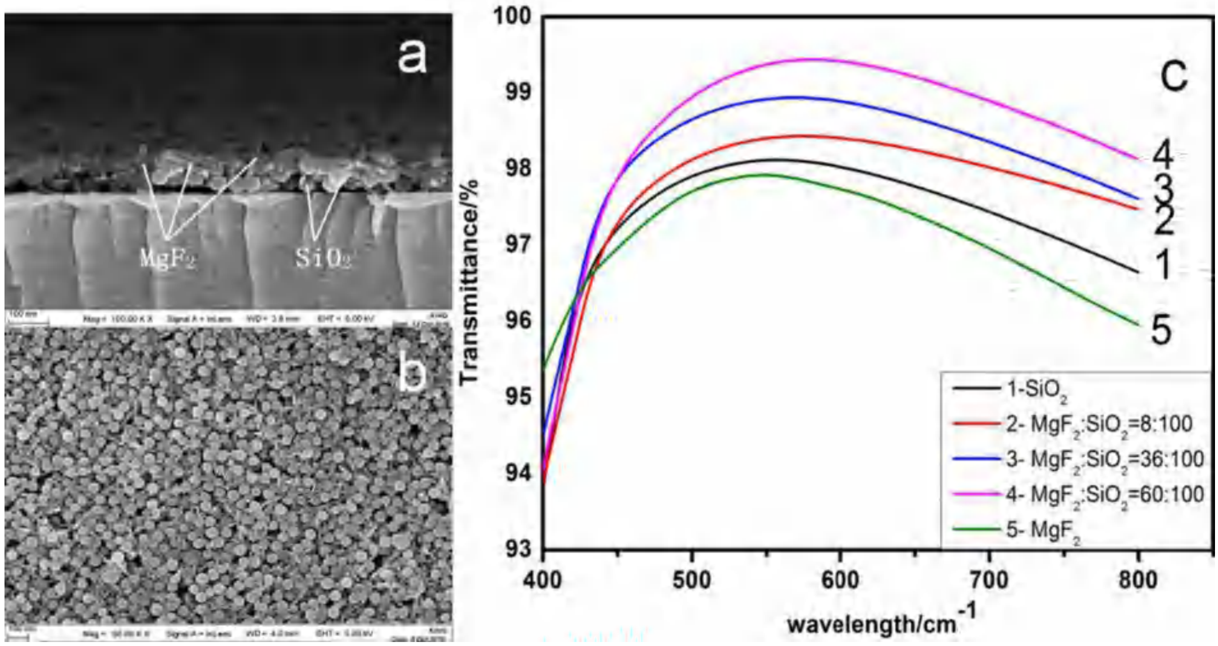

Fig. 2. (a) SEM cross-sectional image and (b) SEM surface image of SiO_2-MgF_2 mixed films. (c) Transmittance curves of SiO_2-MgF_2 mixed films with different molar ratios.

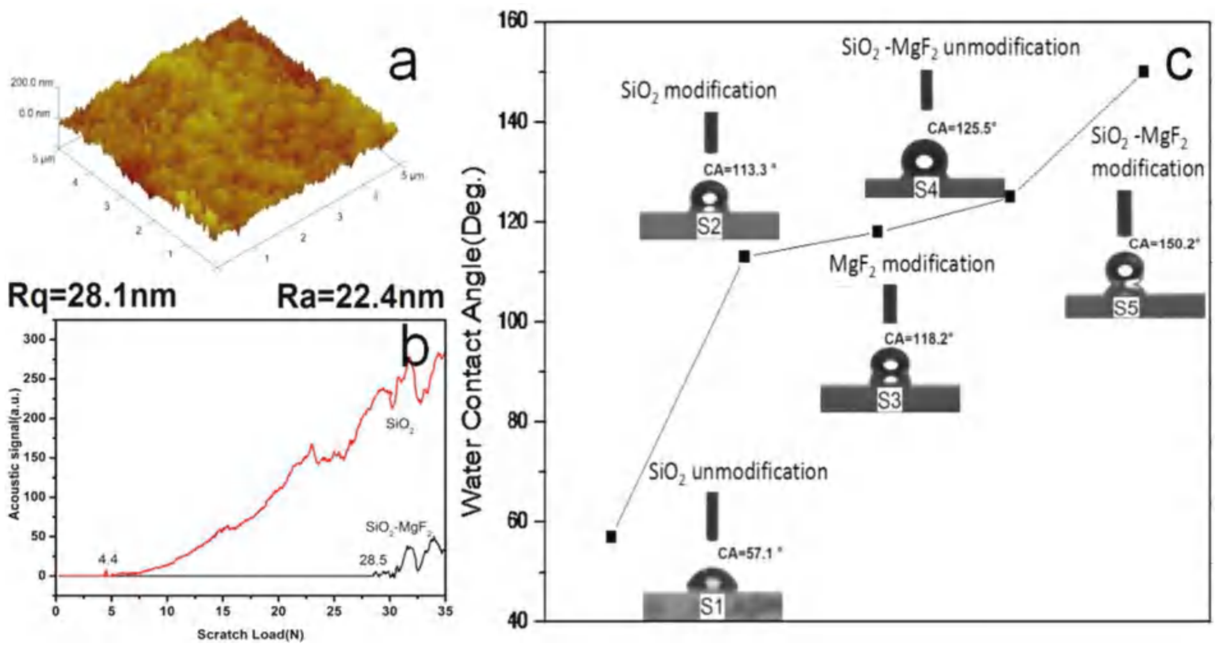

Fig. 3. (a) AFM image of SiO_2-MgF_2 mixed films. (b) Acoustic emission spectrum of scratches between the film and the substrate. (c) Changes in the contact angle of SiO_2-MgF_2 mixed films with different molar ratios.

as opposed to the literature [10]. The strong adhesion to the surface may be due to the hydrogen bonding of F^- in the MgF_2 to the hydroxyl groups on the surface of the silica (Fig. 1g). Fig. 1h shows the zeta potential of both SiO_2 and MgF_2 sols as a function of pH value. The zeta potentials of SiO_2 and MgF_2 sol are positive when pH is below 2, which results in the mixture of two samples with the same polarity (Fig. 1i-4). The pH of SiO_2 sol after removal of ammonia was about 7. When the sol was mixed with MgF_2 sol, the sedimentation occurred after 2 h and the uniform mixed sol could not be formed (Fig. 1i-3).

A stable and uniform SiO_2-MgF_2 mixed sol was obtained. The pH of SiO_2 sol was adjusted to 1.5–2.5, and then mixed with various quantities of MgF_2 sols. Fig. 1c shows the hollow rod-like MgF_2 evenly dispersed between the spherical SiO_2 particles without agglomeration. Mixed sols remained transparent after one month. The preparation showed good reproducibility through many experiments.

3.2. Optical properties of SiO_2-MgF_2 self-cleaning antireflective films

Fig. 2c shows the transmittance curves of MgF_2, SiO_2 and SiO_2-MgF_2 mixed sols with different molar ratios at 400–800 nm. The results show that the maximum transmittance of the mixed films attains 99.4% and the refractive index is 1.23 [11] at 400–800 nm

(Fig. 2b). All the mixed films mentioned below have a molar ratio of MgF_2: SiO_2 = 60:100.

SEM images of SiO_2-MgF_2 mixed films are shown in Fig. 2a and b. The film is composed of spherical SiO_2 and rod-like MgF_2, which dispersed uniformly with closely packed pattern. The thickness of the film is about 120 nm and jagged with irregular protrusions.

3.3. Hydrophobic and mechanical properties of SiO_2-MgF_2 self-cleaning antireflective films

The hydrophobicity of SiO2 film, MgF2 film, and SiO2-MgF2 mixed films were modified with HDTMOS by the CVD method. The results of contact angle test are compared in Fig. 3c. With the increase of the proportion of rod-like MgF_2 in the films, the hydrophobic angle of the surface increases gradually. At the molar ratio of MgF_2:SiO_2 = 60:100, after modified with HDTMOS the hydrophobic angle reaches 150.2°. The AFM images of the mixed films also show that the surface is rough and its Rq and Ra values are 28.1 nm and 22.4 nm, respectively (Fig. 3a). The SEM cross-sectional image of the mixed films (Fig. 2a) shows that the rod-like MgF_2 bulges on the surface of the film, forming the air groove, and the air is easily trapped in the valley of the rough structure by water droplets, forming air vesicles. Water droplets easily float over the air and rely on the bulging solid support to achieve the apparent hydrophobic effect. It is a typical Cassie heterogeneous interface [12], which can the hydrophobic angle of the mixed films from being unmodified with HDTMOS reaches 125.5°. The acoustic emission signal-load curve of the mixed films is shown in Fig. 3b. The critical load of the mixed films is 28.5 N [13], which is much larger than that of SiO_2 film. With the increase on the ratio of rod-like MgF_2 in the films, the bonding force between the film and the substrate increases gradually. Likewise, the pencil hardness (ISO 15184) of the mixed films can reach 4–5 H [8].

4. Conclusions

The nano-hollow rod-like MgF_2 sol with ultra-low refractive index was synthesized using a solvothermal method. By adjusting the zeta potential of nano-silica sol, a mixed sol with long-term stable nanoparticles and nanorods was successfully prepared. The SiO_2-MgF_2 mixed films showed high transmittance at 400–800 nm. As the rod-like MgF_2 formed air grooves on the film surface due to protrusions, the surface hardness reached 4–5 H. The contact angle reached 150.2° after HDTMOS modification on the surface, which showed the substance to have significant value for outdoor use.

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