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Morphology modification of TiO_2 film by adding ammonium nitrate in precursor sol

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ABSTRACT

The surface morphology of TiO_2 film was modified with pore or particle by adding ammonium nitrate into TiO_2 precursor sol and controlling the humidity of air during drying of dip-coated TiO_2 sol film over glass substrate. Water vapor in the surrounding air condenses to the coated sol film during drying process and decreases the compatibility between the precursor and the solvent. Introduction of ammonium nitrate into the TiO_2 sol causes a further increase of interfacial tension, which results in the formation of different morphologies of TiO_2 film due to a phase separation between the precursor and the solvent. The formation process of pores or particles in TiO_2 film is closely related to the condensation rate of water vapor. The RMS roughness of TiO_2 film is significantly increased after the surface is modified with pore or particle, and can be controlled by varying the coating times. Adding NH_4NO_3 into the precursor sol cannot only modify the surface morphology but can also cause N element doping into the TiO_2 film.

1. Introduction

Titanium dioxide with high chemical and physical stability exhibits high photocatalytic activity for environmental purification [1–5]. The photo-induced superhydrophilicity of TiO_2 film has been applied for antifogging or self-cleaning materials (window glass, automobile mirror and other ecological building) [6,7]. The photocatalytic activity and photo-superhydrophilicity of TiO_2 are induced by the irradiation of light in the ultraviolet wavelength range, which limits the application of TiO_2 in the case of light in the visible wavelength range. Furthermore, water contact angle of TiO_2 film gradually increases when the film was stored without irradiation of UV light [8]. Therefore, the enhanced hydrophilicity of TiO_2 under the condition without irradiation of UV light is an important issue. The wettability of water is usually evaluated with contact angle of water, depending on not only the surface energy but also the surface morphology of a given material when a water droplet on a given rough surface fills all the concaves under it. The apparent contact angle (θ) is related to Young contact angle (θ_y) on ideally flat surface as follows [9]:

$$\cos\theta/\cos\theta_y = r. \tag{1}$$

The r value (≥ 1) represents the roughness parameter. Eq. (1) indicates that an increase in the surface roughness parameter leads to an increase of the hydrophilicity for a wettable film. Some researchers improved the wettability by modifying the surface of TiO_2 film through the formation of pores. For example, Murakami et al. [10] obtained a porous TiO_2 film with pores in a mesoscale range by radio frequency magnetron sputtering using $LiTiO_3$ target and subsequent carbonation route. In addition, polymer template has usually been combined with sol–gel technique to prepare porous TiO_2 thin films [11–16]. Hsu et al. [15] synthesized a TiO_2–WO_3 film with homogenously distributed ordered pores, using polystyrene microspheres as a template. The pore size distribution was controlled by varying the size and amount of polystyrene spheres. Wang et al. [16] used polyethylene glycol as the pore-directing agent in the preparation of a porous TiO_2 thin film. On the other hand, Liu et al. [17] used an anatase TiO_2 colloid solution as a coating precursor to fabricate a self-cleaning TiO_2–SiO_2 bilayer film with particle-modified rough surface. In the present work, pore- or particle-modified TiO_2 thin films have been prepared by adding ammonium nitrate into a TiO_2 sol solution and controlling air humidity during the coating process. The purposes of this work are to develop a method to modify the surface of TiO_2 film, to study the mechanisms of the formation of pore and particle induced by ammonium nitrate, and to investigate the influences of humidity of air and repeating times of dip-coating process on the surface morphology and roughness of TiO_2 film.

2. Experimental details

2.1. Preparation TiO_2 sol solution

Tetrabutyltitanate ($Ti(OBu^n)$), TBT, purity >98.5 mass%, Sinopharm, China), acetylacetone, water and ethanol (99.7 mass%) were mixed at a volume ratio of 5:2:1:40. Before the mixing, TBT and acetylacetone (as a stabilizing agent for hydrolysis of TBT) were diluted with ethanol to form a TBT solution. Deionized water was also mixed with ethanol,

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and then its pH was adjusted to pH 3–4 with HNO_3 solution, and finally the water–ethanol solution was added into the TBT solution by dropwise under stirring. After 1 h stirring, the mixed solution was transferred to a reactor with Teflon internal cylinder and aged at 80 °C for 24 h to form a sol solution. The thermal aging was used to form fine microstructure netwok with nanosize crystalline particles and pores. The sol solution was further diluted with ethanol to 1/4 of an original concentration, and then ammonium nitrate (shortened as AN) was dissolved into the sol solution at the molar ratio of $n_{AN}/n_{TBT}=1.3$. Then the sol solutions with and without ammonium nitrate were used to prepare TiO_2 films, and the remainder sol solutions were dried at room temperature and subsequently heated at 500 °C for 30 min to form TiO_2 powders for phase identification.

2.2. Preparation of TiO_2 film

A dip-coating technique was used to prepare TiO_2 films. A glass substrate was dipped in the sol solutions and then was pulled out at a rate of 6 cm/min in air with relative humidity (RH) of 45%, 65% and 75% respectively. After being dried at 100 °C for 20 min, the gel film coated glass substrate was heat-treated at 500 °C for 30 min in air. The dip-coating process was repeated for 1–4 times. The surface modified TiO_2 films prepared from the precursor sol with ammonium nitrate were denoted as F45 − n, F65 − n and F75 − n, in which n represents the repeating times, and 45, 65 and 75 represent the relative humidity of air. The corresponding gel films were denoted as G45 − n, G65 − n and G75 − n, respectively. A smooth surface film prepared from the sol without ammonium nitrate at 45% RH was denoted as FS − n.

2.3. Characterization of TiO_2 film

X-ray diffraction measurement for the heated TiO_2 powder was performed on a DMax2500 Rigaku X-ray diffractometer with Cu Kα radiation ($\lambda=0.15406$ nm) at a scan rate of $0.1^\circ s^{-1}$ to determine the crystal structure and phase purity of the as-prepared TiO_2 films. The accelerating voltage and applied current were 40 kV and 100 mA, respectively. The structure of TiO_2 film was examined by scanning electron microscope (SEM, JSM-6360LA, JEOL, Japan) at an accelerating voltage of 15 kV. For SEM specimens, the glass substrate coated with TiO_2 film was placed on a carbon tape attached to a brass stupa and the TiO_2 film was linked with the brass using carbon tape to ensure a good conductivity of the film. The TiO_2 film was then coated with platinum via plasma sputtering system (JFC-1600 auto fine coater, JEOL, Japan). The topography of the film samples was analyzed by atomic force microscopy (AFM, Nanoscope III Weeco, USA). X-ray photoelectron spectroscopy measurements were performed on an ESCALAB 250 surface analyzer (ThermoFisher Scientific Co.) equipped with a monochromatic AlKα X-ray source. Survey spectra were recorded with a pass energy of 100 eV, and high resolution spectra with a pass energy of 30 eV. Light absorption measurement on the TiO_2 films was conducted with an ultraviolet-visible spectrophotometer (UV-mini1240, Japan). The size distribution of precursor particles in TiO_2 sol solution was analyzed by a ZETASIZER (ZEN3600 Malvern, England).

3. Results and discussion

3.1. Morphology of TiO_2 film

3.1.1. Influence of ammonium nitrate and humidity of air

Fig. 1 shows the X-ray diffraction patterns of the TiO_2 powders prepared by heating the TiO_2 precursor sols with and without ammonium nitrate at 500 °C. Both patterns are assigned to anatase TiO_2 and no peak for contamination was found in the two patterns. The crystalline particle size estimated using Scherrer equation is 13 nm for both the powders from the precursor with and without ammonium nitrate. During the annealing, ammonium nitrate may react with the coated gel film to form N-doped TiO_2. This will be discussed in Section 3.2.

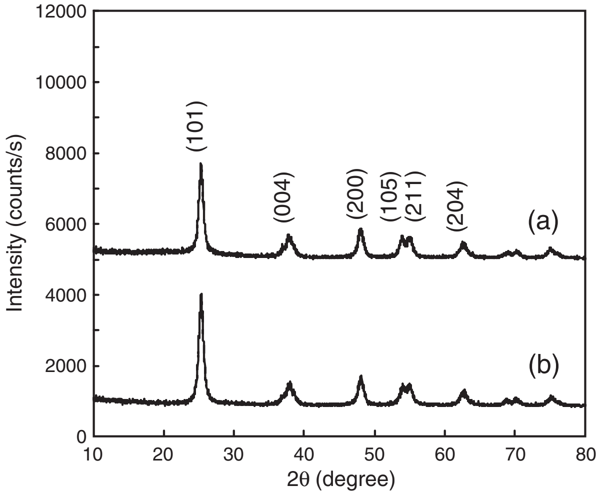

Fig. 1. X-ray diffraction patterns of (a) TiO_2 powder from the sol with NH_4NO_3 and (b) TiO_2 powder from the sol without NH_4NO_3 by heating at 500 °C.

The TiO_2 films prepared under different conditions were observed using scanning electron microscope. The SEM images in Fig. 2 show the microstructures of two TiO_2 films (one coating process) prepared from the precursor sol without ammonium nitrate at relative humidity of 45% RH (29 °C) and 75% RH (12 °C). Both microphotographs show relative smooth surface without any crack, pore or particle formed on the surface. Although the precursor sol was thermally aged, it retained transparent and homogenous, which indicates that the colloid particles in the sol were extremely small. As a result, the small colloid particles deposited on the substrate and formed the smooth film during the dip-coating process. No significant difference is observed between the two film surfaces in Fig. 2, which suggests that the relative humidity has little effect on the surface morphology.

The SEM images in Fig. 3 show the microstructures of the TiO_2 films formed using precursor sol containing ammonium nitrate by repeating dip-coating process for 4 times. The films prepared at 45% RH (29 °C), 65% RH (32 °C), and 75% RH (12 °C) show morphologies of homogeneously distributed multilayer pores, coral-like particles and spherical particles, respectively. These types of morphology are related to the composition variation of the dip-coated sol film during drying process. The formation mechanism is detailed as follows. When a glass plate is pulled out of the TiO_2 sol solution, a liquid film is formed on the substrate surface. The ethanol in the sol film evaporates rapidly, which cools the surrounding air through heat absorption. As a result, water vapor in air condenses into the sol film. This leads to the formation of an ethanol/water mixture solvent. The saturated vapor pressure (P_0) of H_2O is reported to be 1402, 4006 and 4755 Pa at 12, 29, and 32 °C, respectively [18]. The H_2O vapor pressure (P) of 75% RH at 12 °C, 45% RH at 29 °C and 65% RH at 32 °C in this work is calculated to be 1052, 1803 and 3091 Pa, respectively. The difference of H_2O vapor pressure, $\Delta P=P_0-P$, increases in the following order: 350 Pa (75% RH at 12 °C)<1664 Pa (65% RH at 32 °C)<2203 Pa (45% RH at 29 °C). The condensation rate of water is influenced by ΔP of H_2O vapor pressure and increases at a lower value of ΔP. In order to investigate the effect of volume ratio between water and ethanol (V_w/V_e) on the behavior of the sol solution, water was mixed into the aged sol solution in different fraction. The sol solution kept transparent at $V_w/V_{sol}<1$. However, the transparent sol solution changed to a translucent and cloudy system if more water was added. The obtained cloudy system could be changed reversibly to a transparent solution when ethanol was added more. Fig. 4 shows the particle size distributions for the sol systems with different