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Effects of carboxylic acids on the microstructure and performance of titania nanocrystals

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Abstract

Effects of carboxylic acids with different molecular structures on the microstructure and performance of nano-crystalline titania have been investigated. It was found that autoclaving $TiCl_4$ aqueous solution in the presence of acetic acid led to the formation of rod-like titania with pure rutile phase, whereas in the case of tartaric acid, citric acid, propylenedi-aminetetraacetic acid or lysine, pure anatase titania with different microstructure was obtained. The change of the phase composition, crystal size and microstructure of titania should be contributed to the coordinating effects of carboxylic acids with titanium ions and their adsorption on the surface of titania nanoparticles. The investigation on photocatalytic activity suggested that rutile titania prepared exhibited a poor photocatalytic activity for the degradation of methyl orange, but a relative high activity for the degradation of rhodamine B. Compared with P25, anatase titania prepared in the presence of citric acid or L-lysine demonstrated high photocatalytic activity for the degradation of methyl orange and rhodamine B.

Keywords: Titania; Hydrothermal process; Carboxylic acid; Chelate; Photocatalytic activity; $TiCl_4$

1. Introduction

In the past decades, new applications for titania have been developed, such as elimination of organic pollutants in gas or liquid phases [1–5], solar cells [6,7] and water splitting for hydrogen generation [8,9]. It has been well accepted that the performance of titania depends on many parameters such as surface area, phase composition, crystallinity, morphology and surface state, etc. Titania with anatase phase generally showed higher activity than rutile in many oxidation reactions [10–13], while the improvement of crystallinity benefited to titania photocatalytic activity [14]. Degussa P25 was an recognized photocatalyst because of its special bicrystalline phase composition [15,16]. Thus, successful control and tailor of the parameters is very important during the synthesis of titania with a high photoactivity.

In general, the titania photocatalyst is synthesized from $TiCl_4$, $TiOSO_4$ and $Ti(OR)_4$, etc., which are very sensitive to moisture. For the controllable synthesis of titania, it is very crucial to control the vigorous hydrolysis and condensation of titanium precursor. In view of the chelating stabilizing effects for transitional metal ions, different chelating agents, including polyol [17], alcamines [17], β-diketone [17], α-hydroxycarboxylic acids [17–19] have been successfully employed in a sol–gel process to prepare titania film, mesoporous titania or monodispersed mixed titanium oxides with fine microstructure. Simultaneously, the influence of chelaing agents on the molecular structure of titanium precursors and the microstructure of titania obtained have also been particularly investigated [20,21]. However, sol–gel processes generally carry out at low temperature. Titania prepared with this method needs to sinter at high temperature to improve crystallinity, which will result in the obvious aggregation and the growth of particles as well as the great decrease of surface hydroxyl groups and surface area. Calcinations at high temperature possibly destroyed the fine structure, too. Previous work has demonstrated that large particle size, low surface hydroxyl groups, small surface area and poor crystallinity are basic factors for lower photocatalytic activity of titania [22].

Comparing with sol–gel process, hydrothermal techniques are considered as one of the most promising approaches because of the high crystallinity of products. Considering the higher tem-

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perature and autoclaving higher pressure in the hydrothermal process, it was necessary to renewedly understand the role of chelating agents in the controllable synthesis of titania nanocrystals. Titania nanocrystals actually have been synthesized, in the past years, by the hydrothermal treatment of amorphous titania gels or $TiCl_4$, $TiOSO_4$, $Ti(OR)_4$ in pure water or organic solvent [23–25]. However, the influence of chelating agents on the performance of titania nanocrystals have been few reported.

In the present work, carboxylic acids such as acetic acid, α-hydroxycarboxylic acids and α-aminocarboxylic acids were used in the hydrothermal process to systematically investigate their effects on the microstructure and property of titania prepared. The work would provide some common information to effectively control and tailor the structural parameters of titania in a strong acidic medium and hydrothermal process.

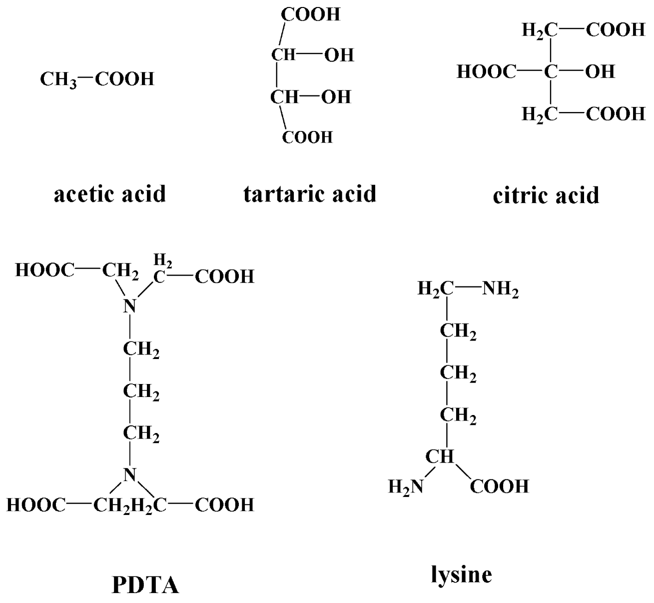
2. Experimental

2.1. Materials

Analytic grade reagents $TiCl_4$, glacial acetic acid, citric acid, β-alanine, ethylene glycol, propylenedi-aminetetraacetic acid (PDTA), methyl orange (MO) and rhodamine B (RhB), tartaric acid and triethanolamine were purchased from Beijing Chemical Reagent Co. L-lysine was obtained from the Institute of Microbiology, CAS. The molecular structures of different carboxyl acids were given in Scheme 1. Commercial TiO_2 (Degussa P25; a mixture of crystalline rutile and anatase phases with the surface area of 50 m^2/g) was from Degussa Co. All the reagents were used as received.

2.2. The preparation of titania

The titanium precursor aqueous solution was prepared by diluting $TiCl_4$ with ice-cooled deionized water and the detailed procedure was described. Under vigorous stirring, about 80 ml of $TiCl_4$ (99%) was slowly added into a glass beaker in an ice-water bath, in which contained ice-cooled deionized water (∼0 °C). After continuously stirring at temperature lower than 5 °C for about 2 h, the solution was leached to remove the indissoluble substances. The concentration of titanium precursor aqueous solution was determined with gravimetric analysis and NH_4OH as precipitator.



Scheme 1. Molecular structures of different carboxylic acids.

Titania powder was synthesized from the titanium precursor aqueous solution by a hydrothermal method as introduced below. 16.77 mmol of carboxylic acids were added into proper amount of titanium precursor aqueous solution obtained, followed by ultrasonication for about 5 min. After magnetic stirring for about one hour at room temperature, a certain amount of deionized water was added to adjust the concentration of titanium to about 0.52 mol/L and the mole ratio of Ti to carboxylic acid was maintained at 1:1. Then, the solution was heated step by step. After maintained at 50 °C for 30 min, 60, 70 and 80 °C for 1 h, respectively, the solution was transferred into an 80 cm^3 teflon-lined stainless steel autoclave. The autoclave was heated to 140 °C and kept for about 18 h. The system was then allowed to cool to room temperature naturally. After the treatment, the powder resulted was washed repeatedly with deionized water, ethanol and at last, with deionized water to remove HCl produced and the acetic acid added. To eliminate the citric acid and L-lysine introduced, repeatedly washing with deionized water, 0.1 mol/L HNO_3 aqueous solution, ethanol and at last deionized water was adopted. Because of the poor dissolution of tartaric acid and PDTA in water and the strong interaction of tartaric acid, PDTA with titanium, 0.1 mol/L NaOH aqueous solution was used to remove tartaric acid and PDTA remained in the titania powder. After washing, the resulted titania powder was dried in air at room temperature.

2.3. Characterization

X-ray diffraction (XRD) was carried out using a Rigaku DMax-RB X-ray diffractometer with the Cu Kα radiation oper-

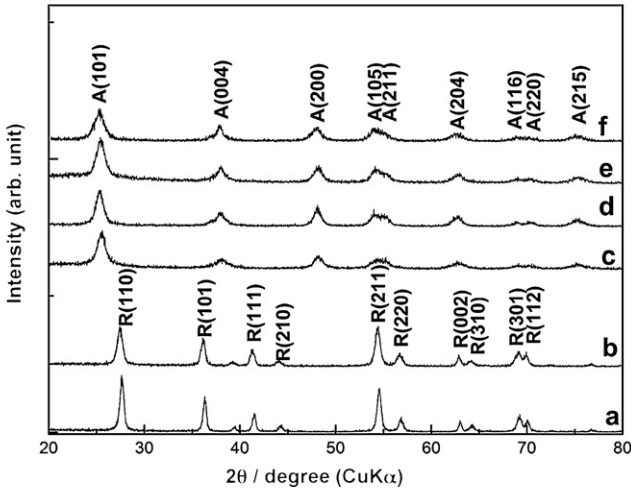


Fig. 1. XRD patterns of titania prepared in the presence of carboxylic acids: (a) no any carboxylic acids; (b) acetic acid; (c) tartaric acid; (d) citric acid; (e) lysine; (f) PDTA.

Table 1
Effects of carboxylic acids on the phase composition and size of titania crystals

Sample carboxylic acid used	Ti-D no any acids	Ti-A acetic acid	Ti-T tartaric acid	Ti-C citric acid	Ti-P PDTA	Ti-L lysine
Phase composition	Rutile	Rutlie	Anatase	Anatase	Anatase	Anatase
Crystal size (nm)	18.4	12.3	9.6	8.7	6.8	7.3

ated at 40 kV and 150 mA. The crystalline size of titania was calculated by means of the Scherrer's equation from the broadening of the (1 0 1) reflections for anatase and the (1 1 0) reflections for rutile. A JEOL JEM-CX200 transmission electron microscope (TEM) operating at 160 kV was used to observe the morphology of the titania obtained. The TEM samples were prepared by ultrasonicating dispersion of corresponding powders in deionized water, and then dropped onto a Formvar coated copper grid. UV–vis spectra of the titania aqueous solutions dispersed by ultrasonication were recorded by UV–vis spectrophotometer (UV-1601, SHIMADZU). The IR spectra of the products were recorded with a Bio-Rad FTS 165 Fourier transform infrared (FTIR) spectroscopy with resolution of 4 cm^{-1} and scan times of 49.

2.4. The measurements of photocatalytic activity

In order to evaluate the photocatalytic behavior of the synthesized titania, MO and RhB were used as molecular probes. Typically, titania powder was added into the aqueous solu-

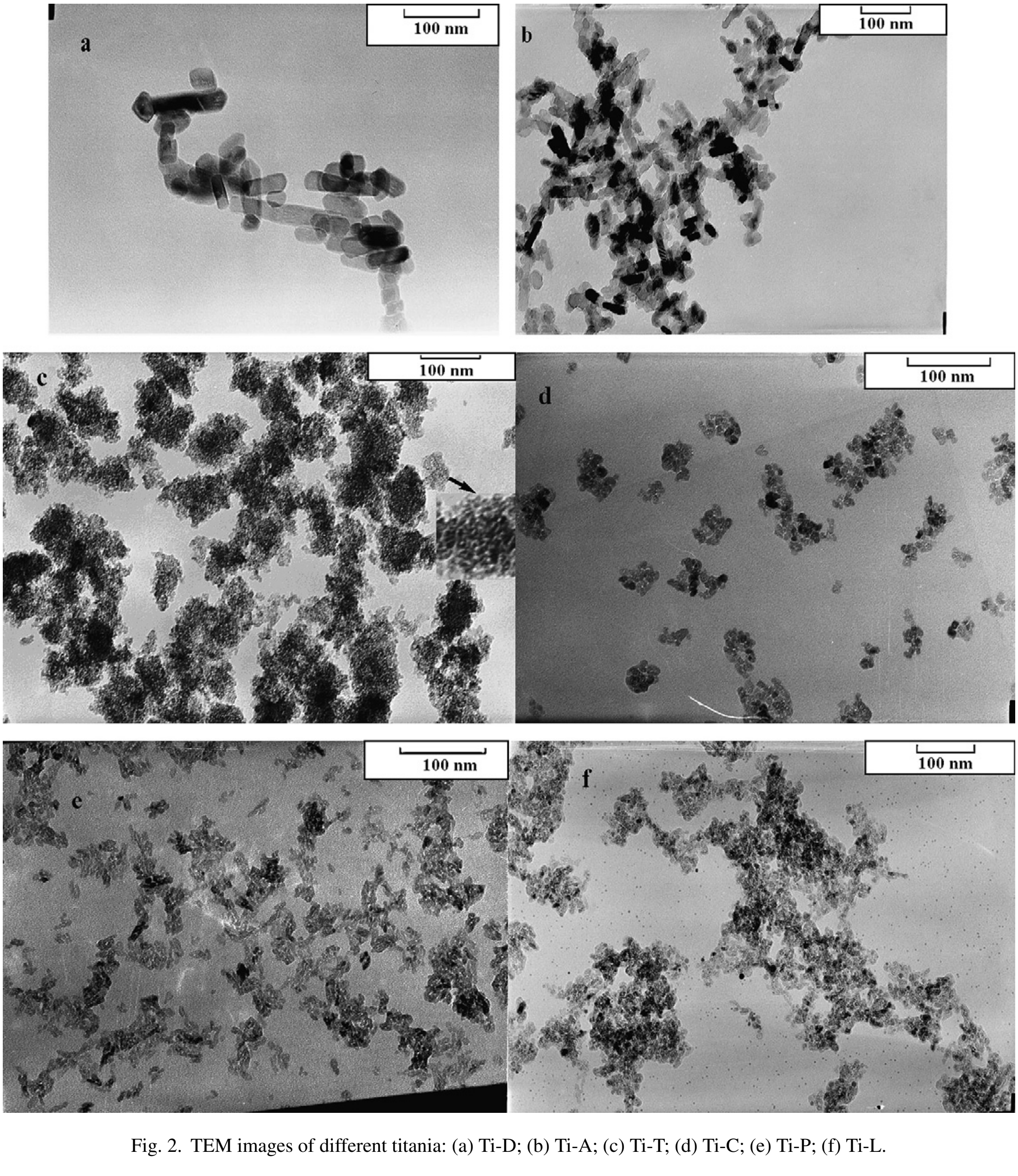


Fig. 2. TEM images of different titania: (a) Ti-D; (b) Ti-A; (c) Ti-T; (d) Ti-C; (e) Ti-P; (f) Ti-L.

tion of MO (4×10^{-5} mol/L) to prepare titania dispersion. The pH value of titania dispersion was adjusted to 3 by 0.1 mol/L hydrochloride aqueous solution. After ultrasonication for about 20 min, the dispersion was stirred and purged with oxygen gas for about 10 min. Then, a photocatalytic reaction was carried out under illumination with wavelength longer than 340 nm. During the photocatalytic reaction, stirring and a stream of oxygen gas was maintained. At a given interval, 5 ml of aliquots were collected and then centrifuged to remove titania particulates. The supernatant was analyzed by recording UV–vis spectra. The experimental procedure of the degradation of RhB was similar to that of MO, except no adjusting pH of the reaction solution. The initial concentration of RhB was 10^{-5} mol/L.

3. Results and discussion

3.1. Phase composition of titania

The sample of titania prepared in the presence of acetic acid, citric acid, PDTA, tartaric acid and lysine were denoted as Ti-A, Ti-T, Ti-C, Ti-P and Ti-L, respectively, and the blank product was wrote as Ti-D. Their XRD patterns were presented in Fig. 1. All the diffraction peaks for the sample Ti-D and Ti-A can be readily indexed to the pure rutile titania (JCPDS, no. 21-1276), while the diffraction peaks for the sample Ti-T, Ti-C, Ti-P and Ti-L could be assigned to pure anatase titania (JCPDS, no. 21-1272). That meant pure rutile was obtained in the absence of carboxylic acid during the preparation. Acetic acid gave little influence on the phase composition of titania. Tartaric acid, citric acid, PDTA and L-lysine resulted in the formation of titania of pure anatase phase. Table 1 showed the crystalline size of different titania calculated by Scherrer's equation. The introduction of acetic acid made the crystal size of rutile titania decreased from 18.4 to 12.3 nm. And the size of anatase titania decreased in the sequence of Ti-T < Ti-C < Ti-L < Ti-P, which suggested that not only the phase composition but also the crystal size of titania was very sensitive to the carboxylic acid used.

3.2. Microstructure of titania

Fig. 2 showed the influence of carboxylic acids on the microstructure of titania. Obviously, in the absence of carboxylic acid, rod-like particles with the diameter of about 19 nm were obtained (Fig. 2a). Acetic acid made the rod diameter decreased to about 13 nm (Fig. 2b). When acetic acid was replaced by α-hydroxycarboxylic or α-aminocarboxylic acids, rod-like structure completely disappeared. Tartaric acid induced porous aggregates with the size of 20–170 nm (Fig. 2c). Citric acid resulted in the formation of aggregates with the size of 15–80 nm (Fig. 2d) and in the case of PDTA and lysine, random aggregation was observed (Fig. 2e and f). In addition, there were well dispersed spherical particles with the mean size of 2–3 nm in Fig. 2f.

3.3. Optical properties of titania

Fig. 3 described the UV–vis absorbance (α) of titania prepared. In Fig. 3a there was a typical absorption band centered at about 310 nm for Ti-D and Ti-A. Compared with Fig. 3a, obvious absorption change occurred in Fig. 3b, possibly induced by the crystalline change from rutile to anatase. Evidently, the absorption of titania in ultraviolet region was sensitive to their phase composition.

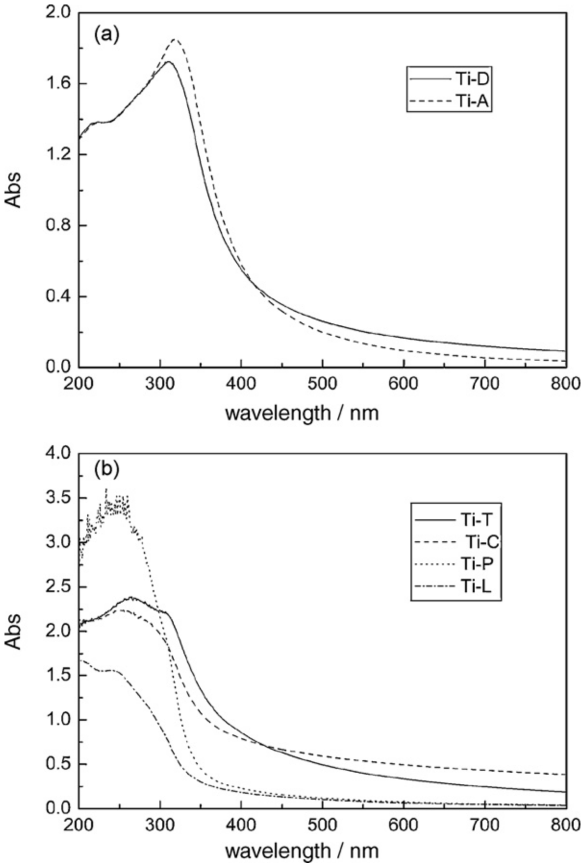


Fig. 3. UV–vis absorption spectra of Ti-D; Ti-A; Ti-T; Ti-C; Ti-P and Ti-L.

The band gap (Eg) of titania was estimated by the plot of $\alpha^{1/2}$ versus photon energy ($h\nu$) [26]. For the sample of Ti-D and Ti-A, the band gaps estimated were around 3.0 eV, coincided with the reported value of bulk rutile (3.0–3.1 eV). The band gap for the sample of Ti-T, Ti-C, Ti-P and Ti-L were 3.14, 3.35, 3.48 and 3.46 eV, respectively. The band gap calculated for Ti-C, Ti-P and Ti-L were slightly larger than the reported value of anatase titania (3.2–3.3 eV), which may be caused by the quantum size effect [27].

3.4. Photocatalytic activity of titania

Titania activities were firstly assessed by the degradation of MO and the corresponding degradation rates were determined by the absorption of MO at about 500 nm. As showed in Table 2, the degradation rates of MO catalyzed by Ti-D, Ti-A, Ti-T, Ti-C, Ti-P, Ti-L and P25 were 2.42, 3.61, 4.67, 9.99, 8.03, 20.32 and 8.53×10^{-3} min^{-1} mol^{-1} L, respectively. Obviously, for the degradation of MO, rutile titania showed very low activity. Anatase titania of Ti-C, Ti-L and Ti-P exhibited higher activity than P25.

Detailed investigating the adsorption properties of various titania demonstrated that Ti-L and Ti-P had excellent adsorption

Table 2
The degradation rate constant and residual amount of MO at irradiation time of 60 and 120 min

	Photocatalysts						
	Ti-D	Ti-A	Ti-T	Ti-C	Ti-P	Ti-L	P25
Initial degradation rate (10^{-3} min^{-1} mol^{-1} L)	2.42	3.61	4.67	9.99	8.03	20.32	8.53
Residual percentage of MO at 60 min	0.901	0.79	0.745	0.356	0.583	0.102	0.443
Residual percentage of MO at 120 min	0.69	0.55	0.459	0.027	0.097		0.125

for MO in acidic media, suggested that for the fast degradation of MO, the adsorption ability of the photocatalyst played an important role. Another factor was special microstructure. For example, Ti-C and P25 had comparative capability for MO adsorption but showed a very different activity. The adsorption capability of Ti-L and Ti-P was similar, whereas the activity of Ti-L was great higher than Ti-P. Conclusively, for the degradation of MO, anatase phase composition, good adsorption property and special microstructure were important factors for the high activity of titania.

In addition to MO, RhB was also used as a model probe to estimate the activity of titania. Although the λ_{max} of RhB shifted during the degradation, the absorbance change at λ_{max} versus irradiation time still could be used to test the photocatalytic activity of titania qualitatively [28,29]. As suggested by Fig. 4, for the degradation of RhB, the activity of the rutile titania was just slower than P25, while anatase titania prepared in the presence of tartaric acid and PDTA (Ti-D and Ti-P) showed very low activity. In contrast, the samples prepared in the presence of citric acid and lysine (Ti-C and Ti-L) could photocatalyze the degradation of RhB as efficiently as P25.

Detailed investigating the adsorption of RhB on various titania concluded that the adsorption capability changed in the order of Ti-C < Ti-D < Ti-A < Ti-T < Ti-L < Ti-P. Obviously, it was not consistent with the activity change of various titania. As indicated by Watanabe et al. [28] and Wu et al. [29], at the initial period of the RhB degradation, the competition between the cleavage of chromophore ring structure and the de-ethylation process of RhB occurred and after the de-ethylation process, the chromophore was further destroyed. The de-ethylation process is a surface-reaction [28,29]. Titania with good adsorptive property would rather benefit the de-ethylation process and thus decrease the cleavage of chromophore ring structure of RhB at the initial period. In a word, for the total degradation of RhB, the adsorptive property of photocatalyst was not so crucial and microstructure of photocatalyst played a more important role.

3.5. Formation mechanism of titania microstructure

In the pure $TiCl_4$ aqueous solution with the concentration higher than 0.40 mol/L, titanium ions mainly exist as six-fold coordinated monomer of $[TiO(OH_2)_5]^{2+}$ and its polynuclear hydrolysis species [30], which was favored the rutile crystallites [31]. Deng et al. [32] indicated that in an aqueous solution with pH of 2, citric acid could tightly chelate titanium ions through deprotonated alcoholic group and dissociated carboxylic groups. Yin [33] concluded that in the mixture aqueous solution of $TiCl_4$ and citric acid, citric acid could interact with $TiCl_4$ or its hydrolysis species. These suggested that α-hydroxycarboxylic or α-aminocarboxylic functional groups would make the citric acid, tartaric acid, PDTA and lysine chelated with titanium octahedrons to form a relatively stable titanium complex, even in strong acidic aqueous solution. Due to the large steric hindrance of carboxylic acidic ligands, the titanium complexes should combine together by sharing equatorial or apical edges, which benefited the formation of anatase crystallites [31,34]. To further clarify the fact, ethylene glycol, triethanolamine and β-alanine were also used during the preparation of titania in our experiments, and rod-like rutile titania was obtained, concluding that in strong acidic media, additives with both carboxylic acidic

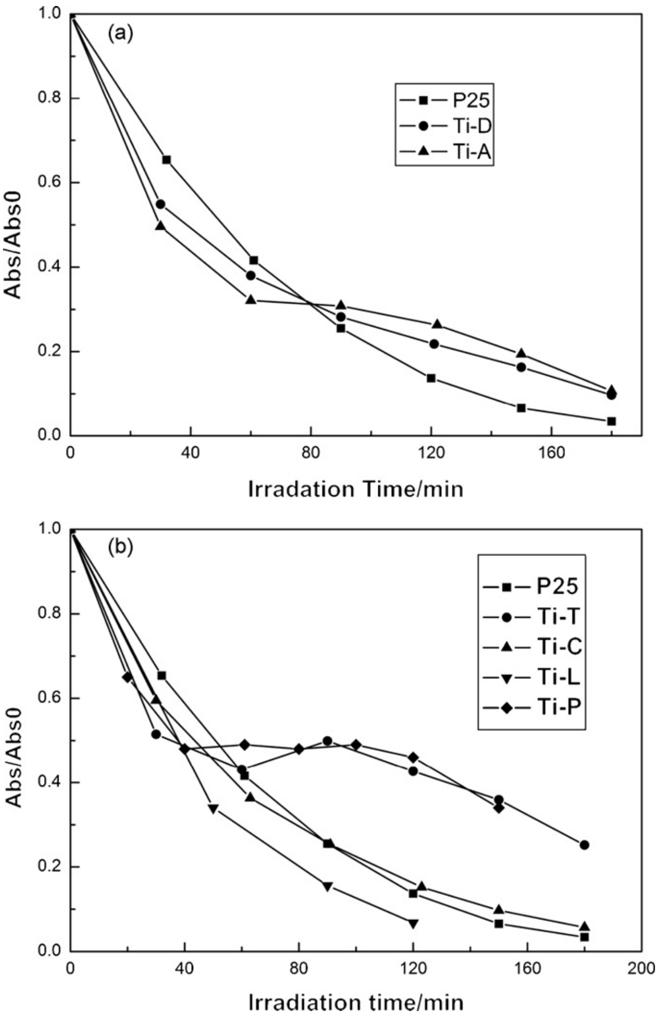


Fig. 4. Photodegradation of RhB in the presence of various titania.

group and α-coordinative group would give an crucial influence on the formation of anatase titania.

As well known if a chemical additive could effectively adsorb on the surface of particles, the growth of particles would be prevented or decreased [35]. During the hydrolysis and condensation of titanium complexes, the ligands of carboxylic acids could be released to the solution and adsorbed on the surface of titania particles freshly formed during the hydrothermal process, thereby the growth of particle was inhibited to some extent, which explained the smaller size of titania particles prepared in the presence of carboxylic acids. The microstructure change of titania might be related to the adsorption of the carboxylic acid on a certain face of titania crystals, however, some in detail are not very clear now and need to be studied further.

4. Conclusion

This work revealed that through carefully selective chelating agents, titania nanocrystals with a different phase composition and crystal size could be synthesized by the hydrothermal process. Coordination group of chelating agents played a key role to the phase composition of final product. The measurement of photocatalytic activity demonstrated that anatase titania prepared in the presence of citric acid or lysine showed an excellent performance for the degradation of MO and RhB. Comparing with adsorption property, microstructure and phase composition was more important for the activity of photocatalysts. Although only pure anatase or pure rutile titania was exclusively obtained in the present work, it was expected that through introduction of proper chelating agents, bicrystalline or tricrystalline titania could be obtained in the future.

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References

[1] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.

[2] I.K. Konstantinau, T.A. Albanis, Appl. Catal. B 42 (2003) 319.

[3] K. Pirkanniemi, M. Sillanpaa, Chemosphere 48 (2002) 1047.

[4] L. Zhang, J.C. Yu, Chem. Commun. (2003) 2078.

[5] C. Burda, Y. Lou, X. Chen, A.C.S. Samia, J. Stout, J.L. Gole, Nano Lett. 3 (2003) 1049.

[6] U. Bach, et al., Nature 395 (1998) 583.

[7] A. Hagfeldt, M. Gräzel, Acc. Chem. Res. 33 (2000) 269.

[8] A. Kasahara, K. Nukumizu, G. Hitoki, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, K. Domen, J. Phys. Chem. A 106 (2002) 6750.

[9] H. Kato, A. Kudo, J. Phys. Chem. B 106 (2002) 5029.

[10] B. Ohtani, Y. Ogawa, S.I. Nishimoto, J. Phys. Chem. B 101 (1997) 3746.

[11] K. Nagaveni, M.S. Hegde, N. Ravishankar, G.N. Subbanna, G. Madras, Langmuir 20 (2004) 2900.

[12] G. Riegel, J.R. Bolton, J. Phys. Chem. 99 (1995) 4215.

[13] T. Sumita, et al., Appl. Surf. Sci. 200 (2002) 21.

[14] K.L. Yeung, A.J. Maira, J. Stolz, E. Hung, N.K.-C. Ho, A.C. We, J. Soria, K.-J. Chao, P.L. Yue, J. Phys. Chem. B 106 (2002) 4608.

[15] D.C. Hurum, K.A. Gray, T. Rajh, M.C. Thurnauer, J. Phys. Chem. B 109 (2005) 977.

[16] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh, M.C. Thurnauer, J. Phys. Chem. B 107 (2003) 4545.

[17] Y. Gao, K. Koumoto, Cryst. Growth Design 5 (2005) 1983, and their references.

[18] D.-W. Lee, S.-K. Ihm, K.-H. Lee, Chem. Mater. 17 (2005) 4461.

[19] (a) P.A. Venz, J.T. Kloprogge, R.L. Frost, Langmuir 16 (2000) 4962;
(b) Z.Y. Zheng, J.B. Pang, K.Y. Qiu, Y. Wei, J. Mater. Chem. 11 (2001) 3367;
(c) K. Inumaru, T. Kasahara, M. Yasui, S. Yamanaka, Chem. Commun. (2005) 2131.

[20] (a) J. Galo, A.A. de, C. Soler-Illis, B. Sanchez, J. Lebeau, Patarin, Chem. Rev. 102 (2002) 4093;
(b) C. Sanchez, G.J. de, A.A. Soler-Illis, F. Ribot, T. Lalot, C.R. Mayer, V. Cabuil, Chem. Mater. 13 (2001) 3061.

[21] (a) U. Schubert, Chem. Mater. 13 (2001) 3487;
(b) V. Torma, N. Hüsing, H. Peterlik, U. Schubert, C. R. Chime 7 (2004) 495;
(c) G. Fornasieri, L. Rozes, S. Le Calve, B. Alonso, D. Massiot, M.N. Rager, M. Evain, K. Boubekeur, C. Sanchez, J. Am. Chem. Soc. 127 (2005) 4869.

[22] A. Fujishima, X. Zhang, C. R. Chimie 9 (2005) 750.

[23] (a) Y.V. Kolen, B.R. ko, M. Churagulov, L. Kumst, C. Mazerolles, Colbeau-Justin, Appl. Catal. B: Environ. 54 (2004) 51;
(b) G. Demazeau, J. Mater. Chem. 9 (1999) 15;
(c) A. Chemseddine, T. Moritz, Eur. J. Inorg. Chem. (1999) 235.

[24] (a) H. Yin, Y. Wada, T. Kitamura, S. Kambe, S. Murasawa, H. Mori, T. Sakata, S. Yanagida, J. Mater. Chem. 11 (2001) 1694;
(b) K. Yanagisawa, J. Ovenstone, J. Phys. Chem. B 103 (1999) 7781;
(c) Y.V. Kolen'ko, A.A. Burukhin, B.R. Churagulov, N.N. Oleynikov, Mater. Lett. 57 (2003) 1124.

[25] S.T. Aruna, S. Tirosh, A. Zaban, J. Mater. Chem. 10 (2000) 2388.

[26] H. Luo, C. Wang, Y. Yan, Chem. Mater. 15 (2003) 3841.

[27] V.F. Stone Jr., R.J. Davis, Chem. Mater. 10 (1998) 1468.

[28] (a) T. Watanabe, T. Takizawa, K. Honda, J. Phys. Chem. 81 (1977) 1845;
(b) T. Inoue, T. Watanabe, A. Fujishima, K. Honda, K. Kohayakawa, J. Electrochem. Soc. 124 (1977) 719.

[29] T. Wu, G. Liu, J. Zhao, H. Hidaka, N. Serpone, J. Phys. Chem. B 102 (1998) 5845.

[30] (a) P. Comba, A. Merbach, Inorg. Chem. 26 (1987) 1315;
(b) J.D. Ellis, G.A.K. Tompson, A.G. Sykes, Inorg. Chem. 15 (1976) 3172.

[31] M. Henry, J.P. Jolivert, J. Livage, in: R. Reisfeld, C.K. Jorgensen (Eds.), Structure and Bonding, vol. 77, Springer-Verlag, Berlin, 1992, p. 155.

[32] Y.-F. Deng, Z.-H. Zhou, H.-L. Wan, Inorg. Chem. 43 (2004) 6266.

[33] H. Yin, Y. Wada, T. Kitamura, T. Sumida, Y. Hasegawa, S. Yanagida, J. Mater. Chem. 12 (2002) 378.

[34] Y. Li, N.-H. Lee, D.-S. Hwang, J.-S. Song, E.G. Lee, S.-J. Kim, Langmuir 20 (2004) 10838.

[35] Y. Jun, M.F. Casula, J.-H. Sim, S.Y. Kim, J. Cheon, A.P. Alivisatos, J. Am. Chem. Soc. 125 (2003) 15981.