



Morphology modification of TiO₂ film by adding ammonium nitrate in precursor sol

Rulin Dong ^{a,*}, Min Fang ^a, Yoshihiro Hirata ^b, Zhidong Chen ^a, Changchun Jin ^a

^a School of Petrochemical Engineering, Changzhou University, Changzhou 213164, Jiangsu, PR China

^b Department of Chemistry, Biotechnology, and Chemical Engineering, Graduate School of Science and Engineering, Kagoshima University, 1-21-40, Korimoto, Kagoshima 890-0065, Japan

ARTICLE INFO

Article history:

Received 11 January 2012

Received in revised form 12 August 2012

Accepted 13 August 2012

Available online 19 August 2012

Keywords:

Titanium dioxide

Thin films

Ammonium nitrate

Surface modification

Sol–gel deposition

ABSTRACT

The surface morphology of TiO₂ film was modified with pore or particle by adding ammonium nitrate into TiO₂ precursor sol and controlling the humidity of air during drying of dip-coated TiO₂ 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 TiO₂ sol causes a further increase of interfacial tension, which results in the formation of different morphologies of TiO₂ film due to a phase separation between the precursor and the solvent. The formation process of pores or particles in TiO₂ film is closely related to the condensation rate of water vapor. The RMS roughness of TiO₂ film is significantly increased after the surface is modified with pore or particle, and can be controlled by varying the coating times. Adding NH₄NO₃ into the precursor sol cannot only modify the surface morphology but can also cause N element doping into the TiO₂ film.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Titanium dioxide with high chemical and physical stability exhibits high photocatalytic activity for environmental purification [1–5]. The photo-induced superhydrophilicity of TiO₂ 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 TiO₂ are induced by the irradiation of light in the ultraviolet wavelength range, which limits the application of TiO₂ in the case of light in the visible wavelength range. Furthermore, water contact angle of TiO₂ film gradually increases when the film was stored without irradiation of UV light [8]. Therefore, the enhanced hydrophilicity of TiO₂ 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]:

$$\cos\theta/\cos\theta_y = r. \quad (1)$$

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 TiO₂ film through the formation of pores. For example, Murakami et al.

[10] obtained a porous TiO₂ film with pores in a mesoscale range by radio frequency magnetron sputtering using LiTiO₃ target and subsequent carbonation route. In addition, polymer template has usually been combined with sol–gel technique to prepare porous TiO₂ thin films [11–16]. Hsu et al. [15] synthesized a TiO₂–WO₃ film with homogeneously 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 TiO₂ thin film. On the other hand, Liu et al. [17] used an anatase TiO₂ colloid solution as a coating precursor to fabricate a self-cleaning TiO₂–SiO₂ bilayer film with particle-modified rough surface. In the present work, pore- or particle-modified TiO₂ thin films have been prepared by adding ammonium nitrate into a TiO₂ 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 TiO₂ 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 TiO₂ film.

2. Experimental details

2.1. Preparation TiO₂ 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,

* Corresponding author. Tel.: +86 519 86330253; fax: +86 519 86330234.
E-mail address: dongrl@cczu.edu.cn (R. Dong).

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 network 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 $n_{\text{AN}}/n_{\text{TBT}} = 1.3$. 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 $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm) at a scan rate of 0.1°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 $\text{AlK}\alpha$ 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

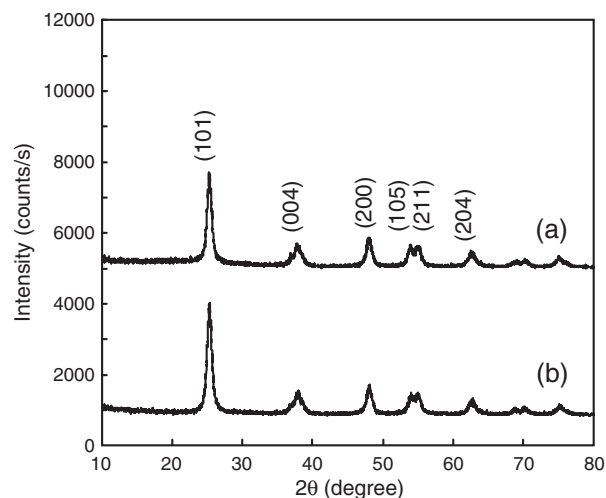


Fig. 1. X-ray diffraction patterns of (a) TiO_2 powder from the sol with NH_4NO_3 and (b) TiO_2 powder from the sol without NH_4NO_3 by heating at 500 °C.

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.

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 $V_w/V_{\text{sol}} < 1$. 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

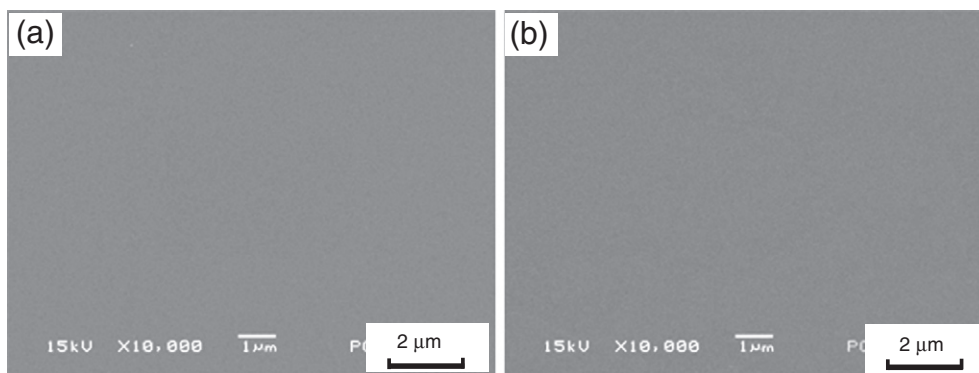


Fig. 2. SEM images of the smooth TiO₂ films prepared using the sol without NH₄NO₃: (a) the film prepared at 45% RH (29 °C); (b) the film prepared at 75% RH (12 °C).

V_w/V_{sol} . The measured median size of the precursor particle increases from 35 nm for the aged sol to 160 nm for the system with $V_w/V_{sol} = 3$. The above results indicate that the precursor particle size depends on the volume ratio of V_w/V_e , and tends to increase as the fraction of water in the system is increased.

Water vapor in the surrounding air condenses to the coated sol film during drying process and decreases the compatibility of the precursor and the solvent. Nevertheless, the films prepared using sol without ammonium nitrate at the same condition show a relatively smooth surface as seen in Fig. 2. Consequently, we believe that ammonium

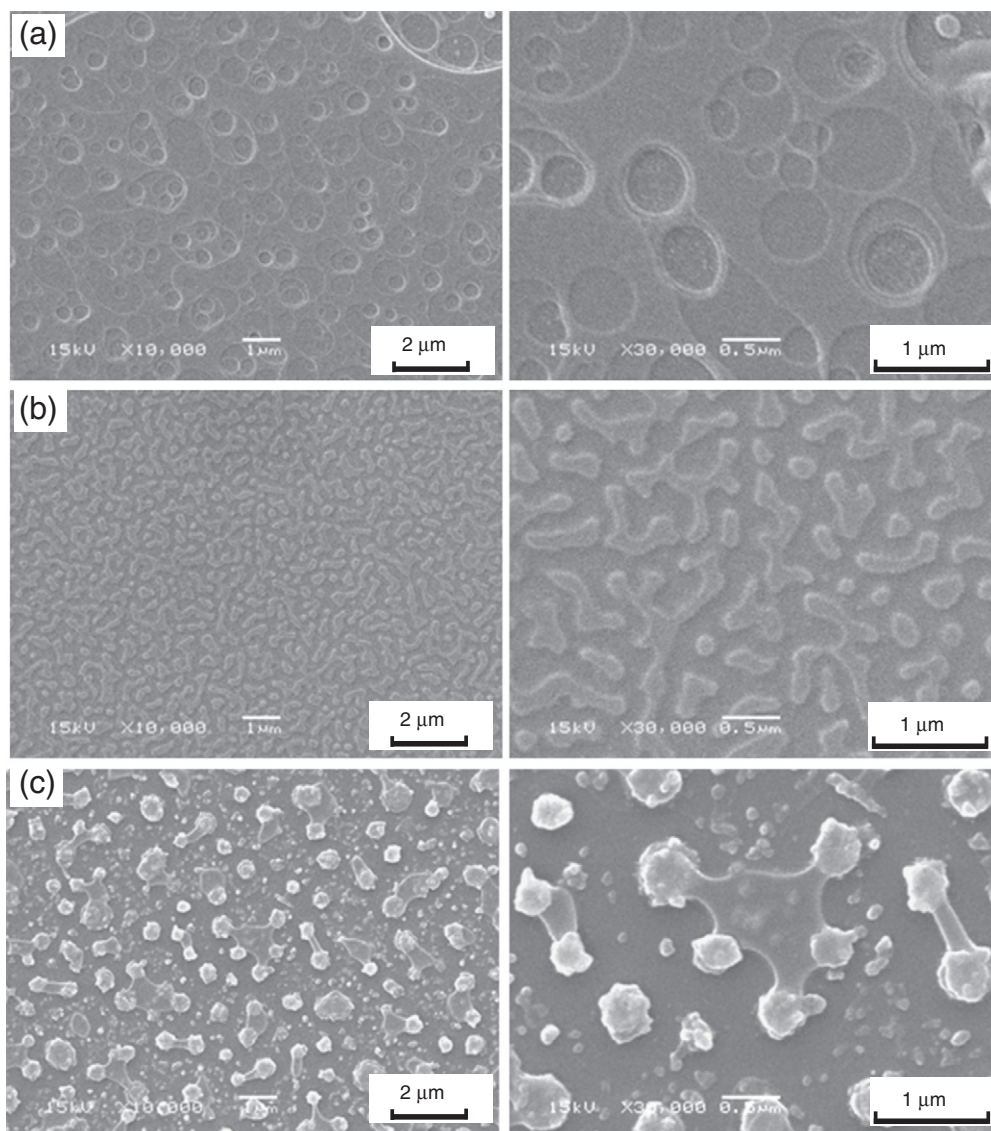


Fig. 3. SEM images of (a) F45-4, (b) F65-4, and (c) F75-4 films.

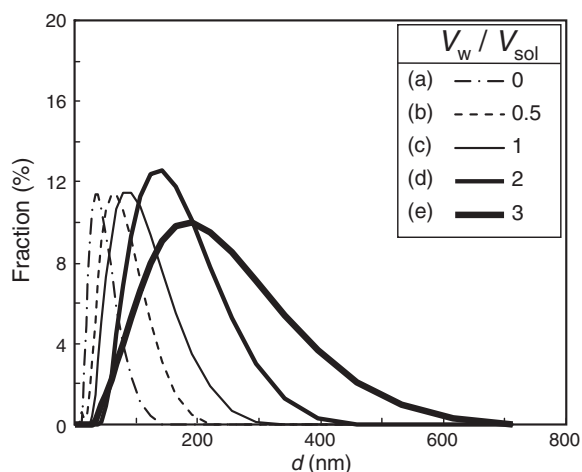


Fig. 4. Size distributions of the particles measured for the TiO_2 sol solutions with different V_w/V_{sol} .

nitrate plays an important role in the formation of the pore or particle modified surface. Introduction of ammonium nitrate into the TiO_2 sol causes a further increase in the surface tension of the solvent, which leads to a phase separation of the precursor and the solvent before the sol begins to gel. The initial uniform sol film can be changed to two types of dispersed systems, depending on the condensation rate of water vapor. When the dip-coating process is performed in air with humidity of 45% RH, the condensation rate of water vapor is relatively low and less water is condensed into the sol film. Hence, when the sol film begins to gel during the drying process, a small amount of water disperses in the form of droplet on the gel surface. Here, ammonium nitrate increases the surface tension of water, which leads to the formation of relatively small droplets. After being dried at 100 °C, the droplets are completely evaporated and pores are left on the film surface. When dip-coating process is repeated, water droplets of bigger size are formed because an increase of the surface roughness, which results in the formation of bigger pores on the film surface. Such a bigger pore contains several smaller pores formed previously. The microphotograph (Fig. 3(a)) shows an evidence of a maximum of four layers of pore. When the humidity rises up to 75% RH, the condensation rate of water vapor becomes relatively high and a larger amount of water vapor is condensed into the sol film during the pulling process. Under this condition, a size increase of the precursor particles is observed as seen from Fig. 4. After complete evaporation of the mixed solvent at 100 °C, the substrate is covered by relatively large particles. When the dip-coating process is carried out in air with humidity of 65% RH, the condensation rate of water vapor is lower than that under the condition of 75% RH. Thus, smaller particles are formed just before the sol gelling. When the coating process is repeated, the precursor source tends to

adhere to the particles formed in the previous process, and some of the particles are joined together, which leads to an irregular morphology (Fig. 3(b)). Therefore, less water mixed into the sol results in the microstructure of Fig. 3(a) and more water mixed into the sol forms the microstructure of Fig. 3(b) and (c). In the mechanisms for the formation of pore or particle, temperature affects both the saturated vapor pressure of water and the evaporation rate of ethanol. The effect of temperature on the saturated vapor pressure has been involved in the calculation of ΔP . A higher temperature leads to a larger evaporation rate of ethanol, which means that the condensed water in the case of F45-n and F65-n is less than that in the case of F75-n. The formation of pore or particle is therefore attributed to the comprehensive effect of humidity and temperature. As the temperature (12–32 °C) selected in the present experiment is relatively low, humidity is considered as the major factor affecting the morphology of the TiO_2 films. Further investigation about the temperature effect will be continued.

The coated films before annealing at 500 °C were also checked by scanning electron microscope. Fig. 5 shows the SEM images of the coated gel films (one dip-coating process) dried at room temperature. Sample (a) was prepared using sol with $n_{\text{AN}}/n_{\text{TBT}} = 1.0$ at 45% RH (29 °C) and sample (b) was prepared using sol with $n_{\text{AN}}/n_{\text{TBT}} = 1.3$ at 75% RH (12 °C). It can be seen from Fig. 5 that pores about 600 nm and particles about 50 nm in diameter had formed on the surfaces of sample (a) and sample (b), respectively. These results indicate that the pores or particles are not formed by the precipitation and pyrolysis of ammonium nitrate during the drying and annealing process, which is in a good agreement with the above discussion about the formation mechanism of pore and particle. Additionally, as compared with primary pores in Fig. 3(a), the pores in Fig. 5(a) are almost two times larger, which suggests that the primary pore size depends on the amount of ammonium nitrate in the precursor sol. The related investigation will be continued further.

3.1.2. Influence of dip-coating times

The SEM images in Fig. 6 show the effect of dip-coating times on the microstructure of the film prepared at 75% RH. After first dip-coating, fine TiO_2 particles of 50 nm are uniformly produced (Fig. 6(a)). However, a bimodal particle size distribution is observed after 3rd dip-coating (Fig. 6(b)). A similar result is also observed in the film after 4th dip-coating (Fig. 6(c)). The average sizes of the larger and smaller particles are 200 and 50 nm, respectively, in Fig. 6(b), and 400 and 50 nm, respectively, in Fig. 6(c). During the repeating dip-coating process, TiO_2 precursor source adheres to the superficial particles previously formed, and the particles become larger.

3.1.3. Roughness of TiO_2 film

SEM observation implies that pore or particle modification as well as dip-coating repeating lead to a variation in the roughness of TiO_2 film. Fig. 7 shows the AFM images of FS-2, F45-2, F75-2 and F75-4.

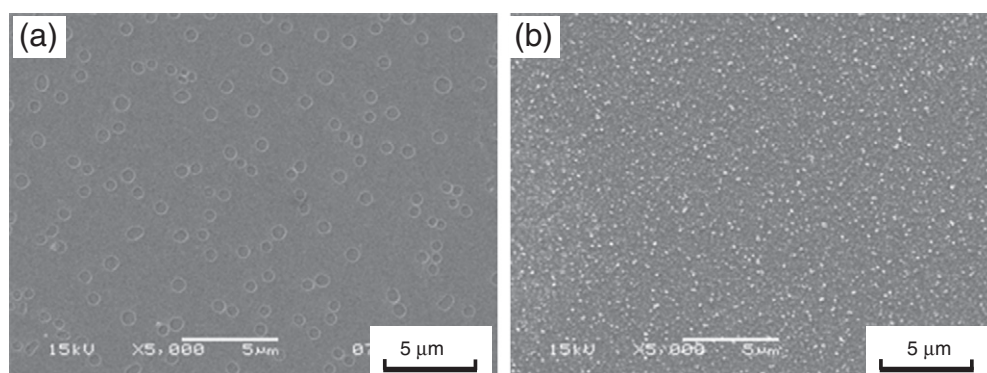


Fig. 5. SEM images of (a) G 45-1, and (b) G75-1 gel films.

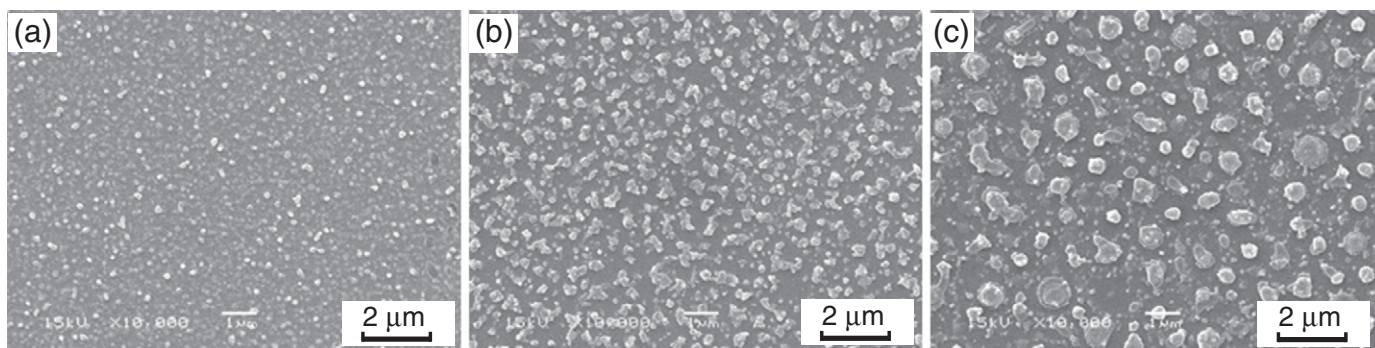


Fig. 6. SEM images of (a) F75-1, (b) F75-3, and (c) F75-4 TiO₂ films.

The surface of FS-2 film is relatively smooth, while the surface of F45-2 shows a honeycomb-like microstructure with pore size of about 1 μm. The surface of F75-2 and F75-4 films is constructed with particles about 0.5–1.5 and 3 μm in diameter, respectively. A RMS roughness measured for FS-2, F45-2, F75-2, F45-4, and F75-4 films is 2.0, 28.6, 30.2, 21.2 and 12.2 nm, respectively. This result reveals that the roughness of TiO₂ film increases significantly as the surface is modified with pore or particle, and has a high value for F45-2 and F75-2 as compared with that for F45-4 and F75-4. For the films prepared at 75% RH (12 °C), when dip-coating process is performed for 1–2 times, the amount of particle per area, namely particle concentration, is relatively high as shown in Fig. 7(c). As dip-coating process is repeated, the TiO₂ precursor fills the space among the particles and

connects some particles together, which results in the formation of large flat particles and the decrease of the particle concentration as shown in Fig. 7(d). Consequently, the RMS roughness tends to decrease when dip-coating repeating times exceeds a certain value. A similar mechanism can also be deduced to explain the change of RMS roughness for those pore modified films.

3.2. Composition of TiO₂ film

The effect of NH₄NO₃ on the chemical composition of the prepared TiO₂ films was analyzed by X-ray photoelectron spectroscopy. Fig. 8 presents N1s XPS spectra of FS-3 and F45-3 films. Both spectra show a peak N1s at a binding energy of 399.8 eV. This binding energy

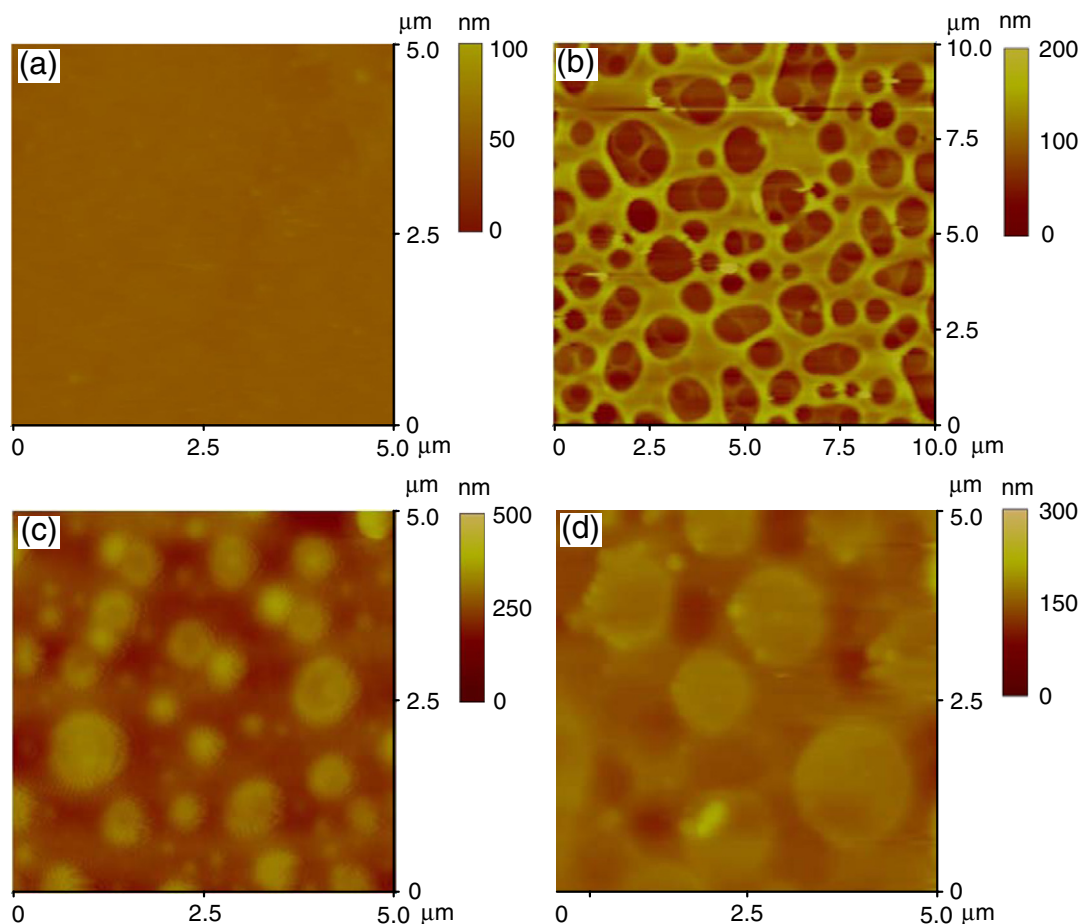


Fig. 7. AFM images of (a) FS-2, (b) F45-2, (c) F75-2, and (d) F75-4 TiO₂ films.

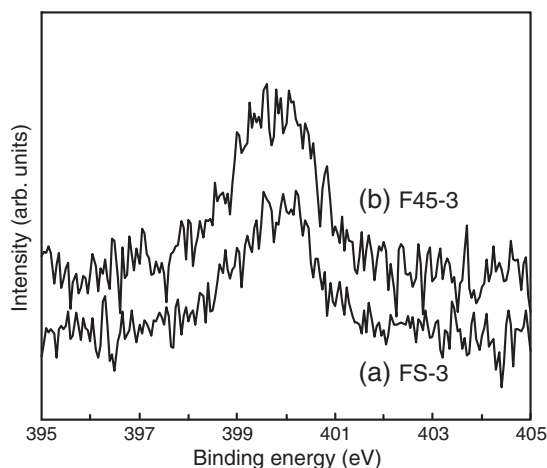


Fig. 8. N1s XPS spectra of FS-3 and F45-3.

value is close to that reported by Wang J. et al. [13] who obtained N and S co-doped TiO_2 mesoporous photocatalyst. Fig. 8 suggests that although no NH_4NO_3 was contained in the precursor sol, the resultant FS-3 film was doped with N element. In the preparing process of the precursor sol, HNO_3 solution was used to adjust the pH value of the system within acidic range. The hydrolysis of titanium alkoxide in the acidic solution results in the formation of nanometer sized Ti-oxo clusters which is positively charged and can be expressed as $\text{Ti-OH}_2^+\text{NO}_3^-$. N element is therefore doped into TiO_2 lattice as TiO_2 crystallite is formed during the heat treatment at 500°C . In the case of F45-3 film, N element can also be doped into TiO_2 through the reaction of NH_4NO_3 with the dried gel during the annealing process because the precursor sol contained NH_4NO_3 besides of HNO_3 . According to the mechanisms of the formation of different surface morphologies discussed in Section 3.1, phase separation occurs during drying of coated sol film. It can be deduced that the concentration of NH_4NO_3 is higher in “water phase” than that in “oil phase”, namely gel, which means that the concentration of N element doped in the surface region of pore in the case of pore modified film or space among the particles in the case of particle modified film is high as compared with that in the other regions. Fig. 9 shows Ti2p XPS spectra of FS-3 and F45-3 films. The binding energy of Ti2p for FS-3 and F45-3 was measured to be 458.2 and 458.5 eV, respectively, which suggests that titanium is in the fourth coordination and in the form of titanium dioxide. This is also confirmed by the O1s peak with a

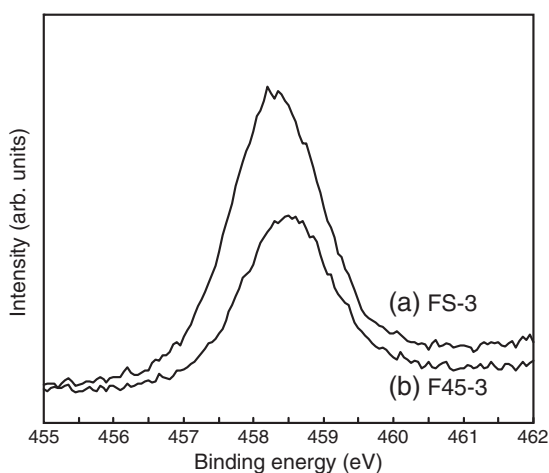


Fig. 9. Ti2p XPS spectra of FS-3 and F45-3.

binding energy of 529.9 eV. As compared to the binding energy of Ti2p for FS-3, a positive shift of about 0.3 eV of Ti2p for F45-3 sample indicates that positive charge of surface Ti increases with the increase of N doped amount. The atom ratio of N/O is calculated to be 0.0167 and 0.0383 for FS-3 and F45-3, respectively, based on the calculation of XPS peak areas of individual elements. N doped TiO_2 can be described as $\text{TiO}_{2-1.5x}\text{N}_x$. As a result, the surface chemical composition for FS-3 and F45-3 is calculated as $\text{TiO}_{1.951}\text{N}_{0.033}$ and $\text{TiO}_{1.891}\text{N}_{0.072}$, respectively. Consequently, 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.

3.3. Optical absorption

Fig. 10 presents the UV-visible absorption spectra of FS-1, F45-1, F65-1 and F75-1 films. Although absorbency curves of F45-1 and F65-1 in the wave length range of 400–800 nm are similar to that of FS-1, a shift of optical absorption edge to the visible light region can be found in the spectra of F45-1 and F65-1 films. It also confirms the fact that the concentration of doped N element is higher in the surface modified film due to the reaction of ammonium nitrate with the gel film during annealing process. An improvement of visible light absorption of TiO_2 film due to N-doping has been reported [13]. As compared with F45-1 and F65-1, F75-1 showed high absorbency in the visible light region. This result is mainly related to the thickness difference of the films. The temperature (12°C) for preparing F75-1 film was lower than that ($29\text{--}32^\circ\text{C}$) for F45-1 and F65-1. As a result, the viscosity of the sol used was higher, which results in a higher thickness of the films.

4. Conclusions

The morphology of TiO_2 film can be modified with pore or particle by adding ammonium nitrate into the precursor sol. The surface modification is mainly attributed to the phase dispersion induced by ammonium nitrate. Simultaneously, the morphology of TiO_2 film was closely affected by the humidity of air. A low humidity produced uniformly distributed pores in the TiO_2 film and a high humidity formed the microstructures consisting of particles. The modification of TiO_2 film with pore or particle leads to a significant increase of RMS roughness. However, the RMS roughness tends to decrease when dip-coating repeating times exceeds a certain value. Besides of the morphology modifying function, ammonium nitrate also acts as N source to form N-doped TiO_2 film.

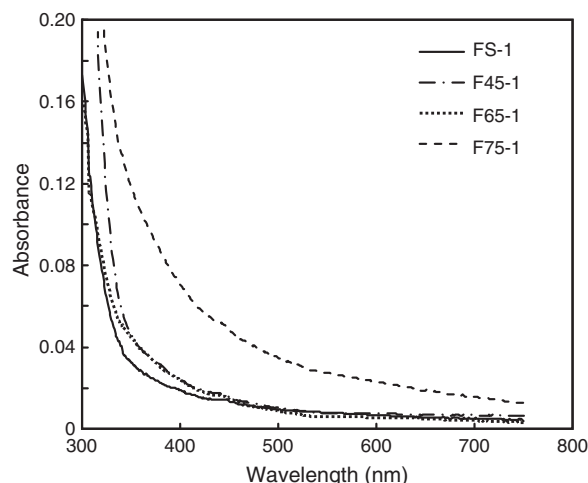


Fig. 10. UV-visible absorption spectra of FS-1, F45-1, F65-1, and F75-1 TiO_2 films.

References

- [1] X. Zhao, M.H. Liu, Y.F. Zhu, *Thin Solid Films* 515 (2007) 7127.
- [2] Y.M. Chen, F. Chen, J.L. Zhang, *Appl. Surf. Sci.* 255 (2009) 6290.
- [3] R. Doong, S.M. Chang, Y.C. Hung, I.L. Kao, *Sep. Purif. Technol.* 58 (2007) 192.
- [4] C.H. Lu, W.H. Wu, R.B. Kale, *J. Hazard. Mater.* 154 (2008) 649.
- [5] S. Sakthivel, M.C. Hidalgo, D.W. Bahnemann, S.U. Geissen, V. Murugesan, A. Vogelpohl, *Appl. Catal., B* 63 (2006) 31.
- [6] S. Karupuchamy, J.M. Jeong, D.P. Amalnerkarc, H. Minourab, *Vacuum* 80 (2006) 494.
- [7] S. Song, L.Q. Jing, S.D. Li, H.G. Fu, Y.B. Luan, *Mater. Lett.* 62 (2008) 3503.
- [8] J.G. Yu, M.H. Zhou, H.G. Yu, Q.J. Zhang, Y. Yu, *Mater. Chem. Phys.* 95 (2006) 193.
- [9] R.N. Wenzel, *Ind. Eng. Chem.* 28 (1936) 988.
- [10] A. Murakami, T. Yamaguchi, S. Hirano, K. Kikuta, *Thin Solid Films* 516 (2008) 3888.
- [11] E. Ortel, S. Sokolov, R. Kraehnert, *Microporous Mesoporous Mater.* 127 (2010) 17.
- [12] M. Wark, J. Tschirch, O. Bartels, D. Bahnemann, J. Rathousky, *Microporous Mesoporous Mater.* 84 (2005) 247.
- [13] J.S. Wang, H. Li, H.Y. Li, C. Zou, *Solid State Sci.* 12 (2010) 490.
- [14] Y.N. Fu, Z.G. Jin, Z.F. Liu, W. Li, *J. Eur. Ceram. Soc.* 27 (2007) 2223.
- [15] C.S. Hsu, C.K. Lin, C.C. Chan, C.C. Chang, C.Y. Tsay, *Thin Solid Films* 494 (2006) 228.
- [16] J.J. Wang, D.S. Wang, J. Wang, W.L. Zhao, C.W. Wang, *Surf. Coat. Technol.* 205 (2011) 3596.
- [17] Z.Y. Liu, X.T. Zhang, T. Murakami, A. Fujishima, *Sol. Energy Mater. Sol. Cells* 92 (2008) 1434.
- [18] In: *Chemical Handbook, Basic Part II*, third edition, The Chemical Society of Japan, Maruzen, Tokyo, 1984, p. 117.