J Mater Sci (2007) 42:4926–4934
DOI 10.1007/s10853-006-0553-2

Synthesis of titanium oxide layers on glass substrates with aqueous refluxed sols (RS) and photocatalytic activities

Lei Ge · Mingxia Xu · Haibo Fang

Received: 29 September 2005 / Accepted: 9 June 2006 /

Abstract Nanocrystalline anatase films were prepared on glass substrates by the dip-coating method from aqueous refluxed sols and calcined at 100, 300 and 500 °C. FT-IR, TEM, SEM, XRD, UV–VIS and XPS analysis were used to characterize the microstructure, phase evolution and chemical composition of the refluxed sols (RS) sols and TiO_2 films. The photocatalytic activities of the TiO_2 films were evaluated by photocatalytic degradation of aqueous methyl orange solutions. It was found that the RS sols were flavescent, alkalescent and contained anatase crystals. The TiO_2 thin films contained not only Ti and O elements, but also a small amount of N and Na elements. The TiO_2 films were transparent and its maximal light transmittance exceeded 80% under visible light region. Calcined at 300 °C, the TiO_2 thin film showed the highest photocatalytic activity, when the calcination temperature is higher than 300 °C, the decrease in photocatalytic activity is due to sintering and growth of TiO_2 crystallites resulting in the decrease of surface area. The results suggested that RS sols are promising novel precursors for synthesizing TiO_2 films, and refluxing technique is quite efficient in preparing titania nanocrystalline films.

L. Ge (✉)
Department of Materials Science and Engineering,
China University of Petroleum, Beijing 102249, P.R. China
e-mail: gelei08@eyou.com

M. Xu · H. Fang
School of Materials Science and Engineering, Key
Laboratory for Advanced Ceramics and Machining
Technology of Ministry of Education, Tianjin University,
Tianjin 300072, P.R. China

Introduction

Nanocrystalline titania films have attracted sustained great scientific and technological interests because of their potential applications in the fields of photoelectronic optical devices [1], solar cells [2], gas sensors [3] and photocatalysts [4–7]. The ulfrafine crystals in the films lead to unusual properties arising from the quantum confinement effects and high surface area, titania is a very important photocatalyst for its strong oxidizing power, nontoxicity, and long-term photostability. In order to maintain higher surface area, it is necessary to use low temperature processing to prepare titania film [8, 9]. Wet-chemical synthesis routes, such as sol–gel processing, have emerged as one of the most promising techniques for growing TiO_2 thin films. The main advantages of sol–gel technique for the preparation of materials are low temperature of processing, versatility, flexible rheology allowing easy shaping and embedding [10–12]. The most frequently used precursors for the titania film through sol–gel processing are the titania sols obtained from organic titanium alkoxides [13]. Nevertheless, subsequent heat treatment should be carried out to remove the organic contents from the complexing species of titanium or the precursors to obtain crystalline phase. Other inorganic synthesis ways to lower the crystallization temperature should be taken into account during the preparation of titania films. Among these, the peroxo titanic acid (PTA) sol is of great interest because it has neutral pH and low material cost [14]. The study about the formation of TiO_2 film using the PTA has been recently performed by Ichinose et al. [15]. Gao et al. [16] have reported the synthesis of anatase TiO_2 thin films using the aqueous peroxotitanate solution obtained by dissolving metatitanic acid (H_2TiO_3) in a mixture of H_2O_2 and ammonia in water. Lee et al. [17] prepared PTA sol using $TiCl_3$ as raw materials. However, the PTA sol contains no anatase crystals, the TiO_2 film on substrate should be calcined at high temperature to obtain anatase structure after the sol was coated on the substrates. Since it should be calcined at high temperature, the choice of the substrate is limited. The refluxing or autoclaving method is efficient to achieve crystalline phase at relatively lower temperature [18], and the TiO_2 thin films are prepared on various substrates after dried in air and calcined at relative low temperatures.

In this paper, we show a new method in which anatase TiO_2 thin films are deposited on glass slides substrates by dip-coating method. The refluxed sols (RS) containing anatase crystals were synthesized by refluxing the PTA sol at relative low temperature and pressure condition, and the TiO_2 thin films with anatase phase were prepared on glass slides substrates after dried in air or calcined at relative low temperatures. In addition, we investigated the photocatalytic activities of the TiO_2 thin films using the methyl orange solution as pollutant. This work may provide new insights into the preparation of highly photoactive TiO_2 thin films in low temperature and low cost.

Experimental

For the preparation of the anatase TiO_2 sol, the following materials were used: titanyl sulfate ($TiOSO_4 \cdot nH_2O$, 23.2% TiO_2); hydrogen peroxide (H_2O_2, 30%); ammonia solution ($NH_3 \cdot H_2O$, 3 mol/l); methyl orange.

The anatase TiO_2 sol (RS) was prepared in the following way: 17.3 g titanyl sulfate was slowly added to the distilled water at room temperature, then precipitated by adding ammonia solution (NH_4OH, 3 mol/l) resulting in the formation of white precipitate [$Ti(OH)_4$]. The white precipitate was filtered and sufficiently washed with distilled water to remove the NH_4^+ and SO_4^{2-} formed in the reaction, and then added 450 ml distilled water to disperse the precipitate homogeneously. The precipitate was peptized in 50 ml aqueous hydrogen peroxide (30%), continual magnetic stirring was required to avoid the immediate dense gel formation during dissolution and to keep the reactant mixed uniformly. The obtained transparent sol was kept under reflux condition (around 100 °C) for 2 h. The sol was refluxed in a flask, the evaporation of water was prevented by cool running water, the temperature of the refluxed sol was detected with a thermometer. Finally, the pure RS sol with anatase TiO_2 crystals was obtained, which was used to prepare thin films and equivalent powders after dried in air oven. This sample was denoted as sample RS-2. Sample RS-6 and RS-10 were prepared by the same procedure, but the reflux time was 6 and 10 h, respectively.

Glass slides were used as substrates. Before the deposition, substrates were ultrasonically cleaned in dilute HNO_3, acetone and absolute ethanol for 30 min, respectively. Finally, they were thoroughly rinsed with distilled water. TiO_2 thin films were deposited on substrates by a dip-coating process at room temperature. Substrates were immersed into the RS sol for 10 min. Upon withdrawing from the RS sol with a dip-coating rate of 6 cm/min, the substrates were dried under infrared light at 60 °C for 30 min. Afterward, the substrates were ultrasonically rinsed with water and then the dried films were calcined at 100, 300 and 500 °C for 30 min in air. Films so obtained were well adhered. TiO_2 layers on substrates could be thickened by means of consecutive 6 dip-coating cycles. In such cases, substrates were only ultrasonically rinsed with water and dried at the end of the whole deposition process.

The surface ζ potential of the particles in the RS sols was measured by JS94G+ micro electrophoresis meter. The FT-IR spectra of the dried gel were measured by the KBr pellet method (BIO-RAD FTS-3000). The structure of the RS particles dried in air and TiO_2 thin films prepared from RS sols were determined by X-ray diffractometer (Rigaka D/max 2500v/pc, Japan) using graphite monochromatic copper radiation (CuKα) at 40 kV, 30 mA over the 2θ range 20–80°. The morphology and size of the RS sol crystals were examined by transmission electron microscopy (JEM-1200 EX II). The adhesion of the TiO_2 films was evaluated by scratching method using abrasive paper. The morphology and crystallinity of dried TiO_2 thin films were observed by a Field Emission Scanning Electron Microscope (FESEM JEDL JSM-6700F). Spectroscopic analysis of the TiO_2 films was performed using UV–VIS spectrophotometer (7230G, Shanghai, China) with wave range of 300–800 nm.

The photocatalytic activity of TiO_2 thin films was evaluated by the photocatalytic discoloration of methyl orange solution at ambient temperature. Experiments were as follows: Two pieces of 25 mm × 75 mm glass plate coated with TiO_2 films were settled in an 80 ml methyl orange aqueous solution with a concentration of 10 mg/l (30.55 μmol/l) in a cylindrical glass reactor of 130 ml capacity (30 mm in height, 75 mm in diameter). A 25 W 254 nm UV lamp (Yaming Instrument Co, Shanghai) was used as a light source. One face of the TiO_2 thin films was irradiated along the normal direction. The average light intensity striking on the TiO_2 film was about 120 $\mu W/cm^2$ (254 nm). The concentration of methyl orange was determined by UV–Visible spectrometry. Prior to photocatalytic reaction, the methyl orange aqueous solution with TiO_2 thin films was kept in a dark condition for 20 min to establish an adsorption–desorption equilibrium. UV–VIS absorption spectra of irradiated samples were measured every 20 min with a UV–VIS spectrophotometer (7230G, Shanghai China). The changes in concentrations of methyl orange were estimated from the changes in absorbance of the absorption maximum at 500 nm. The product of methyl orange degradation was determined by ion chromatograph with a conductivity detector (Dionex, DX-100).

Results and discussion

Properties and characterization of RS sols

The RS sols were flavescent, semitransparent and alkalescent; their pH values were about 7–8 and increased a little with extending reflux time. The RS sols kept stable and did not change over periods of 6 months at room temperature, no coagulation and precipitate appeared. The variation of surface ζ potential of the particles in the RS sols are shown in Fig. 1, the RS sol treated at 100 °C for 2 h with Ti^{4+} concentration of 0.1 mol/l was about –28.51 mV, which indicated that colloidal particles in RS sols contained negative charges. From Fig. 1, the absolute value of surface ζ potential of RS sols increased with increasing reflux time, the transparent PTA sol became translucence and yellow color decreased, which illustrated that more PTA molecules decomposed and crystallized to anatase crystals with extending reflux time. When the reflux time exceeded 10 h, the sample became white precipitate instead of stable RS sol, the result illustrated that most of PTA molecules decomposed and crystallized to anatase crystals, the RS sols became unstable, and then the reflux time should be kept under10 h.

The FT-IR spectra of RS sols prepared by refluxing PTA sol at different conditions are shown in Fig. 2. The as-dried RS gel exhibited peaks at 900, 1,130, 1,400 and 1,630 cm^{-1}, as well as a broad band at 3,000–3,600 cm^{-1}. It is known that a stretching mode frequency of the first-order O–O bond (a peroxo group) is around 900 cm^{-1} [14]. The absorption peak at 900 cm^{-1} is detected for RS sol, which is attributed to the peroxo groups. The absorption peak at 1,130 cm^{-1} is caused by the SO_4^{2-} remained in refluxed-sol. The absorption from 3,000 to 3,600 cm^{-1} can be assigned to the stretching vibration of the hydrogen-bonded OH groups of the adsorbed water. The absorption around 1,630 cm^{-1} is due to the bending vibration of water molecules. The peaks around 1,400 cm^{-1} are due to the stretching vibration of the N–H bonds in NH_4^+ that remained. With increasing reflux time, the peak intensity at 900 cm^{-1} obviously decreased and disappeared completely when the reflux time reached 10 h, and the RS sol became precipitate, the result illustrated that most of PTA molecules decomposed and crystallized to anatase crystals. The transparent sol became translucence and yellow color decreased with increasing reflux time, which was the result of decomposition of PTA molecules and increasing content of anatase crystals.

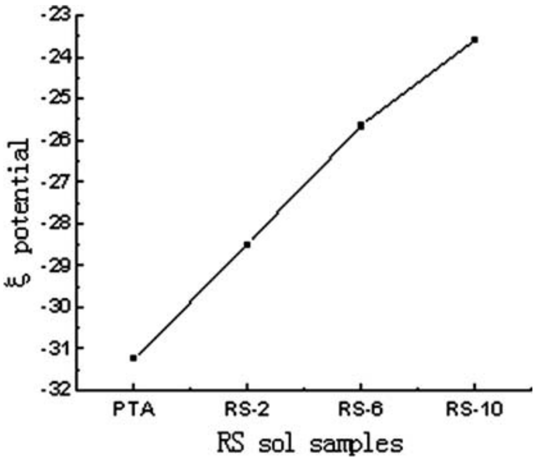


Fig. 1 Variation of ζ potential of RS sols with different reflux time

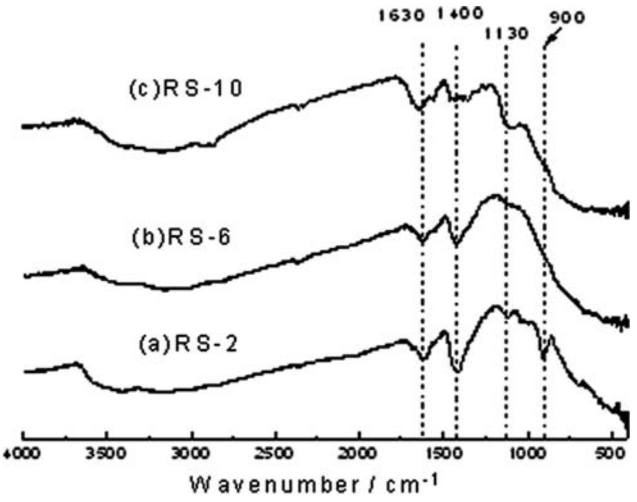


Fig. 2 FT-IR spectra of the RS gel prepared at 100 °C. The heating times represented are: (a) 2 h, (b) 6 h and (c) 10 h

XRD patterns of TiO_2 particles from the RS sols synthesized at different conditions are presented in Fig. 3. For comparison, the FT-IR spectra PTA sol is presented as well. As shown in the figure, the PTA samples without reflux treatment show no anatase peaks. While, the samples after autoclaved had formed anatase phase since the samples give five distinctive TiO_2 peaks at 25.3°, 37.9°, 48.0°, 54.6° and 62.8°, corresponding to anatase (101), (103, 004 and 112), (200), (105 and 211), (204) crystal planes (JCPDS 21-1272), respectively. The TiO_2 crystal phase in RS sol obtained from this method was exclusively anatase. It is commonly accepted that high temperature calcinations, at least 400 °C, is required to obtain anatase TiO_2 powder. However, we prepared anatase nanocrystalline particles at 100 °C without further treatment in the present work, in which $TiOSO_4$ was used as a starting material. The intensities of the XRD peaks increase and widths become narrower as shown in Fig. 3b–d compared with Fig. 3a. The finding indicates that the crystallinity of obtained RS anatase particles increase with increasing reflux time. The *d* (101) peak at 25.3° was used to calculate the mean crystallite size of the crystal particles. The average size by the length and diameter of needle-like crystal calculated from Scherrer equation is about RS-2: 5 nm, RS-6: 33 nm and RS-10: 40 nm. It is noted that the crystal size of anatase TiO_2 crystals in RS sol increase with extending reflux time. However, the crystal size of TiO_2 crystals obtained from this method is small in spite of having high crystallinity.

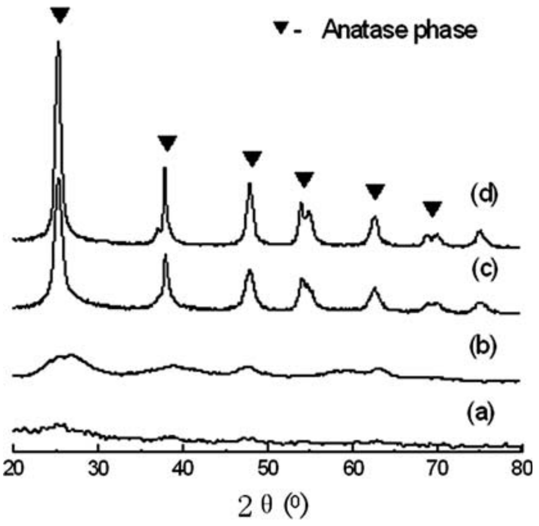


Fig. 3 XRD patterns of the RS gel prepared at 100 °C. The reflux time represented are (a) 0 h PTA, (b) 2 h, (c) 6 h and (d) 10 h

Figure 4. illustrates the size and morphological development in RS sol particles prepared at different conditions, and the needle-like anatase particles are found in the sol. It can be seen from Fig. 4a that needle-like particles with an approximate length of 11–15 nm appeared and uniformly dispersed in the whole aqueous solution. As the treating time was increased to 6 h, a few larger and longer anatase particles of about 40–50 nm in length started to form in comparison with Fig. 4a. As shown in Fig. 4b and c, uniform and well-dispersed anatase TiO_2 particles of about 50–60 nm in length and 10–15 nm in diameters appeared in the RS

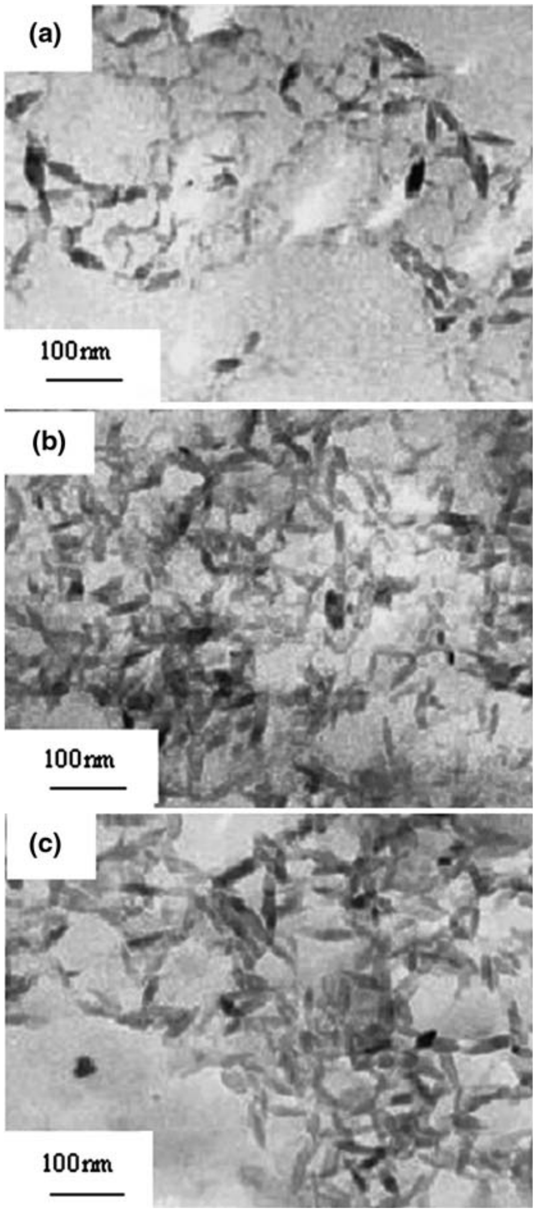


Fig. 4 TEM micrographs of anatase TiO_2 sol (RS) samples prepared at different reflux time: (a) 2 h, (b) 6 h, (c) 10 h

sol. The fact suggests that the longer treating time favor to the formation of larger needle-like anatase crystals, and the more PTA molecules decompose and crystallize to anatase phase with increasing reflux time. However, the size was different from the crystal size calculated from the Scherrer equation, this because the crystals are randomly distributed, the estimated crystal size from XRD is the average size of the length and the accuracy of Scherrer equation is affected by many factors such as diffraction line width, defects, surface tension and instrumental broadening effects, so the Scherrer formula may induce some inexact data in measuring the absolute values of the crystallite size.

Characterization of the TiO_2 films

To determine the crystallinity of the TiO_2 films, the XRD patterns of the TiO_2 thin films calcined at different temperatures are shown in Fig. 5. For comparison, the XRD pattern of glass substrate is given as well. The presence of the broad peak region in XRD pattern of glass substrates should be attributed to the diffraction peaks of SiO_2 in glass substrates. The XRD results of TiO_2 thin films deposited on glass indicate that the TiO_2 thin films calcined at 100, 300 and 500 °C show the some preferential orientation for anatase in the (101) direction. At 100 °C, the width of the anatase (101) plane diffraction peak ($2\theta = 25.3°$) shows wider, which indicate the formation of fine crystallites in the film. With increasing calcination temperature, the peak intensity of anatase increases and the width of the (101) peak becomes narrower, which is due to the growth of crystallites and improvement of crystallization. From Fig. 5, the phase transition temperature of amorphous to anatase seems to be obviously lower than that observed for the TiO_2 thin film prepared by sol–gel method (about 400 °C). This is ascribed to the fact that the anatase crystals form in the RS sols in reflux treatment, and the crystallization is easy to happen on the surface of existed crystals, therefore the calcination temperatures are reduced obviously in this method.

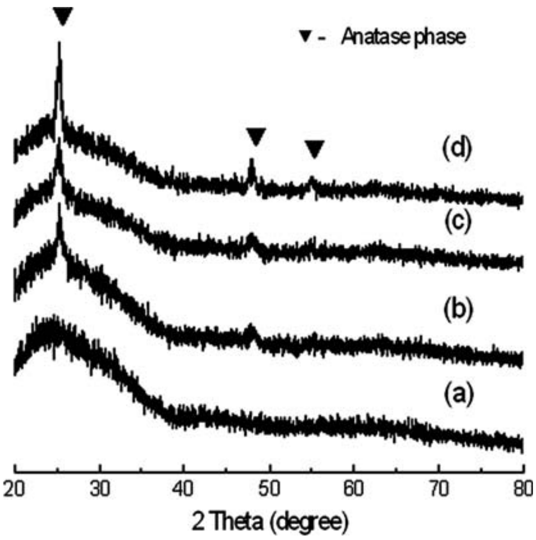


Fig. 5 XRD patterns of TiO_2 films prepared from anatase TiO_2 sol (RS-6) and calcined at different temperatures for 30 min: (a) substrates, (b) 100 °C, (c) 300 °C, (d) 500°C

Figure 6 shows SEM micrographs of the TiO_2 thin films deposited on glass slide substrates and calcined at 100 °C (a), 300 °C (b) and 500 °C (c), respectively. It can be observed that the surface morphologies and roughness of the TiO_2 thin films are different at different calcination temperatures. At 100 °C, the film consists of spherical particles with a diameter range from 30 to 50 nm. When the calcination temperature is 300 °C, the diameters of anatase particles reach about 70–90 nm, the surface morphology and roughness of the TiO_2 thin films alters. At 500 °C, the surface morphology and roughness of the thin films occur to change significantly and the anatase particles grow and connect together on the surface and the film shift into the agglomerated state, diameters of some large particles reaches about 200 nm.

However, the particle morphologies of RS sols and TiO_2 thin films were different. As we known, the growing process of anatase crystals in solutions and calcination conditions are different. According to principle of lowest surface energy of crystal growth [19], the crystals can keep stable by regulating their morphologies and grow into round particles through diffusion to maintain their lowest surface free energy under heating conditions. Then the needle-like anatase crystals in RS sols may become unstable under calcination conditions for their large diameters in length, and the crystals may adjust their morphologies into round figures to achieve the lowest surface free energy. Therefore, we concluded that needle-like anatase crystals with large length–diameter ratio may decrease in length and gradually become approximative round figures with smaller diameters under heating conditions, the changing process was achieved by the diffusion and transformation of TiO_2 crystals. At the same time, the residual PTA molecules decomposed and crystallized into anatase phase on the surface of existing anatase crystals under heating conditions, and the length of anatase crystals decreased and regulated into approximative round figures through diffusion to obtain the lowest surface free energy, the volume of crystals became larger for growth of crystals. The larger needle-like crystals formed bigger nuclei and grew

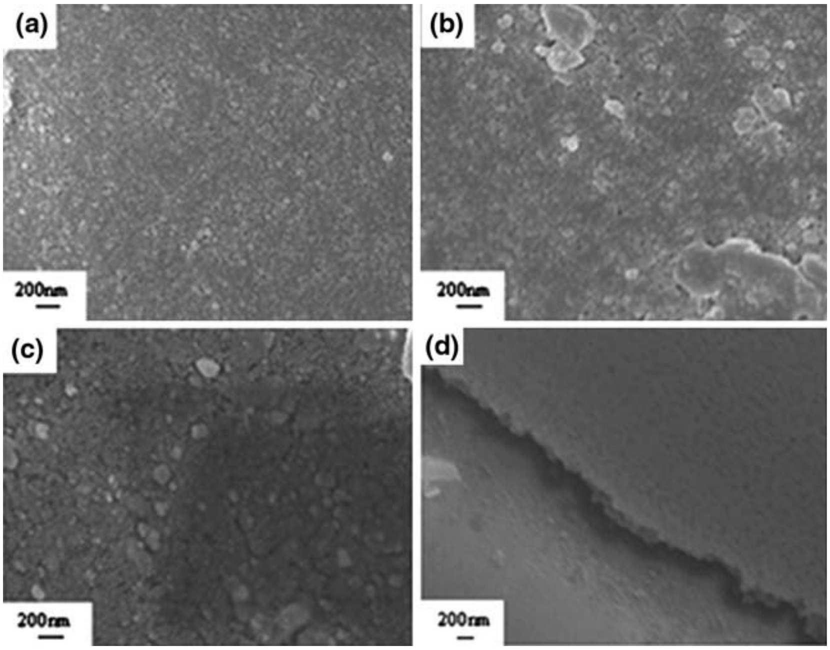


Fig. 6 FE-SEM micrographs of TiO_2 thin films prepared from RS-6 sol and calcined at different temperatures: (**a**) 100 °C; (**b**) 300 °C; (**c**) 500 °C; (**d**) fracture cross-section (FCS) of RS-6 thin films calcined at 100 °C

into larger round particles, so the particles on surface of films increased with increasing calcination temperatures. Therefore, the RS sols and TiO_2 thin films have different particle morphologies.

The compositions of TiO_2 thin films calcined at 100, 300 and 500 °C were characterized with XPS. The corresponding XPS survey spectra for the TiO_2 thin films calcined at 100, 300 and 500 °C are shown in Fig. 7. The XPS results show that TiO_2 thin films deposited on glass substrates contain not only Ti and O elements, but also some N, and Na elements. The photoelectron peak for Ti2p appears clearly at a binding energy of 458.05 eV, O1s at 531 eV and C1s at 284.6 eV. The peak positions are in agreement with the literature values [7]. The XPS peak for C1s due to the adventitious hydrocarbon from the XPS instrument itself. The XPS peaks for N with a binding energy of 400 eV are observed in the films calcined at 100 °C, which are due to the residual elements from starting materials ammonia solution, the content of N element decreases with increasing calcination temperatures. The corresponding high-resolution XPS region spectra of O1s for the TiO_2 thin films calcined at 100, 300, and 500 °C are provided in Fig. 8. The Na element comes from diffusion in the glass substrates and increases with calcinations temperature. The diffusion phenomenon imply occurrence of some chemical reactions on the interface between the TiO_2 films and glass substrates, but other compositions in the glass such as Si and Ca are not found in the survey spectrum.

Figure 7 also shows the high-resolution XPS spectra of the O1s region, taken on the surface of TiO_2 thin films calcined at 100, 300 and 500 °C, respectively. The O1s region is decomposed into two contributions at 529.3 and 530.9 eV. The main contribution is attributed to Ti–O in TiO_2, and the other oxygen contributions can be ascribed to the OH in Ti–OH. Although some H_2O is easily adsorbed on the surface of TiO_2 films

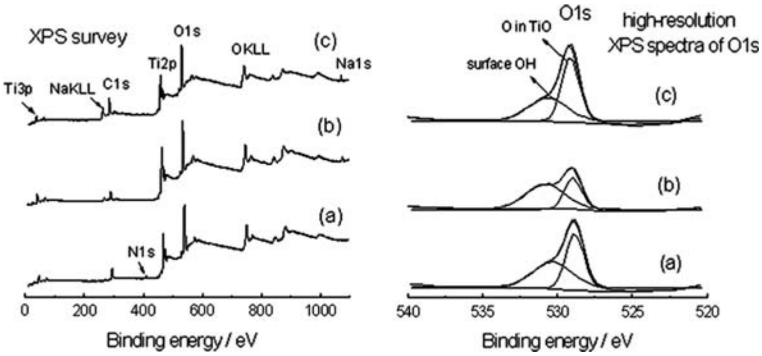


Fig. 7 XPS survey and high resolution XPS spectra of TiO_2 thin films heated at different temperatures (a) 100 °C, (b) 300 °C, (c) 500 °C

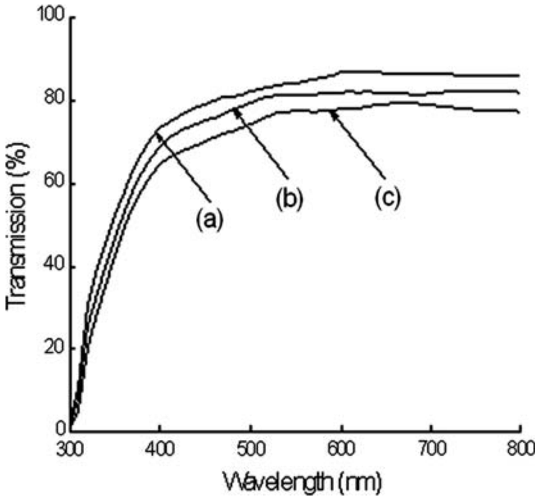


Fig. 8 UV–VIS spectra of TiO_2 thin films prepared from RS-6 sol under different temperatures: (a) 100 °C; (b) 300 °C; (c) 500 °C

during deposition process, the physically absorbed H_2O on TiO_2 is easily desorbed under the ultrahigh vacuum condition of the XPS system. Therefore, the hydroxyl on the surface can be attributed to the Ti–OH on the thin films. The contributions of OH groups in O1s on the surface of TiO_2 thin films calcined at 100, 300 and 500 °C samples are 30.8, 46.2 and 26.7%, respectively. Usually, an increase in the hydroxyl content on the surface of TiO_2 films can enhance the photo-induced super-hydrophilicity and photocatalytic activity, but the photocatalytic activity of TiO_2 films are also affected by other factors such as the crystallinity of titania, diameters of crystal particles. At 500 °C, the TiO_2 thin films still contain a small amount of hydroxyl. This is probably due to the fact that the films easily adsorb water vapor in air, leading to the formation of hydroxyl on the films.

The TiO_2 thin films deposited on glass slides and calcined at various temperatures are transparent. The corresponding UV–VIS spectra for the TiO_2 thin films calcined at 100, 300 and 500 °C are provided in Fig. 8. A significant decrease in the transmittance below 400 nm can be assigned to absorption of light caused by the excitation of electrons from the valence band to the conduction band of titania. The transmission of titania thin films calcined at 300 and 500 °C is about 70–80% over the visible light spectra region and is lower than that of the TiO_2 thin films heated at 100 °C. This can be ascribed to the formation of larger particles with on the surface of TiO_2 thin films (according to Fig. 6), which causes the scattering of light. With increasing calcination temperature, the changes in the transmittance and absorption edge wavelength of the TiO_2 thin films are ascribed to the difference in surface morphologies, crystallite size within the films. The UV–VIS transmittance spectra show that absorption edge shifts to longer wavelength with increasing temperatures, and the ‘‘red-shift’’ of absorption edge wavelength can be attributed to the growth of TiO_2 crystallites. Also, the existence of surface defects in the film will result in the decrease of the transmittance due to scattering of light.

The difference in absorption edge wavelength for the TiO_2 thin films clearly indicates a decrease in the band gap of TiO_2 with increasing calcination temperatures. In order to obtain a quantitative estimate of the bandgap energies, the UV–VIS spectra were processed in order to obtain the energy band gap E_g, from the expression corresponding to indirect gap semiconductors:$(\alpha h\nu)^{1/2} = A_{\mathrm{i}}\left(h\nu - E_{\mathrm{g}}\right)$.

Where α is the absorption coefficient (cm^{-1}) and $h\nu$ (eV) is the energy of excitation. A_i is a constant which does not depend on photo energy.

The intercepts of the tangents to the $(\alpha h\nu)^{1/2}$ versus photon energy (E) plots will give an estimate of the band gap energies of TiO_2 thin films. Plots of $(\alpha h\nu)^{1/2}$ versus photo energy (E) for TiO_2 thin films calcined at different temperatures are shown in Fig. 9. The band gap energies for TiO_2 films calcined at 100, 300 and 500 °C are estimated to be 3.56, 3.47 and 3.39 eV, respectively. It is found that the bandgap energies of the films decrease and red shift in the absorption edge appears with increasing calcination temperature. The difference between the band gap energies of TiO_2 thin films calcined at different temperatures may be due to the difference in crystallite size. The size of nano particles on surface of TiO_2 thin films increased with calcinations temperature according to the SEM analysis,

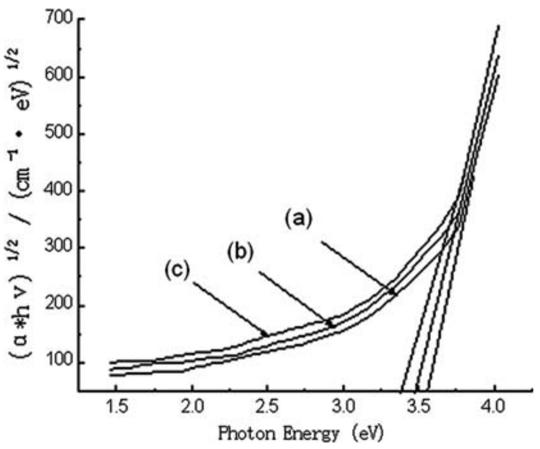
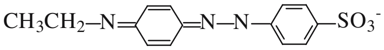


Fig. 9 Determination of the bandgap energies of the TiO_2 films heated-treated under different temperatures. (a) 100 °C; (b) 300 °C; (c) 500 °C

the larger anatase crystals has lower energy band gap caused by the quantum size effects.

Photocatalytic properties of TiO_2 films

The structure of methyl orange is shown below:



Based on the results before [6], the methyl orange can be easily photocatalytic degradated when its pH value is 3, so we adjusted the pH value of MO to 3 in this experiment.

Figure 10 presents the degradation of methyl orange with the TiO_2 films calcined at different temperatures. It was found from the figure that the TiO_2 films heated at 300 °C had the best photocatalytic activity compared with other two kinds of films. The photocatalytic activity of TiO_2 films calcined at 500 °C is slightly lower than those treated at 300 °C. The degradation rate of methyl orange solution reached 99% after irradiated for 160 min, which implied that almost all the methyl orange was oxidized. The blank sample also shows the degradation of methyl orange, the degradation rate reach about 82% after irradiated for 2 h, which is much lower than the samples with TiO_2 thin films.

It is worth noting that the calcination temperature is very important to photoactivity of TiO_2 thin films. The correlation between photocatalytic activity and calcination temperature is well consistent with the effect of calcination temperature on the crystals sizes of TiO_2 thin films according the SEM analysis (Fig. 6). It is believed the TiO_2 thin films calcined at 300 °C should have excellent photocatalytic activity due to high specific surface areas and relative small crystals sizes compared with other two kinds of films. The TiO_2 film heated at 100 °C contains little anatase TiO_2 crystals and most of TiO_2 are amorphous, then it has lower photoactivity than films heated at 300 and 500 °C. The crystallinity of TiO_2 films is enhanced after calcined at 500 °C according to XRD analysis (Fig. 5), more anatase phase favors to improve the photocatalytic activity. However, the diameters anatase crystals in 500 °C heated films increase with calcination temperature and some large particles exceed 200 nm in diameters. When the crystals size become lager, the growth of TiO_2 crystallites result in the significant decrease of surface area of the TiO_2 thin films, the average path length of a charge carrier to the surface is longer, which has negative effect on the photoactivity. Therefore, the photocatalytic activity of TiO_2 films calcined at 500 °C is slightly lower than those treated at the lower temperature (300 °C). The TiO_2 thin films heated at 300 °C have better crystallinity than films heated at 100 °C and smaller crystal size than films heated at 500 °C, and the hydroxyl content on the surface of the 300 °C calcined films are greater than others according to XPS analysis, these factors are beneficial to the enhancement of photocatalytic activity. Therefore, the films heated at 300 °C have the best photoactivity.

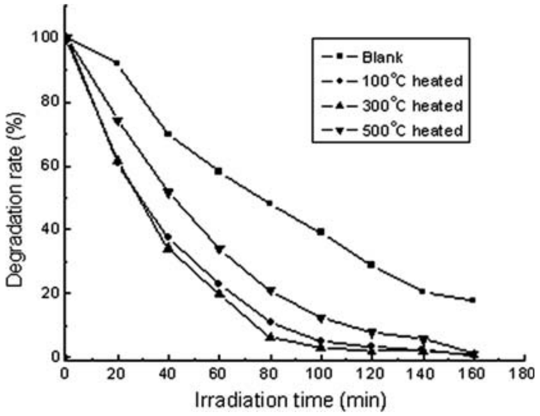


Fig. 10 Photodegradation of methyl orange over TiO_2 thin films as a function of UV light irradiation time

Decoloration does not means degradation, to resolve the problem, the photocatalytic products were analyzed by ion chromatograph with a conductivity detector (Dionex, DX-100). The anion of SO_4^{2-} is one of the main profucts of MO degradation. The SO_4^{2-} have been detected in the solution after photocatalytic reaction, which confirmed that the methyl orange had been photocatalytic degradation (see Table 1). A SO_4^{2-} ion concentration of 24.2 μmol/l was detected in the solution after the photocatalytic reaction over the 100 °C heated TiO_2 thin films under visible light irradiation, which indicated that 79.2% of sulphur from MO was converted to sulphate. When the TiO_2 films were heated at 300 and 500 °C, the concentration of SO_4^{2-} ion reached 27.9 and 21.6 μmol/l, indicating that 91.3 and 70.7% of the sulphur in MO was degradation. We could deduce that MO should have been decomposed to many fragments from the increase of SO_4^{2-} concentration after the photocatalytic reaction.

Table 1 The value of SO_4^{2-} concentration in the solution after methyl orange photocatalytic degradation

Film samples	100 °C heated	300 °C heated	500 °C heated
SO_4^{2-} concentration (μ mol/l)	24.2	27.9	21.6

Conclusions

The flavescent, semitransparent and alkalescent RS sols were synthesized by refluxing PTA sol at 100 °C for 2–10 h. The RS sols contain needle-like TiO_2 anatase crystals which are 10–70 nm in length, 5–15 nm in diameters. The RS sols keep stable by the mutual repulsion between the peroxo groups remain on the surface of the anatase crystals. It is found that the TiO_2 thin films contain not only Ti and O elements, but also a small amount of N and Na elements. The N element comes from the precursor solution. The Na element in the TiO_2 thin films can be attributed to the diffusion of Na element from the surface of glass substrate into thin films at high temperature. The TiO_2 films are transparent and their maximal light transmission exceeds 80% under visible light region. At 300 °C, the TiO_2 thin film shows the highest photocatalytic activity. When the calcination temperature is 100 °C, the films show low photocatalytic activity because the thin films are composed of amorphous TiO_2. When the calcination temperature is higher than 300 °C, the decrease in photocatalytic activity is due to sintering and growth of TiO_2 crystallites resulting in the decrease of surface area.

Acknowledgement This work was financially supported by the Doctor Foundation (Grant No. 20030056001).

References

1. Djaoued Y, Badilescu S, Ashrit PV (2002) J Sol-Gel Sci Technol 24:247
2. Gebeyehu D, Brabec CJ, Sariciftci NS (2002) Thin Solid Films 403/404:271
3. Sankapal BR, Lux-steier MCh, Ennaoui A (2005) Appl Surf Sci 239:165
4. Sonawane RS, Kale BB, Dongare MK (2004) Mater Chem Phys 85:52
5. Wu L, Jimmy YC, Wang XC, Zhang LZ, Yu JG (2005) J Sol State Chem 178:321
6. Ge L, Xu MX, Fang HB, Li Y (2005) Chin J Ceram Soc 33(3):330
7. Yu JG, Yu HG, Cheng B, Zhao XJ, Yu JC, Ho WK (2003) J Phys Chem B 107:13871
8. Hu Y, Yuan CW (2005) J Cryst Growth 274:563
9. Djaoued Y, Badilescu S, Ashrit PV (2002) J Sol-Gel Sci Technol 24:257
10. Ge L, Xu MX, Lei E, Tian YM, Fang HB (2005) Key Eng Mater 280–283:809
11. Hwang KS, Jeong JH, Jeon YS, Jeon KO, Kim BH (2005) J Sol-Gel Sci Technol 35:237
12. Bu SJ, Jin ZG, Liu XX, Yang LR, Cheng ZJ (2005) J Eur Ceram Soc 25:673
13. Buscema CL, Malibert C, Bach S (2002) Thin Solid Films 418:79
14. Ichinose H, Terasaki A, Katsuki H (1996) J Ceram Soc Japan 104:715
15. Ichinose H, Terasaki M, Katsuki H (2001) J Sol-Gel Sci Technol 22:33
16. Gao Y, Masuda Y, Koumoto K (2004) Chem Mater 16:1062
17. Lee CK, Kim DK, Lee JH, Sung JH, Kim I (2004) J Sol-Gel Sci Technol 31:67
18. Yang J, Mei S, Ferreira JMF (2004) J Eur Ceram Soc 24:335
19. Zhang KC, Zhang LH (1981) Crystal growth. The Science Publishing House, China, p 79