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Sol–gel SiO_2/TiO_2 bilayer films with self-cleaning and antireflection properties

Zhaoyue Liu, Xintong Zhang, Taketoshi Murakami, Akira Fujishima *

Photocatalyst Group, Special Research Laboratory for Optical Science, Kanagawa Academy of Science and Technology, KSP Building West 614, 3-2-1 Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan

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ABSTRACT

We report here that a facile sol–gel dip-coating technique can be used to fabricate a SiO_2/TiO_2 bilayer film with self-cleaning and antireflection properties. The bottom SiO_2 layer acts as an antireflection coating due to its lower refractive index; the top TiO_2 layer acts as a self-cleaning coating generated from its photocatalysis and photo-induced superhydrophilicity. The maximal transmittance of SiO_2/TiO_2 bilayer film at normally incident light can be reached 96.7%, independent of the high refractive index and coverage of TiO_2 nanoparticles. However, the photocatalytic activity of the bilayer film shows a close dependence on coverage of TiO_2 nanoparticles. After illuminated by ultraviolet light, the SiO_2/TiO_2 bilayer films are superhydrophilic with water contact angle less than 2°, which favors greatly the self-cleaning function of the films.

1. Introduction

In recent years, TiO_2 self-cleaning property can be bestowed on many different types of surface, and some TiO_2-based self-cleaning products such as tiles, glass, and plastics have been commercially available [1,2]. The self-cleaning property of TiO_2 film derives from its two unique photo-induced phenomena [3–5]: photocatalysis [6,7] and photo-induced superhydrophilicity [8–10]. That is, organic pollutant adsorbed on the surface of TiO_2 film can be decomposed under illumination of ultraviolet light (UV). Subsequently, the contaminant and dust can be washed off by rainwater due to its photo-induced superhydrophilicity [4].

TiO_2 nanoparticles can be deposited on a substrate by various techniques, such as sol–gel dip-coating, spin-coating and spray pyrolysis [11–16]. However, the film of TiO_2 increases the reflection of the substrate due to its high refractive index ($n\sim2.5$ for anatase phase [17]). For some applications, such as solar collectors, greenhouses and windows, a high transmittance for visible light is desirable [18]. The reduction of surface reflection can be achieved by applying an antireflection layer on the substrate [19–23]. Such an idea has already been examined by our and several other groups [18,20,24–30]. In our previous work, we deposited TiO_2 nanoparticles or nanosheets on a SiO_2 antireflection layer via layer-by-layer (LbL) assembly technique to fabricate a self-cleaning film with a low refractive property [29,30]. The compositions and structures of the films can be conveniently modulated by the parameters of LbL assembly.

However, preparation of the double-functional film via LbL assembly is complex, which usually needs much time. A facile technique is necessary for some forthcoming developments. Sol–gel dip-coating technique, as a widely adoptive methodology in the productions of antireflection and color effect interference filters, is time-saving, low-cost, and suitable for large-area optical films [31,32]. Herein, we report that we can use this facile technique to fabricate a double-functional SiO_2/TiO_2 bilayer film with self-cleaning and antireflection properties.

2. Experimental

2.1. Preparation of SiO_2/TiO_2 bilayer films

SiO_2 colloid solution in isopropanol (30 wt%, IPA-ST, Nissan Chemical Industries, LTD, Japan) was diluted ultrasonically with 80 vol% of isopropanol. The diluted solution was filtered with an inorganic 0.8 μm membrane filter (Whatman) and then coated on the glass substrate (S-1126, Matsunami Corporation, Japan) by dip-coating at a speed of 0.25 mm/s. The SiO_2 film was calcined at 500 °C for 30 min to remove any organic substances and reinforce the film.

TiO_2 nanoparticles were deposited on the surface of the SiO_2 film, also by dip-coating technique. A commercially available anatase TiO_2 colloid solution with a primary size of 7 nm in isopropanol (20 wt%, TDK-701, Tayca Corporation, Japan) was diluted ultrasonically with appropriate volume of isopropanol. After the diluted solution was filtered, it was coated on the surface

* Corresponding author. Tel.: +81 44 819 2020; fax: +81 44 819 2038.
E-mail address: fujishima@newkast.or.jp (A. Fujishima).

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of SiO_2 film. The SiO_2/TiO_2 bilayer film was also calcined at 500 °C for 30 min. By changing the concentration of TiO_2 colloid and the speed of dip-coating, the coverage of TiO_2 nanoparticles on SiO_2 film can be tuned. In this paper, the concentration of TiO_2 colloid was about 2, 1 and 0.5 wt%, and the speed of dip-coating was 0.13 mm/s. These bilayer films were labeled as TS-2, TS-1 and TS-0.5. The bilayer film with a larger TiO_2 coverage was prepared in 2 wt% TiO_2 colloid solution at a speed of 0.25 mm/s, which was labeled as TS-2T.

2.2. Characterizations

Transmission spectra of the SiO_2/TiO_2 bilayer film under normally incident light were recorded on a Shimadzu UV-2450 spectrophotometer. Morphologies and cross-sections of the bilayer films were investigated by a Hitachi S-4700 scanning electrons microscope (SEM). Surface roughness (Root mean square, Rms) of the bilayer films was analyzed on a Nanoscope IV (Digital Instrument) scanning probe microscope (SPM). The scanning range was 2 μm × 2 μm. Two points were measured and the roughness was averaged. The water contact angles were measured with a contact angle meter (Kyowa CA-X) in the sessile mode at room temperature and analyzed with a commercially FMAS software. This software also enabled us to measure the transient contact angle during the spreading of the liquid on the surface. The refractive indices of the glass substrate and SiO_2 film were measured with an ellipsometer (J. A. Woollam, M-2000U) in the wavelength region of 250–1000 nm.

2.3. Photocatalytic experiment

N-octadecyldimethylmethoxysilane (ODMS, 93%, Wako chemicals) monolayer was deposited on the surface of SiO_2/TiO_2 bilayer film by a reaction in the vapor phase. Typically, SiO_2/TiO_2 bilayer films were preheated in a custom-built sealed vessel full of argon atmosphere at 120 °C for 30 min. Then, the hot argon atmosphere within the vessel was evacuated, and the fresh argon atmosphere was introduced into the vessel. This degassing/gas-filling process was repeated three times to remove the water adsorbed on the film thoroughly. After that, 0.2 ml of ODMS was added to a separate shallow bottle inside the vessel and heated at 120 °C for another 3 h. The vaporized silane reacts with the hydroxyls on the surface of the TiO_2 and SiO_2, and formed a monolayer on the films. Finally, the films were rinsed by plenty of dehydrated ethanol (Wako chemicals) to remove physicsorbed silane molecules, and dried with airflow. After modification by ODMS monolayer, the surfaces of the films were hydrophobic. The photocatalytic activities were evaluated by measuring the evolution of the water contact angle of the films irradiated by a mercury-xenon lamp (Hayashi LA-310UV-1, wavelength range of 250–450 nm). The irradiance of the UV light was 5 mW/cm^2, measured by a UV power meter (Hamamatsu Photonics, C9536-01).

3. Results and discussion

3.1. Morphologies of SiO_2/TiO_2 bilayer films

Fig. 1 shows the top view images of SiO_2 film, TS-0.5, TS-1, TS-2 and TS-2T bilayer films. The cross-sectional image of TS-2T bilayer film is also shown in Fig. 1. As shown in Fig. 1a–e, SiO_2 layer is stacked from SiO_2 particles with a size of about 20 nm. The bilayer films are comprised of TiO_2 particle aggregates with average size of 52 nm (standard deviation: 12) based on 30 aggregates counted from SEM, which randomly distribute on the surface of SiO_2 film. TiO_2 particles can also form larger aggregates with size of about 150 nm (Fig. 1d and e). Fig. 1a–e also indicates that an increase in the concentration of TiO_2 colloid increases the coverage of TiO_2 particles on the surface of SiO_2 film under a constant dip-coating speed. Additionally, at a constant TiO_2 colloid concentration, an increase in the dip-coating speed also increases the coverage of TiO_2 particles slightly, as evidenced by Fig. 1d and e. From the cross-sectional image of TS-2T film, we can identify the bilayer structure of the film. The thickness of SiO_2 film is about 128 nm. The TiO_2 film is not uniform, and aggregated TiO_2 particles distribute randomly on the surface of SiO_2 film. The refractive index of TiO_2 film is determined by the volume ratio of TiO_2 particles to air [29]. A high-volume ratio of air in TiO_2 film ensured a low refractive index, which favors the antireflection properties of SiO_2/TiO_2 bilayer films.

3.2. Transmission spectra of SiO_2/TiO_2 bilayer films

Fig. 2 shows the transmission spectra of SiO_2 film, TS-0.5, TS-1, TS-2 and TS-2T bilayer films. For comparison, the transmission spectra of a glass substrate and a TiO_2 film on the glass are also shown in Fig. 2. The transmittance of glass substrate in the wavelength range of 350–800 nm is about 92% (Fig. 2a). After it is coated by SiO_2 nanoparticles on both sides, the transmittance increased in the whole measured region of 350–800 nm. The maximal transmittance of SiO_2 film is 96.7% at 490 nm (Fig. 2b). The refractive index of SiO_2 film on glass substrate is 1.36 at 490 nm measured by ellipsometer, which is lower than that of the glass substrate (1.52 at 490 nm). Therefore, SiO_2 film prepared by sol–gel dip-coating methodology can act as an effective antireflection layer. The optical thickness of SiO_2 film is about 123 nm, calculated from the quarter of the wavelength with maximal transmittance [29], which is close to the thickness (128 nm) of the SiO_2 film. After SiO_2 film is coated by TiO_2 nanoparticles on both sides, the position of maximal transmittance shifts to longer wavelength, which indicates that the optical thickness of the film increases. However, the maximal transmittance remains almost unchanged at about 96.7%, independent of the high refractive index of TiO_2 particles. The positions of maximal transmittance for TS-0.5, TS-1, TS-2 and TS-2T bilayer films are at 540, 590, 690 and 800 nm respectively. From Fig. 2, we can also find that an increased TiO_2 coverage decreases the transmittance of SiO_2/TiO_2 bilayer films in the short-wavelength region comparing with that of a glass substrate, which can be ascribed to the absorption and scattering of the TiO_2 nanoparticles. It should be mentioned that, the transmittance of a glass substrate decreases greatly in the whole measured region of 350–800 nm (Fig. 2(g)), if it is only coated by TiO_2 nanoparticles in 2 wt% TiO_2 colloid solution at a speed of 0.25 mm/s. The refractive index of this TiO_2 film is about 1.87 in the wavelength range longer than 600 nm measured by ellipsometry, which is much lower than anatase TiO_2 ($n \sim 2.5$). This means the present TiO_2 film shows a porous structure. The refractive indices (n) of the particle coatings are related to the refractive index and volume fraction of each component (Φ) by the following equation: $n^2 = (n^2_{TiO_2}\Phi_{TiO_2}) + (n^2_{air}(1-\Phi_{TiO_2}))$. We calculate the volume fraction of TiO_2 in the film is about 47%, which ensures a low refractive index of TiO_2 coating. We also try to measure the refractive indices of the bilayer films by ellipsometry. However, we cannot fit the experimental results because the bilayer films are too thick.

3.3. Photocatalytic activities of SiO_2/TiO_2 bilayer films

In order to evaluate the photocatalytic activities SiO_2/TiO_2 bilayer films, monolayer ODMS molecules are deposited on the