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New insights into anatase crystallization behavior in ionothermal synthesis of nanostructured TiO_2

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Abstract The anatase crystallization behaviors in ionothermal synthesis (sol–gel method containing ionic liquid) of nanostructured TiO_2 were studied in this paper. It was found that the specific physical chemical characteristics of the water/ionic liquid mixture caused the formation path and crystallinity of anatase TiO_2 to depend on the H_2O/titanium dioxide precursor (titanium tetraisopropoxide, TIP) molar ratio. Hydroxylated titanium compound was a key intermediate for forming anatase TiO_2. It could be directly formed from hydrolysis of titanium dioxide precursor or ionic liquid-induced water dissolution of the condensation product. X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) data indicated that a higher hydroxyl group ratio content of hydroxylated titanium compound was obtained at medium H_2O/TIP molar ratio and from the system containing hydrophilic ionic liquid, such as 1-butyl-3-methylimidazolium tetrafluoroborate ($[BuMIm]^+[BF_4]^-$). The self organization ability of ionic liquid drove anatase crystallization through dehydration of the Ti–OH group of hydroxylated titanium compound in the thermal annealing process. As for the particle size of TiO_2, TEM results indicated smaller particle size of TiO_2 was obtained at medium H_2O/TIP molar ratio case.

Introduction

Titanium dioxide (TiO_2) is a semiconductor oxide. It has two main crystalline forms, i.e., anatase and rutile. Of these two crystalline forms, anatase TiO_2 is considered the more important material. It is widely used as an environmental photocatalyst and active electrode for dye-sensitized solar cell. TiO_2 can be synthesized from the hydrolysis and condensation of titanium dioxide precursor by sol–gel method [1]. However the initial reaction product of sol–gel reaction is generally amorphous TiO_2. For getting anatase TiO_2 from amorphous product, high-temperature calcination or hydrothermal treatment is required [2, 3].

Over the past two decades, room temperature ionic liquid has received extensive attention for both academic research and industrial investigations. Owing to its pronounced self-organization ability, ionic liquid has been used by many researchers as green reaction media for the sol–gel synthesis of highly organized nanostructural anatase TiO_2 at ambient condition [4]. For example, Zhou and Antonietti [5] synthesized TiO_2 nanocrystals by addition of $TiCl_4$/ionic liquid mixture to water. Nakashima and Kimizuka [6] reported the preparation of hollow TiO_2 microspheres using an interfacial ionothermal system with a toluene solution of titanium tetrabutoxide. Dionysiou and coworkers [7, 8] systematically studied the preparation and characterization of mesoporous TiO_2 using an ionothermal system with aqueous solution of titanium tetraisopropoxide.

In their analysis of the crystallization behavior of synthesizing anatase TiO_2 in an ionothermal system, Zhou and

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Antonietti suggested that the titanium dioxide precursor was hydrolyzed quickly into an amorphous TiO_2 sol within an ionic liquid at the beginning of the reaction. The amorphous TiO_2 sol was gradually ripened into the well defined TiO_2 nanocrystals as the reaction time proceeded. Ionic liquid can favor formation of TiO_2 nanocrystal via specific sites [5]. Dionysiou and coworkers pointed out that rather than the amount of water, the interaction between water and anion part of the ionic liquid was the essential factor in forming anatase TiO_2 [7]. They also found that higher crystallinity anatase TiO_2 was prepared from the system containing 1-butyl-3-methylimidazolium hexafluorophosphate ($[BuMIm]^+[PF_6]^-$) [8]. The capping effect and particle aggregation inhibitor of $[BuMIm]^+[PF_6]^-$ were also proposed by this group in another study [9]. However, Liu et al. [10] thought that ionic liquid could enhance the condensation and anatase crystallization rate in their study on the preparation of nanostructure anatase TiO_2 monoliths by using $[BuMIm]^+[BF_4]^-$.

From these discussions, it can be seen that the factors affecting anatase crystallization behavior in ionothermal synthesis of anatase TiO_2 mentioned by previous authors are diverse and undecided, especially regarding the type of ionic liquid and the role of water. Apparently, to achieve a better understanding of crystallization behavior in the ionothermal synthesis of anatase TiO_2, two things must be clearly identified: (1) the structural chemistry of each sol–gel reaction stage (hydrolysis, condensation, and annealing) and (2) what is the role of ionic liquid in each stage. In recent years, many new findings about the specific physical–chemical characteristics of water/ionic liquid mixture system had been demonstrated in the literature [11]. Hence, based upon these new findings, especially for the interaction between water and ionic liquid, new insights into the anatase crystallization behavior in ionothermal synthesis of nanostructured TiO_2 are presented in this paper.

Experimental

Synthesis of TiO_2 samples

TiO_2 samples were synthesized via a sol–gel reaction with and without ionic liquid by precursors of titanium tetraisopropoxide (TIP, Aldrich). TIP was dissolved in a mixture of isopropanol (IPA, J. T. Barker) and ionic liquids (IL) (1-butyl-3-methylimidazolium hexafluorophosphate, $[BuMim]^+[PF_6]^-$ or 1-butyl-3-methylimidazolium tetrafluoroborate $[BuMIm]^+[BF_4]^-$) and stirring in a 20 mL narrow neck glass bottle. Water was then added into the solution at room temperature. The reaction was continued for 30 min under stirring. The molar ratio of H_2O/TIP was varied from 2 to 100. The IPA/TIP molar ratio was fixed at 30, and the IL/TIP molar ratio was fixed at 3. The powder products of the sol–gel reaction were collected by filtration and washed with de-ionized water, then dried, and annealed at 100 °C for 2 h. Acetonitrile was used to remove any IL residues if necessary. The final product was a white powder.

The temperature and reaction time effect on anatase crystallinity at a constant reactant mole ratio were also examined. Three reaction temperatures were studied in these experiments: 70, 90, and 120 °C. TIP was dissolved in a mixture of IPA and IL ($[BuMim]^+[PF_6]^-$ or $[BuMIm]^+[BF_4]^-$) with stirring. Water was then slowly added to the mixture. The reaction was continued for a specific duration. The final powder was washed with water and acetonitrile, then freeze dried and subjected to thermal annealing.

Characterization methods

The crystalline phase was investigated by using the X-ray diffraction method (Rigaku D-Max) using CuKα radiation ($\lambda = 0.1540$ nm). The scanning speed was 2° $\min^{-1}$, and the scanning range was from 20° to 60°. The major anatase (101) peak at 25.4° was analyzed. The average crystal sizes were calculated from the most intense diffraction peak (101) using the Scherrer formula, where λ is the X-ray wavelength employed, θ is the diffraction angle of the (101) peak, and β is defined as the half-width after subtracting for the instrumental broadening. The TiO_2 sample crystallinity was estimated by comparing the integrated intensity of the anatase peak of the (101) planes with that of a sample annealed at 600 °C, as shown in Fig. 1D. The latter annealed sample was assumed to be wholly crystalline. The chemical structure bonding of the TiO_2 sample was studied using X-ray photoelectron spectroscopy (XPS) measurements on the PHI 1600/3057 (Physical Electronics) with an MgKα source. The weight loss of TiO_2 sample was analyzed in an air ambiance by TGA measurements using Pyris Diamond TG/DTA supplied by Perkin-Elmer Instruments. The heating rate was 20 °C $\min^{-1}$, and the scanning range was from 30 to 1000 °C. The particle size of the sample was examined by transmission electron microscopy (TEM) using a JOEL JEM-2010 instrument with an acceleration voltage of 200 keV.

Results and discussion

Substantial effect of ionic liquid on anatase crystallization

Figure 1 shows the representative XRD curves of samples synthesized by the sol–gel reaction system containing

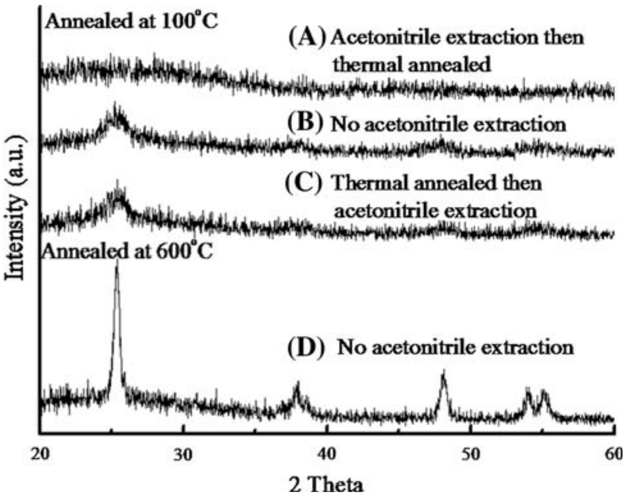

Fig. 1 The XRD curves of sample prepared with the same sol–gel reaction condition but different post-treatment processes. Sample A was first treated by acetonitrile and then annealed at 100 °C for 2 h. Sample B was annealed at 100 °C for 2 h. Sample C was annealed at 100 °C for 2 h and then treated by acetonitrile. Sample D was annealed at 600 °C for 2 h. The molar ratios of IPA/TIP, IL/TIP, and H_2O/TIP were 30, 3, and 100, respectively

$[BuMim]^+[PF_6]^-$ with same preparation condition but different post-treatment process. The molar ratios of H_2O/TIP, IPA/TIP, and IL/TIP were 100, 30, and 3, respectively. The reaction time was 30 min at room temperature. The powder product was collected by filtration, and then annealed at 100 °C for 2 h before or after removing ionic liquid by acetonitrile. Figure 1A shows that the anatase peak was not found in the XRD curve when the synthesized sample was first treated with acetonitrile before annealing. Figure 1B shows the XRD curve for the synthesized sample annealed at 100 °C for 2 h. Figure 1C shows the XRD curve for the sample annealed at 100 °C for 2 h and then treated by acetonitrile. From a comparison of the results of Fig. 1B, C, it can be seen that the acetonitrile treatment process had no effect on anatase peak intensity for the annealed samples. The critical effect of ionic liquid on anatase crystallization of TiO_2 in ionothermal synthesis system can be found from these results.

Table 1 Anatase crystallinity of thermally annealed TiO_2 samples prepared with different ionic liquids and H_2O/TIP molar ratios

Ionic liquid type	H_2O/TIP molar ratio	Crystallinity (%)	Crystal size (nm)
Without IL	2	No anatase peak	–
	5	No anatase peak	–
	10	No anatase peak	–
	100	No anatase peak	–
$[BuMIm]^+[PF_6]^-$	2	No anatase peak	–
	5	42.7	4.17
	10	36.7	4.10
	100	18.6	3.42
$[BuMIm]^+[BF_4]^-$	2	No anatase peak	–
	5	57.0	4.12
	10	51.8	4.02
	100	21.0	4.06

The molar ratios for IPA/TIP and IL/TIP were 30 and 3, respectively. The thermal annealing condition was 100 °C for 2 h

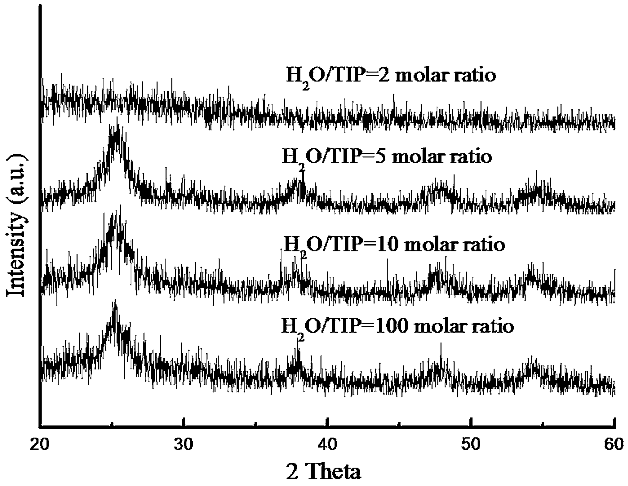

Fig. 2 The XRD curves of the annealed sample prepared from sol gel reaction system containing $[BuMIm]^+[BF_4]^-$for different H_2O/TIP molar ratios. The molar ratios of IPA/TIP and IL/TIP were 30 and 3, respectively. The reaction time was 30 min at room temperature. The thermal annealing condition was 100 °C for 2 h

Effect of H_2O/TIP molar ratio on anatase crystallinity

The anatase crystallinity of TiO_2 samples prepared by the sol–gel process with and without ionic liquid at different H_2O/TIP molar ratios is listed in Table 1. The anatase crystallinity was measured from XRD data. The thermal annealing condition was 100 °C for 2 h. Figure 2 shows the representative XRD curve of an annealed sample prepared from the system containing $[BuMIm]^+[BF_4]^-$. From Table 1, it can be seen that no significant anatase peak was observed for a system without ionic liquid. It was also found that no significant anatase peak was observed at a very low H_2O/TIP molar ratio. However, the highest anatase crystallinity was obtained at medium H_2O/TIP molar ratio (about 5 in this experiment), especially for the system containing $[BuMIm]^+[BF_4]^-$. In comparison with the medium H_2O/TIP molar ratio case, anatase crystallinity was relatively lower in the high H_2O/TIP molar ratio case. These results evidently demonstrated that the H_2O/TIP molar ratio plays an important role in the anatase crystallization in an ionothermal synthesis system.

It has been reported that a water/ionic liquid mixture system is not considered as a homogeneous system and can be regarded as a nanostructured system [12]. Liu et al. and Zhu et al. found that most of ionic liquids were self-associated as tight ion pair in system rich in ionic liquid. On the other hand, most of water molecules were also self-associated in water-rich system. Besides these two extreme cases, ionic liquids are hydrogen-bonded to water molecules [11, 12]. We thought that this specific characteristic of a water/ionic liquid system might make the anatase crystallization behavior dependent on the H_2O/TIP molar ratio in our ionothermal synthesis system.

In general, the initial reaction products of a conventional sol–gel reaction are amorphous mixtures of hydrolysis or/and condensation product. A higher proportion of condensed product with a polymeric Ti–O–Ti chain structure could be formed at a high H_2O/TIP molar ratio [13]. Prior to the investigation of the anatase formation and its crystallinity at high H_2O/TIP molar ratio in our ionothermal synthesis system, we should note our previous study on the hydrothermal analogy role of ionic liquid for post-transforming amorphous TiO_2 to anatase TiO_2 at ambient condition [14]. We found that the coexistence of water and ionic liquid is a critical factor in anatase formation. Ionic liquid actually plays an important role in driving surface crystallization of amorphous TiO_2 to anatase TiO_2 by retaining a suitable amount of water through a dissolution–crystallization mechanism. Further a higher anatase crystallinity can be obtained using a hydrophilic ionic liquid such as $[BuMIm]^+[BF_4]^-$. In this work, the same role of ionic liquid is proposed at high H_2O/TIP molar ratio (about 100 in this experiment). Initially, the sol–gel reaction products are amorphous condensation products, and anatase crystallization could be resulted from the hydrothermal analogy effect of the ionic liquid. In other words, water dissolution of condensation product to form hydroxylated titanium compound was a necessary step before anatase crystallization can occur. The remaining water and ionic liquid around the amorphous condensation product were critical components in formation of hydroxylated titanium compound. However some different formation features appeared in the medium H_2O/TIP molar ratio. Most of the hydroxylated titanium compound was directly formed from initial hydrolysis reaction [15]. Ionic liquid near hydroxylated titanium compound was also acted as a steric stabilizer. After the formation of hydroxylated titanium compound, the self-organization ability of the ionic liquid would drive anatase crystallization through the dehydration of the Ti–OH group in the hydroxylated titanium compound via the following thermal annealing process [16].

Note that the water-inducing dissolution process in the condensation product is a kinetic control process. A sufficient annealing time and annealing temperature are required to obtain suitable water-inducing dissolution. Hence, lower anatase crystallinity was expected at high H_2O/TIP molar ratio for the same thermal annealing condition. A higher temperature and longer annealing time are required to obtain a higher anatase crystallinity, as shown in Table 2. The results in Table 2 also demonstrate that a higher anatase TiO_2 crystallinity was gained for the reaction system containing $[BuMIm]^+[BF_4]^-$. The result that no anatase peak was observed in the very low H_2O/TIP molar ratio case could be because most of the ionic liquids were self-associated as separated and tight ion pairs. An incomplete hydrolysis reaction could be another reason.

Structure characterization of hydroxylated titanium compound

As discussed in the section above, hydroxylated titanium compound was a critical intermediate for anatase crystallization in our ionothermal synthesis system. This can

Table 2 Anatase crystallinity of annealed TiO_2 samples prepared with different temperatures and times

Temperature (°C)	Time (min)	$[BuMIm]^+[PF_6]^-$		$[BuMIm]^+[BF_4]^-$	
		Crytsallinity (%)	Crystal size (nm)	Crytsallinity (%)	Crystal size (nm)
70	30	Amorphous	–	4.8	2.12
	60	4.8	1.38	22.8	2.99
	120	7.3	1.9	28.3	4.0
	240	34.3	3.98	60.8	4.72
90	30	Amorphous	–	24.1	3.49
	60	15.6	4.02	38.0	3.67
	120	32.5	4.73	41.0	3.93
	240	39.8	4.65	63.8	4.8
120	30	30.7	3.5	53.6	4.37
	60	54.0	4.02	59.0	4.9
	120	59.0	4.1	61.4	4.82
	240	60.3	4.32	71.1	5.71

The molar ratios of H_2O/TIP, IPA/TIP and IL/TIP were 100, 30, and 3 respectively be proved by the following XPS and TGA data. For a long time, XPS has been used to examine the structural composition of TiO_2 [17]. The bonding energy of Ti and O was measured in XPS analysis of TiO_2 and the change of the bond type could be characterized by observing the shift in bonding energy. The O1s regions are fitted into three peaks; the main peak is attributed to the Ti–O of TiO_2 and one of the minor two peaks, located at 531.1 eV, is assigned to the hydroxyl group of titanium compound. The other minor peak belongs to the adsorbed water [18]. Figure 3 shows the representative fitting results of the XPS curves of an unannealed TiO_2 sample prepared from the system containing $[BuMIm]^+[BF_4]^-$ at different H_2O/TIP molar ratios. The fitting data of XPS curves for different unannealed TiO_2 samples are shown in Table 3. The results shown in Table 3 indicate that a higher hydroxyl group ratio was obtained at medium H_2O/TIP molar ratio case. Additionally, compared to the TiO_2 samples prepared from the system containing $[BuMIm]^+[PF_6]^-$, the TiO_2 sample prepared from the system containing $[BuMIm]^+[BF_4]^-$ had a higher hydroxyl group ratio. This indicates that the water dissolution effect could be more effective for the system containing $[BuMIm]^+[BF_4]^-$.

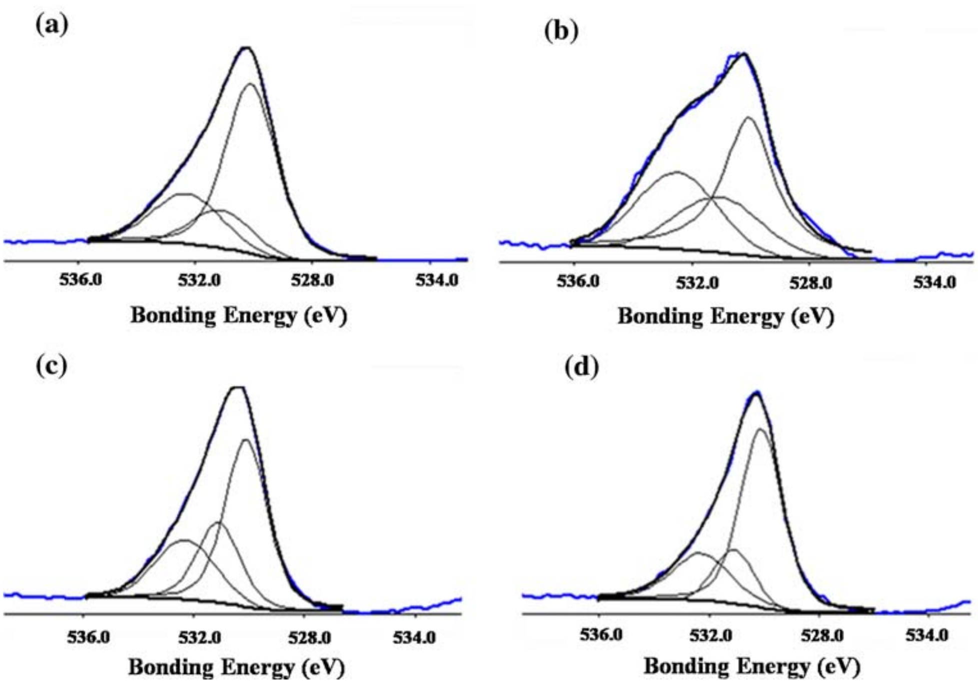

Fig. 3 The representative fitting results of the XPS curves of unannealed TiO_2 samples prepared from sol gel reaction system containing 3 mole $[BuMIm]^+[BF_4]^-$ with different H_2O/TIP molar ratios. The molar ratios of IPA/TIP and $[BuMIm]^+[BF_4]^-$/TIP were 30 and 3, respectively. The reaction time was 30 min at room temperature. **a** $H_2O/TIP = 2$ molar ratio, **b** $H_2O/TIP = 5$ molar ratio, **c** $H_2O/TIP = 10$ molar ratio, **d** $H_2O/TIP = 100$ molar ratio

Table 3 The fitting results from XPS curves of different TiO_2 samples prepared from sol–gel reaction system containing $[BuMIm]^+[PF_6]^-$ or $[BuMIm]^+ [BF_4]^-$ at different H_2O/TIP molar ratios

Ionic liquid type	H_2O/TIP molar ratio	O1s (Ti–O) area ratio (%)	O1s (Ti–O) FWHM (eV)	O1s (OH^-) area ratio (%)	O1s (OH^-) FWHM (eV)
Without IL	2	82.6	1.9	17.4	1.7
	5	75.8	3.20	24.2	2.50
	10	78.1	1.64	21.9	2.03
	100	80.7	2.17	19.3	2.01
$[BuMIm]^+[PF_6]^-$	2	81.5	1.65	18.5	1.88
	5	66.8	1.81	33.2	1.82
	10	72.3	2.62	27.7	2.0
	100	78.9	2.01	21.1	1.99
$[BuMIm]^+[BF_4]^-$	2	77.0	2.46	23.0	2.05
	5	62.9	3.4	37.1	2.01
	10	67.0	1.45	33.0	2.42
	100	77.2	1.73	22.8	1.81

The molar ratios for IPA/TIP and IL/TIP were 30 and 3, respectively

The TGA results for TiO_2 samples prepared at different H_2O/TIP molar ratio are shown in Table 4. Figure 4 shows the representative TGA curves obtained from the TiO_2 samples prepared from the system containing $[BuMIm]^+[BF_4]^-$. In Fig. 4, the weight loss below 120 °C was due to adsorbed water. The weight loss at higher temperatures (>120 °C) resulted from thermal condensation of the surface hydroxyl group of hydroxylated titanium compound [19], as determined from the weight difference at 120 and 600 °C. The result having the higher amount of dehydroxylation of OH group, as shown in Table 4, agrees with the higher content of hydroxylated titanium compound found in the XPS data shown in Table 3.

Table 4 The TGA results of different TiO_2 samples prepared from sol–gel reaction system containing $[BuMIm]^+[BF_4]^-$ with different H_2O/TIP molar ratios

Ionic liquid type	H_2O/TIP molar ratio	Weight loss of adsorbed water (%)	Weight loss for dehydroxylation of bonded OH group (%)
Without IL	2	3.6	7.9
	5	10.6	11.8
	10	5.9	10.0
	100	6.1	7.1
$[BuMIm]^+[PF_6]^-$	2	5.8	6.5
	5	12.5	12.5
	10	6.2	11.9
	100	5.4	9.2
$[BuMIm]^+[BF_4]^-$	2	4.2	5.5
	5	7.2	14.2
	10	6.5	12
	100	4.5	11.6

The molar ratios for IPA/TIP and IL/TIP were 30 and 3, respectively

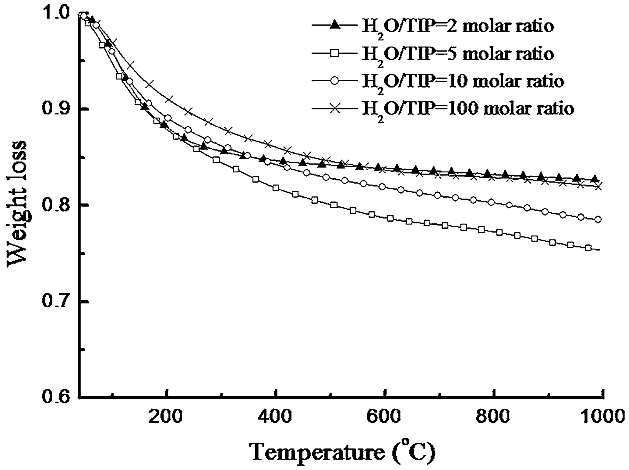

Fig. 4 The TGA results of TiO_2 samples containing $[BuMIm]^+[BF_4]^-$ prepared at different H_2O/TIP molar ratios (The molar ratios of IPA/TIP and $[BuMIm]^+[BF_4]^-$/TIP were 30 and 3, respectively. The reaction time was 30 min at room temperature)

TEM study of thermal annealed TiO_2 sample

As with the anatase crystallinity, particle size is also an important property for environmental photocatalyst and dye-sensitized solar cell application. TEM observations of each thermally annealed TiO_2 samples are presented in Fig. 5. As shown in Fig. 5a-1, it can be seen that the particle size of a TiO_2 sample prepared from the system containing no ionic liquid was about 30 nm at medium H_2O/TIP molar ratio. However, a larger particle size of about 100 nm occurred at higher H_2O/TIP molar ratio, as shown in Fig. 5a-2. On the other hand, Fig. 5b-1, c-1 shows that the particle sizes of thermally annealed TiO_2 sample containing $[BuMIm]^+[BF_4]^-$ and $[BuMIm]^+[PF_6]^-$ were about 20 and 25 nm, respectively, at medium H_2O/TIP molar ratio. The TiO_2 particle size was also slightly increased to 30 nm at higher H_2O/TIP molar ratio, as shown in Fig. 5b-2, c-2. These results show a small TiO_2 particle size occurred in the system containing ionic liquid, indicating the steric control roles of ionic liquid.

Conclusions

Experimental results demonstrate that the anatase crystallization behavior in ionothermal synthesis of nanostructured TiO_2 was related to the H_2O/TIP molar ratio. The anatase crystallization induced from ionic liquid was not found at a very low H_2O/TIP molar ratio. This could be because most of the ionic liquid self-associated as separated tight ion pair. At other H_2O/TIP molar ratios, the hydroxylated titanium compound was a critical intermediate for anatase crystallization. Hydroxylated titanium compound can be directly formed from the hydrolysis of titanium dioxide precursor at medium H_2O/TIP molar ratio. However this hydroxylated titanium compound could from water dissolution of the amorphous condensation product at higher H_2O/TIP molar ratios. In this case, ionic liquid was acted as water adsorption agent. Ionic liquid also acted as a steric stabilizer of the hydroxylated titanium compound after its formation. XPS and TGA data indicated that samples having a higher content of hydroxylated titanium was formed at medium H_2O/TIP mole ratio and for the reaction system containing $[BuMIm]^+[BF_4]^-$. The self-organization ability of

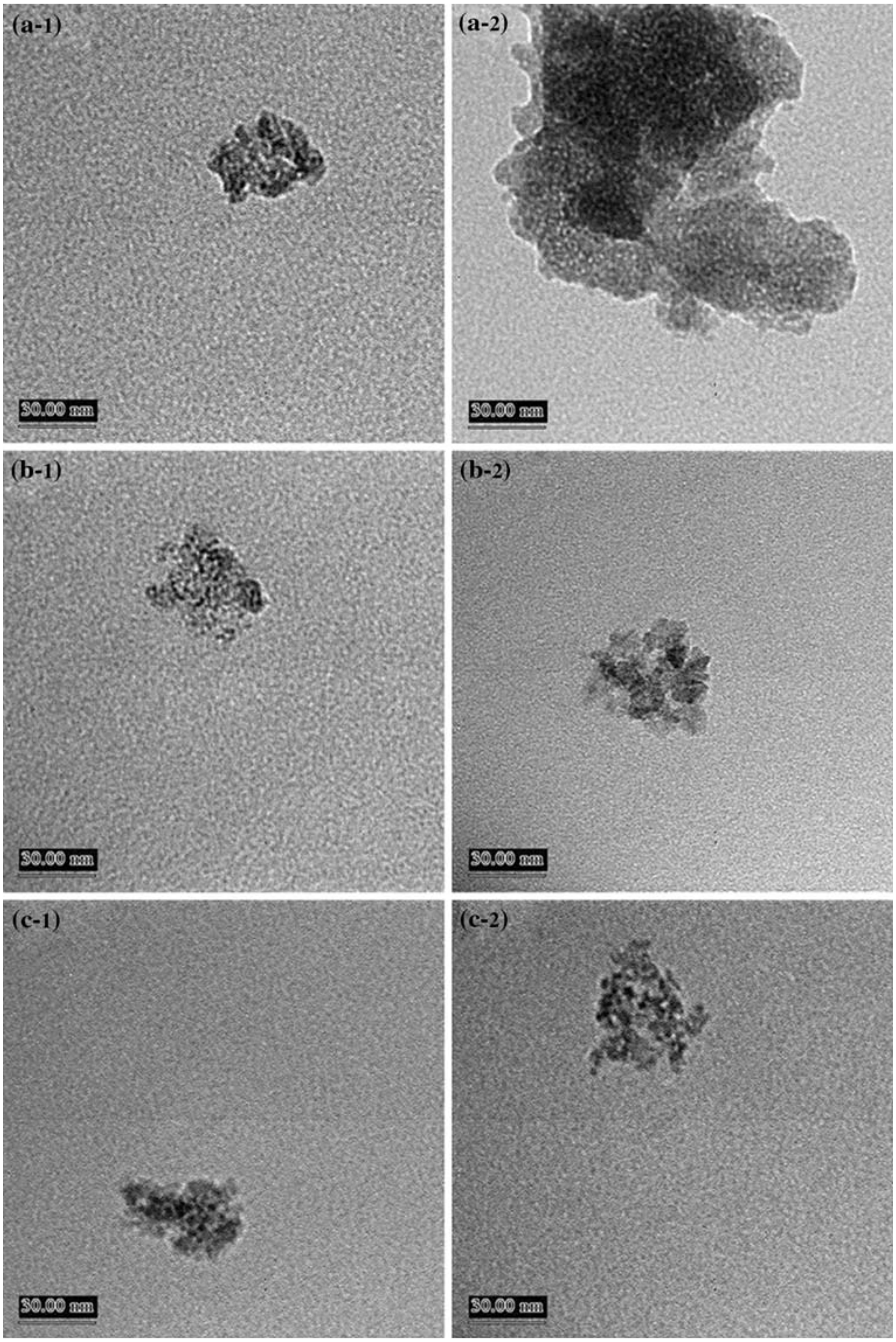

Fig. 5 TEM images of TiO_2 powders prepared from sol gel reaction systems **a-1** and **a-2** containing no ionic liquid, **b-1** and **b-2** containing $[BuMIm]^+[PF_6]^-$, and **c-1** and **c-2**: containing $[BuMIm]^+[BF_4]^-$. The molar ratios of H_2O/TIP were 5 (1) and 100 (2), respectively

ionic liquid drives the formation of the anatase phase TiO_2 through dehydration of the hydroxyl group in the hydroxylated titanium compound in the following thermal annealing process. TEM results indicated that a smaller particle size was obtained at medium H_2O/TIP molar ratio.

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