Preparation and characterization of porous C-modified anatase titania films with visible light catalytic activity

Yi Xie, Xiujian Zhao*, Yunxia Chen, Qingnan Zhao, Qihua Yuan

Key Laboratory of Silicate Materials Science and Engineering, Wuhan University of Technology, Ministry of Education, Wuhan, Hubei 430070, PR China

Abstract

Visible-light-activated C-modified anatase titania films have been synthesized from $TiCl_4$ and carbonic ink by using the sol–gel route. The synthesized photocatalysts were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and optical measurements. The modifying carbon not only produces homogeneous worm-like structure with uniform pores, but also extends the absorbance spectra of the as-prepared films into visible region. The results of visible-light-induced degradation of methyl orange (MO) show that the C-modified titania films exhibits much higher photocatalytic activities than that of pure titania film prepared at the same conditions.
© 2007 Elsevier Inc. All rights reserved.

1. Introduction

Titania has been widely used and explored as a photocatalytic material since it is nontoxic, chemical stable, inexpensive, and has favorable optoelectronic property. However, there have been two typical deficiencies for using of this photocatalyst. First, it is difficult to separate suspended TiO_2 at the completion of each reaction cycle. Second, TiO_2 can work only under ultraviolet (UV) light due to its wide bandgap of 3.0–3.2 eV, which means only ~4% of the incoming solar energy on the surface can be utilized. As for the first problem, it could be avoided by using the TiO_2 films immobilized on substrates [1,2]. In addition, many attempts have been made to improve the optical response of TiO_2 under visible light excitation. In recent years, nonmetal doping of TiO_2 rekindled a great interest in visible light catalysis since the report of the work of Asahi et al. in 2001 [3–7].

Carbon doping was considered to be one of the methods to lower the band gap of TiO_2 and the consequent high photocatalytic activity for degradation of organics under visible light illumination. C-modified or C-doped TiO_2 could be synthesized by various techniques, such as hydrolysis [8], sol–gel [9,10], carbonization under CO gas or ethanol environment [11,12], oxidative annealing of TiC [13,14], magnetron sputtering [15,16]. Chemically modified *n*-type TiO_2 [4] was synthesized by using controlled combustion of Ti metal in a natural gas flame, and the resulting photocatalyst could absorb UV and most of the visible light < 535 nm. Lettmann et al. [17] prepared porous *n*-TiO_2 from titanium alkoxides by a sol–gel process followed by calcination. Irie et al. [13] have synthesized C-doped anatase TiO_2 powders by oxidative annealing of TiC under O_2 flow at 600 °C. Their catalysts showed visible-light-induced photocatalytic activities for the decomposition of 2-propanol to CO_2 via acetone.

In the present work, we prepared anatase C-modified titania films by dip-coating method. The visible-light-induced catalytic activities of C-modified titania films were evaluated by the decomposition of methyl orange (MO) aqueous solution.

2. Experimental details

2.1. Samples synthesis

C-modified anatase titania films were prepared by dip-coating route. In a typical procedure, 6 mL $TiCl_4$ (Sinopharm

*Corresponding author. Fax: +86 27 8766 9729.
E-mail address: opluse@whut.edu.cn (X. Zhao).

Chemical Reagent Co. Ltd, China) was added dropwise into 500 mL distilled water dispersed with carbonic ink (Boss Enterprise, Guizhou, China) in an ice-water bath under strong magnetic stirring. After stirring for 30 min, the pH of this black acidic solution was adjusted to ~7 by dropwise addition of diluted ammonia solution (1:9). After stirring at this pH for 24 h, the obtained blue precipitate was filtered and washed thoroughly with distilled water repeatedly until Cl^- ions were not detected. The precipitate was then dispersed in 400 mL of distilled water by sonication and 45 mL of H_2O_2 (30%) was added dropwise into this mixture under stirring. The resulting solution was heated in a Teflon-lined stainless-steel autoclave at 100 °C for 6 h. Finally, the uniform, stable, and yellow brown transparent titania sol with anatase crystals was obtained, which was used to prepare films. A series of C-modified titania films were prepared by changing the dosage of starting carbonic ink: they were designated as TCx, where "x" represents the dosage of carbonic ink (mL). The obtained sol can maintain homogeneous dispersion for more than 2 years without sedimentation and delamination phenomena. Table 1 shows the preparation condition together with other physicochemical data. Comparatively, light white transparent TiO_2 sol with anatase phase was also prepared without addition of carbonic ink.

Glass slides were used as substrates. Before the deposition, substrates were ultrasonically cleaned in acetone and absolute ethanol for 30 min, respectively. Films were deposited on substrates by a dip-coating process. Substrates were immersed into the C-modified or unmodified titania sol for 30 s and upon withdrawing from the sol with a dip-coating rate of 1–2 mm/s, the substrates were dried at 60 °C. C-modified titania layers on substrates were thickened by means of consecutive 15 and 50 dip-coating cycles, respectively. Finally, the former films were annealed at 500 °C for 5 h in air and the latter at 400 °C for 3 h in argon with a ramp of 3 °C/min.

2.2. Samples characterization

The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB MK II spectro-

meter (VG Scientific Ltd., UK) with non-monochromatic Al $K\alpha$ X-ray (1486.6 eV). The pressure in the chamber during the experiments was less than 10^{-6} Pa. The analyzer was operated at 50 eV pass energy for high-resolution spectra and 100 eV for survey spectra. The binding energy of the C 1s line (284.6 eV) was taken for calibrating the obtained spectra. Background subtraction and peak fitting was performed using a public XPS peak fit program (XPSPEAK4.1 by R. Kwok). Recorded spectra were fitted using Gauss–Lorentz curves and the Lorenz–Gauss ratio for each Ti, O and C species was kept constant.

The crystalline structure of the C-modified titania powders dried from sol was identified by X-ray diffraction (XRD) (D/MAX-βA, Rigaku, Japan) measurements using Cu $K\alpha$ ($\lambda = 0.15418$ nm) radiation at 40 kV, 50 mA in the 20–70° 2θ angle range. Apparent crystal size (ACS) was estimated through Scherrer's formula [18]:

$$D = \frac{k\lambda}{\beta \cos \theta}, \qquad (1)$$

where D is the crystallite size (nm), k is the apparatus constant taken as 0.89, λ is the wavelength of Cu $K\alpha$ line (1.5418 Å), θ is the Bragg's angle(°) and β is the width of the diffraction peak at a half-maximum of intensity (rad) planes of anatase.

The morphologies of the films were observed on an atomic force microscopy (AFM) (Digital Instrument's Nanoscope IV, Veeco, America) and a Hitachi S-4800 FE SEM (Hitachi Ltd., Japan) at an acceleration voltage of 10 kV. All measurements were made with similar temperature and humidity conditions.

Both of the total spectral transmittance (T_λ) and reflectance (R_λ) of C-modified titania films were recorded using an NKD-7000 W system spectrophotometer (AQUILA, Britain). Spectral absorption (A_λ) was obtained from

$$A_\lambda = 1 - T_\lambda - R_\lambda. \qquad (2)$$

2.3. Photocatalytic decomposition of MO

Visible-light induced photocatalytic activity of the as-prepared photocatalysts was evaluated by the degradation

Table 1
Preparation condition, crystal size and XPS analysis for different C-modified titania films

Sample	Ink[a] (mL)	D^{b}_{XRD} (nm)	D^{c}_{AFM} (nm)	XPS: Binding energies of Ti 2p, O 1s and C 1s (eV) (atomic content, at%)					
				Ti 2p	O 1s O^{2-}	O–H	C–C	C 1s C–O	C = O
TC1	1	7	20	458.2 (22.3)	529.4 (42.7)	531.4 (12.8)	284.6 (12.9)	286.9 (6.6)	289.1 (2.7)
TC2	2	8	22	458.1 (21.8)	529.3 (40.6)	531.2 (16.4)	284.6 (16.3)	286.8 (2.1)	288.4 (2.8)
TC3	3	7	24	458.8 (22.9)	529.8 (41.1)	531.7 (11.2)	284.6 (15.8)	286.1 (7.5)	288.4 (1.5)
TC4	4	6	28	458.6 (22.3)	529.9 (41.4)	531.8 (9.2)	284.6 (18.4)	286.3 (7.3)	288.9 (1.4)

[a] Dosage of starting carbonic ink.
[b] Crystal size from XRD (nm).
[c] Grain size of films (annealed at 500 °C in air) from AFM.

of MO aqueous solution in a Pyrex glass vessel (45×45 mm^2). The films (43×43 mm^2) were placed at the bottom of the reaction vessel, and 12 mL of MO solution with 10 mg/L of concentration was added into the vessel, exposed to a high pressure Hg-light (125 W) with the UV cut-off filter. The UV cut-off filter was placed between the beaker and light source to exclude UV radiation under 420 nm. The light intensity at 420 nm on the surface of the MO solution was identified as 197 μW cm^{-2}. At the end of the irradiation time 3 mL MO solution was taken, and the relative concentration is determined through a UV-1601 UV–vis spectrophotometer (Rigaku, Japan) by measuring the absorption spectral change of MO [19].

3. Results and discussion

3.1. XPS analysis

The XPS measurements were carried out to study the chemical state of the C-modified titania photocatalysts. Fig. 1a–c illustrate the high-resolution and curve fittings of C 1s, Ti 2p and O 1s XPS spectra taking on the surface of different C-modified titania films dip-coated for 50 cycles and annealed at 400 °C for 3 h in argon.

It can be seen that the C 1s spectra span over a broad energy range from 291 to 281 eV, which can be well fitted to three peaks. The first peak at 284.60 eV is assigned to the active carbon from carbonic ink or adventitious carbon
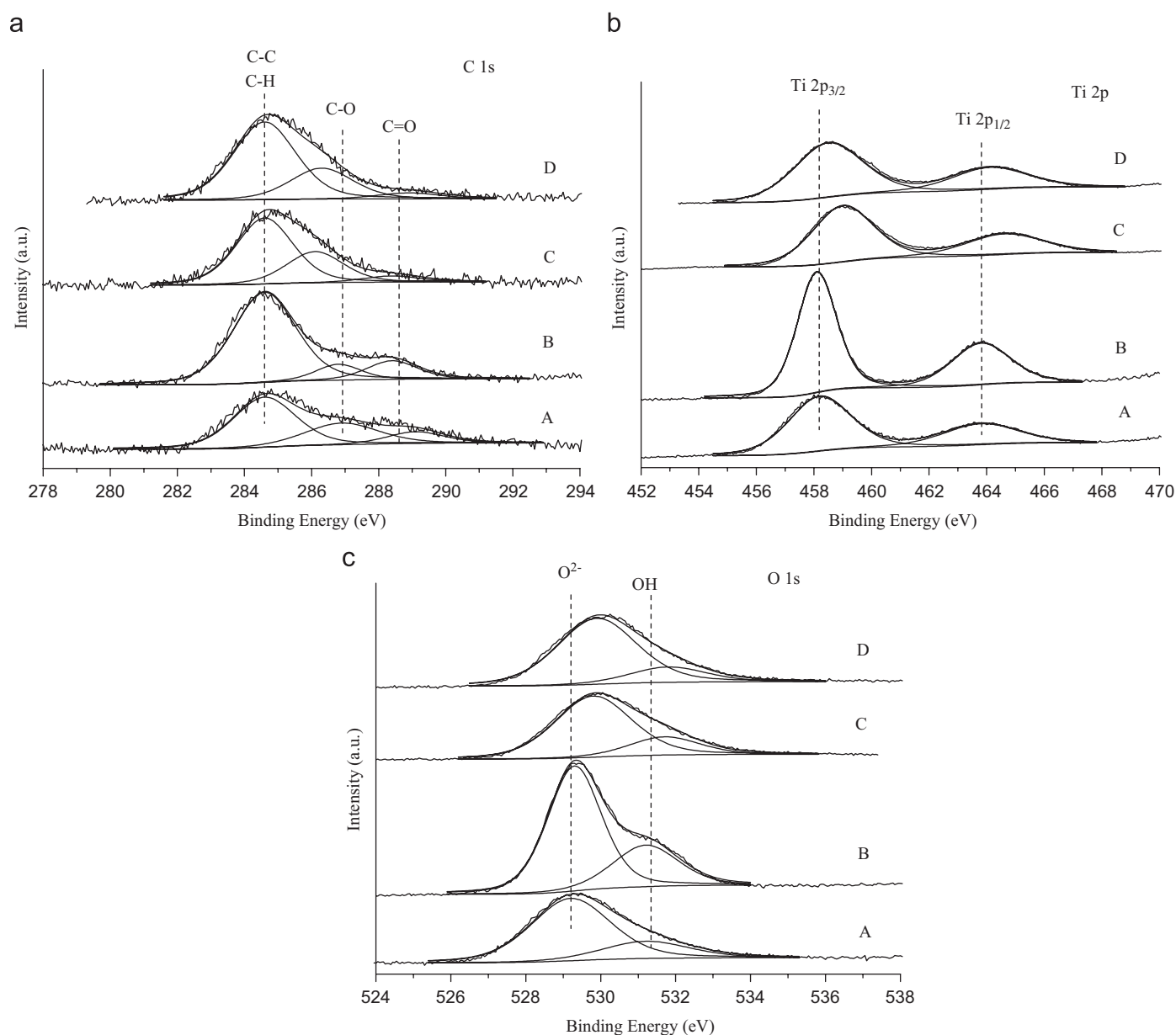

Fig. 1. High-resolution XPS spectra of C 1s (a), Ti 2p (b) and O 1s (c) on the surface of C-modified titania films prepared with starting carbonic ink of (A) 1 mL, (B) 2 mL, (C) 3 mL and (D) 4 mL. The films were dip-coated for 50 cycles and annealed at 400 °C for 3 h in argon.

contamination adsorbed from the atmosphere. The second and the third peaks at 286.1–286.9 and 288.4–289.1 eV can be attributed to C–O and $C = O$ bonds, respectively [20]. Hashimoto et al. [13] observed C 1s XPS peak at 281.8 eV and they assigned this C 1s XPS peak to Ti–C bond in carbon-doped anatase titania by substituting some of the lattice oxygen atom by carbon. Kamisaka et al. suggested that cation-doped carbon atoms formed a carbonate-type structure by theoretical calculation [21]. Jin et al. [22] synthesized carbon-sulfur-codoped TiO_2 and viewed the XPS signals at 281.8 and 282.6 as Ti–C bonds, and that at 285.6 eV as elemental carbon, and two peaks at 288.8 and 289.8 eV as carbonate species. Li et al. [23] prepared C-doped titania by temperature-programmed carbonization of K-contained anatase titania under a flow of cyclohexane and they attributed the peak at 288.2 eV as the presence of one kind of carbonate species. However, according to the literature [24], the XPS peak at 288.6 eV indicated the presence of C–O bonds and carbon might substitute for some of the lattice titanium atoms and form a Ti–O–C structure. Two kinds of carbonate species present in our case, which are similar with that reported by Sakthivel et al. [20,25]. The results by curve fitting are shown in Table 1. The total surface carbon concentration in our sample increased on the whole with the increasing dosage of starting carbonic ink, which was estimated by XPS to be as high as 27.1%.

The XPS spectra of Ti 2p and O 1s regions were also shown in Fig. 1b–c. Fig. 1b reveals the characteristic doublet Ti $2p_{3/2}$ and Ti $2p_{1/2}$ at 458.1–458.8 and 463.8–464.4 eV, respectively. The area ratios of the two peaks, A(Ti $2p_{3/2}$)/A(Ti $2p_{1/2}$), are equal to 2.0 ± 0.2 and the binding energy (BE) difference, E_b(Ti $2p_{1/2}$)–E_b(Ti $2p_{3/2}$), is 5.6–5.7 eV. All of these values indicate that Ti exists in the Ti^{4+} form [26] on the surface of C-modified titania films. The high-resolution XPS spectrum of the O 1s peak is shown in Fig. 1c. It consists of a main peak at 529.3–529.9 eV and a shoulder at 531.2–531.8 eV, which can be assigned to bulk O^{2-} from TiO_2 and –OH adsorbed on the surface of as-prepared film, respectively [27]. Table 1 also summarizes the titanium and oxygen concentrations detected by XPS for the C-modified titania films. As indicated in Table 1, oxygen is deficient in a stoichiometric ratio.

3.2. Crystal structure

Fig. 2 shows the XRD patterns of the dried C-modified titania powders from sol prepared at 100 °C. The diffraction peaks at $2\theta = 25.15°$, $37.79°$, $47.75°$, $54.15°$, $62.67°$ correspond to the (1 0 1), (1 0 3, 0 0 4 and 1 1 2), (2 0 0), (1 0 5 and 2 1 1), (2 0 4) crystal planes of anatase, respectively [28] (JCPDF Card no. 21-1272). All of the XRD peaks are not so sharp as compared to the highly crystalline bulk titania, which indicates the small crystal size of the dried C-modified titania powders from sol. In fact, the particle size calculated from Scherer equation is 7 ± 1 nm, which is of
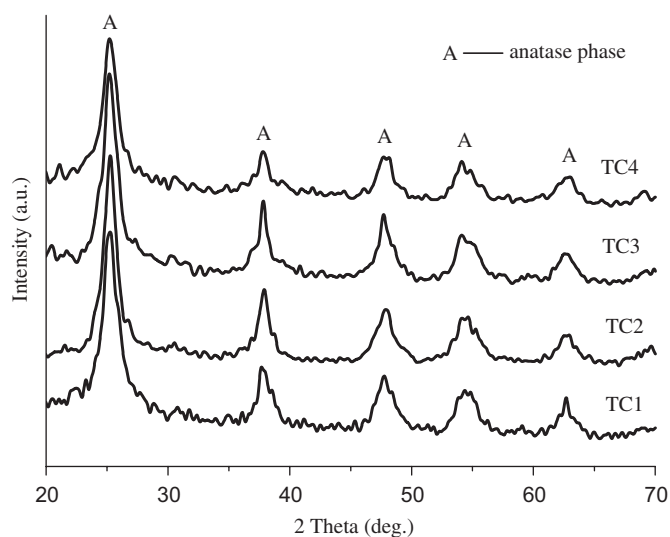

Fig. 2. XRD patterns for dried powders from C-modified titania sol.

nanoscale. Usually, the amorphous-anatase transformation may complete in the temperature range from 250 to 400 °C. All the results mentioned above, however, may inspire us to develop low temperature methods to prepare nanoscale nonmetal-doped TiO_2 photocatalysts with anatase phase. Zhang et al. [24] have prepared visible-light-active carbon-doped TiO_2 photocatalysts using glucose as carbon source at 160 °C using a hydrothermal method. Recently, in our team, F–N-codoped and S–N-codoped titania powders with high visible-light activity were also prepared at temperature as low as 100 °C [29,30].

3.3. Morphological studies

Fig. 3 illustrates the topographic images obtained by AFM measurements in tapping mode of C-modified titania films (dip-coating for 15 cycles and annealing at 500 °C for 5 h in air) surfaces (scanned area is 1000×1000 nm^2) in atmospheric air. The surface morphology of pure TiO_2 film shown in Fig. 3a is obviously much different from that of C-modified titania films. As for the C-modified titania films, uniform, small and interconnected grains are observed (Fig. 3b–e) and their dimensions vary in a narrow range (20–30 nm in diameter), with root mean square surface roughness 5.0 ± 1.0 nm. The analysis of grain sizes from AFM is different from that from XRD of C-modified titania powders dried from sol (Table 1), which indicates that annealing of films influences the grain growth. Furthermore, pores are distributed on the surface of C-modified titania films. This homogeneous and porous structure is also obviously observed on typical scanning electron microscopy (SEM) images of C-modified titania films shown in Fig. 4. It can be seen that all of the films present quite similar worm-like structure with uniform pores regardless the dosage of starting carbonic ink. The pore size varied from 10 to 20 nm, which is typically the mesoporous structure. This structure is undoubtedly
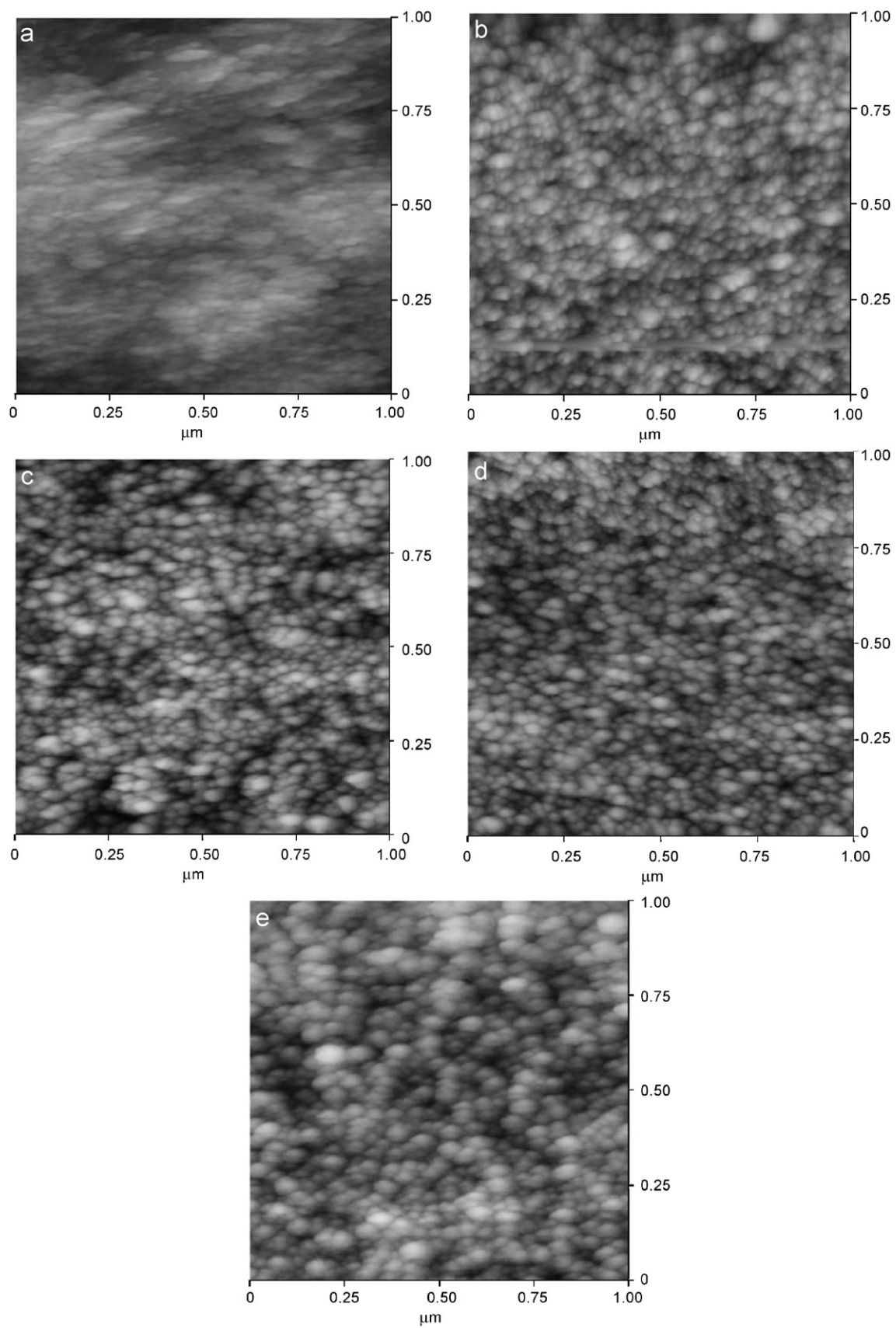
Fig. 3. AFM top view images of different films dip-coated for 15 cycles and annealed at 500 °C for 5 h in air: (a) TiO_2; (b) TC1; (c) TC2; (d) TC3; (e) TC4.
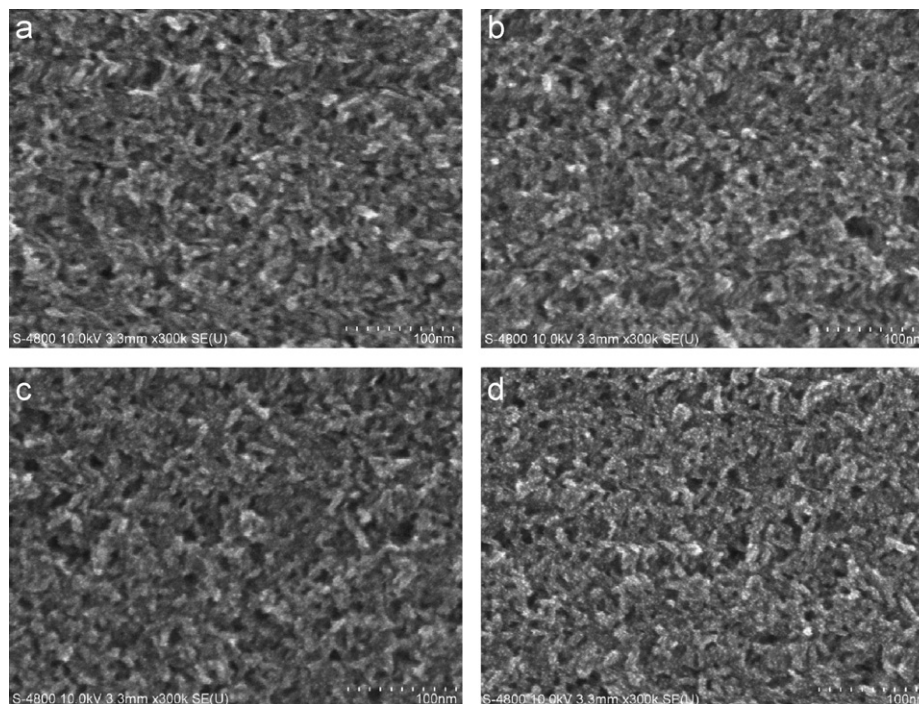
Fig. 4. SEM images of selected C-modified titania films dip-coated for 50 cycles and annealed at 400 °C for 3 h in argon: (a) TC1; (b) TC2; (c) TC3; (d) TC4.

beneficial for the adsorption of organic molecular and thus improves the photocatalytic activity.

3.4. Optical properties of C-modified titania

Fig. 5 shows optical data for unmodified and C-modified titania films. It can be seen that the onsets wavelength for absorption in C-modified titania films shift into the visible region, while the onset of unmodified titania film is close to the UV region. The interference-like pattern probably originates from difficulties in measuring the total reflectance [31]. Hashimoto and coworkers [15] synthesized C-doped anatase titania thin films by magnetron sputtering method, and they observed that the dopant carbons located at the oxygen sites caused the shifts in both the absorbance edge and shoulder to a longer wavelength region. In our case, this shift was influenced by the modifying carbon concentration. Lettmann et al. [17] found that pyrolysis of alcohols led to highly condensed, coke-like carbonaceous species embedded in n-TiO_2 matrix, which contributed to absorption of light in the visible region and enhanced the photocurrent response both in UV and visible region. Khan et al. [32] synthesized carbon-modified (CM)-n-TiO_2, which absorbed well into the visible to near infrared region up to 800 nm and exhibited enhanced photocatalytic activity for the degradation of 4-chlorophenol under visible light illumination. From the results of Figs. 1 and 5, we conclude that different from that of most literatures, the visible light response is caused without the substitution of oxygen by carbon, though the reasons should be further studied.
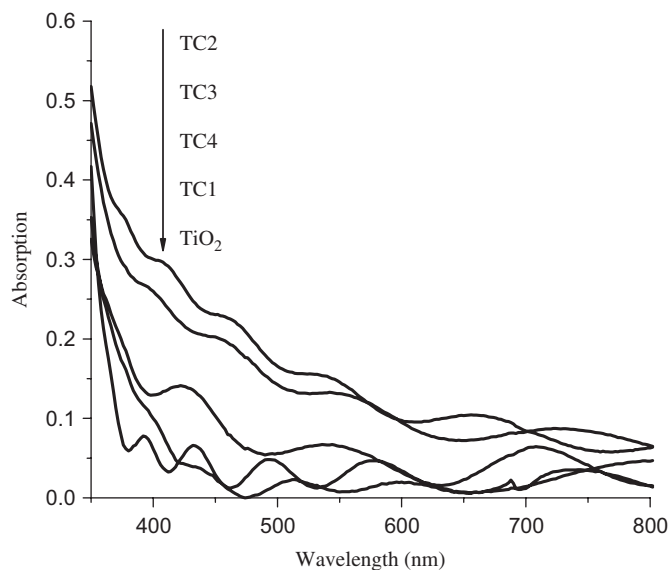

Fig. 5. Spectral absorption for different C-modified titania films. The films were dip-coated for 50 cycles and annealed at 400 °C for 3 h in argon.

3.5. Photocatalytic activity

The photocatalytic degradation of MO with as-prepared films was detected by measuring MO absorption spectral changes after 22 h visible light irradiation (Fig. 6). It can be seen that the dosage of carbonic ink affects the photocatalytic activity. The visible-light driven catalytic activity of various films is in the following order of: pure $TiO_2 <$ TC1 $<$ TC4 $<$ TC3 $<$ TC2. Among them, TC2 film
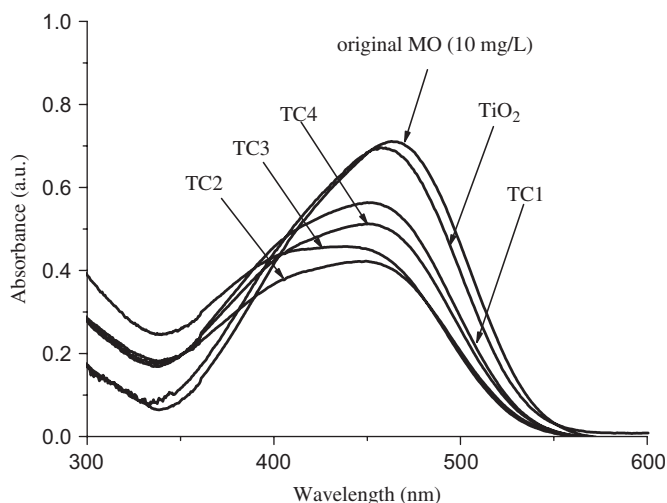
Fig. 6. Absorption spectral changes of MO solution in the presence of various films after irradiation by visible light for 22 h. The films were dip-coated for 50 cycles and annealed at 400 °C for 3 h in argon.

shows the highest photodegradation activity with a MO conversion of 40.63%, which is much higher than that by pure TiO_2 film (2.19%). Obviously, the visible-light absorption of C-modified titania films revealed in Fig. 5 contributes to the visible-light induced catalytic activity. Furthermore, C-modifying leads to the formation of porous structure (Figs. 3 and 4), which benefits for the adsorption of MO and thus improved the photodecomposition. Finally, the surface hydroxyl detected by XPS was as high as 16.4% for TC2 film annealed at 400 °C in argon (Table 1). The Ti^{4+}–$OH^{\bullet}$ entities could be formed by a surface hydroxyl trapping a hole, among which the $OH^{\bullet}$ radicals drive degradation reactions, which can eventually lead to the decomposition of organic pollutants [33]. These results indicate that C-modifying is an effective way to improve the visible-light driven catalytic activity of TiO_2-based catalysts for decomposition of organic compounds.

4. Conclusions

C-modified anatase titania films have been successfully prepared by using the sol–gel and dip-coating methods. Compared with that of pure titania film, UV–vis absorption spectra of C-modified titania films show a shift towards higher wavelengths. Carbon modifying also produces uniform morphology with porous structure on the as-prepared films. All these are beneficial for the high photocatalytic efficiency for the decomposition of MO under visible irradiation.

Acknowledgments

References

[1] Y. Cao, X. Zhang, W. Yang, H. Du, Y. Bai, T. Li, J. Yao, Chem. Mater. 12 (2000) 3445–3448.
[2] H.J. Nam, T. Amemiya, M. Murabayashi, K. Itoh, J. Phys. Chem. B 108 (2004) 8254–8259.
[3] R. Asahi, T. Morikawa, T. Ohwaki, A. Aoki, Y. Taga, Science 293 (2001) 269–271.
[4] S. Khan, M. Al-Shanhry, W.B. Ingler, Science 297 (2002) 2243–2245.
[5] G. Liu, F. Li, Z. Chen, G.Q. Lu, H.M. Cheng, J. Solid State Chem. 179 (2006) 331–335.
[6] M. Sathish, B. Viswanathan, R.P. Viswanath, C.S. Gopinath, Chem. Mater. 17 (2005) 6349–6353.
[7] K. Madhusudan Reddy, Babita. Baruwati, M. Jayalakshmi, M. Mohan Roa, Sunkara V. Manorama, J. Solid State Chem. 178 (2005) 3352–3358.
[8] S. Sakthivel, M. Janczarek, H. Kisch, J. Phys. Chem. B 108 (2004) 19384–19387.
[9] M.E. Rincón, M.E. Trujillo-Camacho, A.K. Cuentas-Gallegos, Catal. Today 107–108 (2005) 606–611.
[10] T.A. Egerton, M. Janus, A.W. Morawski, Chemosphere 63 (2006) 1203–1208.
[11] J.H. Park, S. Kim, A.J. Bard, Nano. Lett. 6 (2006) 24–28.
[12] M. Janus, M. Inagaki, B. Tryba, M. Toyoda, A.W. Morawski, Appl. Catal. B—Environmental 63 (2006) 272–276.
[13] H. Irie, Y. Watanabe, K. Hashimoto, Chem. Lett. 32 (2003) 772–773.
[14] M. Shen, Z.Y. Wu, H. Huang, Y.K. Du, Z.G. Zou, P. Yang, Mater. Lett. 60 (2006) 693–697.
[15] H. Irie, S. Washizuka, K. Hashimoto, Thin Solid Films 510 (2006) 21–25.
[16] A.C. Fernandes, P. Carvalho, F. Vaz, S. Lanceros-Méndez, A.V. Machado, N.M.G. Parreira, J.F. Pierson, N. Martin, Thin Solid Films 515 (2006) 866–871.
[17] C. Lettmann, K. Hildenbrand, H. Kisch, W. Macyk, W.F. Maier, Appl. Catal. B—Environmental 32 (2001) 215–227.
[18] L.Q. Jing, X.J. Sun, B.F. Xin, B.Q. Wang, W.M. Cai, H.G. Fu, J. Solid State Chem. 177 (2004) 3375–3382.
[19] S.M. Paek, H. Jung, Y.J. Lee, M. Park, S.J. Hwang, J.H. Choy, Chem. Mater. 18 (2006) 1134–1140.
[20] A.H. Yuwono, Y. Zhang, J. Wang, X.H. Zhang, H. Fan, W. Ji, Chem. Mater. 18 (2006) 5876–5889.
[21] H. Kamisaka, T. Adachi, K. Yamashita, J. Chem. Phys. 123 (2005) 084704.
[22] H. Sun, Y. Bai, Y. Cheng, W. Jin, N. Xu, Ind. Eng. Chem. Res. 45 (2006) 4971–4976.
[23] Y.Z. Li, D.S. Hwang, N.H. Lee, S.J. Kim, Chem. Phys. Lett. 404 (2005) 25–29.
[24] W.J. Ren, Z.H. Ai, F.L. Jia, L.Z. Zhang, X.X. Fan, Z.G. Zou, Appl. Catal. B—Environmental 69 (2007) 138–144.
[25] S. Sakthivel, H. Kisch, Angew. Chem. Int. Ed. 42 (2003) 4908–4911.
[26] B.M. Reddy, K.N. Rao, G.K. Reddy, P. Bharali, J. Mol. Catal. A—Chemical 253 (2006) 44–51.
[27] H.X. Wu, T.J. Wang, Y. Jin, Ind. Eng. Chem. Res. 45 (2006) 1337–1342.
[28] M. Yoon, M. Seo, C. Jeong, J.H. Jang, K.S. Jeon, Chem. Mater. 17 (2005) 6069–6079.
[29] Y. Xie, Y.Z. Li, X.J. Zhao, J. Mol. Catal. A—Chemical 277 (2007) 119–126.
[30] Y. Xie, Q.N. Zhao, X.J. Zhao, Y.Z. Li, Catal. Lett. 118 (2007) 231–237.
[31] G.R. Torres, T. Lindgren, J. Lu, C.G. Granqvist, S.E. Lindquist, J. Phys. Chem. B 108 (2004) 5995–6003.
[32] C. Xu, R. Killmeyer, McMahan L. Gray, Shahed U.M. Khan, Appl. Catal. B—Environmental 64 (2006) 312–317.
[33] J.R. Xiao, T.Y. Peng, R. Li, Z.H. Peng, C.H. Yan, J. Solid State Chem. 179 (2006) 1161–1170.