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# Diverse effects of microwave heating on anatase crystallization in ionothermal synthesis of nanostructured $TiO_2$

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**Abstract** This article examines anatase crystallization in the ionothermal synthesis [sol gel method in the presence of ionic liquid (IL)] of nanostructured $TiO_2$ under microwave (MW) irradiation. MW heating can lead to rapid temperature increase of chemical reactions. In this study, we found that rapid temperature increasing effects on anatase crystallization were diverse and dependent on initial water concentration, MW irradiation time, and IL concentration. The results indicated that higher anatase crystallinity was obtained at high water amount irrespective of IL concentration. However, at lower water amounts, higher anatase crystallinity occurred only when MW heating was applied after the mixtures reacted for certain duration, especially at lower initial temperature and at a specific IL concentration. Different MW heating effects on the hydrolysis–condensation reaction and the post-treatment stage under MW/IL conditions can explain this diversity. Heating characteristics of IL/water mixtures under MW irradiation were also discussed.

## Introduction

Microwave (MW) heating has been widely used in organic synthesis for many years [1]. The benefits of MW heating are high temperature rising in a short time and high reaction product homogeneity. In material chemistry, MW heating is also used for preparation of inorganic crystalline material including titanium dioxide ($TiO_2$) [2]. Most studies focused on the MW heating treatment of $TiO_2$ sols or $TiO_2$ products. MW irradiation of $TiO_2$ sols or completely amorphous $TiO_2$ samples can obtain rapid crystallization and higher anatase crystallinity of $TiO_2$ [3, 4]. Hydrothermal crystallization of amorphous $TiO_2$ can be conducted under MW irradiation and can also get higher anatase crystallinity in a shorter time [5].

Over the past two decades, ionic liquid (IL) has received significant attention in sol gel synthesis of inorganic crystalline nanomaterials due to its low melting point (below 100 °C) and negligible vapor pressure at elevated temperature [6, 7]. When IL is used as reaction medium in inorganic crystalline nanomaterial synthesis, it can serve as template agent for porous inorganic nanomaterials. Besides, it is also a steric stabilizer and crystallization promoter for

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the formed nanomaterials [8–12]. IL is a MW absorber [13]. In recent years, MW heating coupled with IL (MW/IL) was used to produce inorganic crystalline materials at ambient condition [14]. Combining structure-ordering ability of IL and high heating rate of MW heating, this method became a new and fast route for producing zeolite [15], $TiO_2$ [16], and other inorganic materials [17]. In the last two studies, the conventional ionothermal synthesis was run to produce reaction products, which were post-treated using MW heating.

A typical sol gel preparation of anatase crystalline $TiO_2$ includes a hydrolysis–condensation stage and a thermal heating treatment stage. Unlike conventional thermal heating, when MW irradiation heats a reaction system, a faster temperature increase can occur in a short time. This rapid temperature increase can affect the condensation and thermal heating treatment stages. In this study, the effect of MW irradiation on hydrolysis–condensation stages was also investigated. Three modes with different MW irradiation cycles were conducted and the effects on anatase crystallization characteristics of $TiO_2$ were explored. The multiple roles of IL in anatase crystallization were also discussed.

## Experimental

### MW synthesis of $TiO_2$ by the sol gel method containing IL

$TiO_2$ was synthesized using a sol gel reaction with de-ionized water, pre-dissolved titanium tetraisopropoxide (TIP) (Aldrich) in isopropanol (IPA) (J. T. Barker) and IL. The IL was hydrophilic 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]^+[BF_4]^-$)(Merck). Three different MW irradiation modes were examined. In the F mode, MW irradiation was conducted for the full reaction cycle with an irradiation time of 30 min. In the L mode, the reactant solution was mixed and stirred for 10 min at 4 °C and then MW irradiated for 20 min. In the S mode, the reactant solution was mixed and stirred for 10 min at room temperature and then MW irradiated for 20 min. In these modes, the molar ratio of $H_2O$/TIP was 5 and 100, respectively. The IPA/TIP molar ratio was fixed at 3, and the IL/TIP molar ratio was varied from 0 to 2.

In conducting the sol gel reactions, de-ionized water was slowly added into a constantly stirred mixture of TIP, IPA, and IL. The addition of water was controlled at a flow rate of 20 mL/min, except at five molar ratios of $H_2O$/TIP. The entire reaction time typically was 30 min. The reaction product of the sol gel reaction was collected by filtration of the solution through a PTFE membrane with pore size of 0.2 μm. The precipitate was washed with 75 mL of de-ionized water and then freeze dried (FTS system) at −50 °C under a 0.05 torr vacuum for 2 h. The final product was a white powder.

The MW device used for sample preparation was equipped with a Milestone START D MR system (power 800 W, frequency 2.45 GHz) from Milestone Srl, Italy. It was fitted to a water reflux condenser (cooling water temperature was 10 °C) for operation at atmospheric pressure. The MW reactor vessel had a volume of 500 mL. The temperature of the reaction system was monitored using infrared sensors connected to a computer during irradiation.

### Characterization methods

The chemical structure of the $TiO_2$ samples was examined using X-ray photoelectron spectroscopy (XPS) measurements on the PHI 1600/3057 (Physical Electronics) with a Mg $K_\alpha$ source. The crystalline phase was investigated using X-ray diffraction (Rigaku D-Max). 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 crystallinity of $TiO_2$ sample was estimated by comparing the intensity of the anatase peak of (101) planes with the intensity of a sample annealed at 600 °C. The sample annealed at 600 °C was assumed to be wholly crystalline. Conductivity measurements were conducted with a Zetasizer Nano-ZS (Malvern) instrument. The temperature of the sample was maintained at $25 \pm 0.1$ °C during the measurements.

## Results and discussion

In conventional ionothermal synthesis of $TiO_2$, high water content resulted in lower anatase crystallinity [18]. However, this study obtained different results under MW irradiation, where low water contents resulted in lower anatase crystallinities at a composition of five molar ratios of $H_2O$/TIP (Table 1). Hence, specific MW heating effects might exist, which could affect anatase crystallization behavior of $TiO_2$ under IL/MW condition.

Figure 1 demonstrates temperature profiles at different amounts of IL and two molar ratios of $H_2O$/TIP in the F mode. The temperature was around or below 100 °C at 100 molar ratios of $H_2O$/TIP irrespective of containing IL (Fig. 1). However, the temperature increased much faster to 160 °C at five molar ratios of $H_2O$/TIP. The lower temperature at 100 molar ratios of $H_2O$/TIP could occur, because it is difficult to heat water to higher temperatures than 100 °C in open vessels under MW irradiation [19]. On the other hand, comparing the data of Fig. 1 and Table 1 suggest that the initial high temperature increase may have

**Table 1** Anatase crystallinity of $TiO_2$ samples prepared with different IL/TIP and $H_2O$/TIP molar ratios

| IL/TIP molar ratio | Crystallinity (%) | |
|---|---|---|
| | $H_2O$/TIP molar ratio | |
| | 5 | 100 |
| 0 | Amorphous | 22 |
| 0.5 | 25 | 33 |
| 1 | 36 | 52 |
| 2 | 34 | 54 |

MW irradiation was applied in the F mode

caused the lower anatase crystallinity at five molar ratios of $H_2O$/TIP. To examine this statement, two more MW irradiation modes were conducted. The L and S irradiation modes differed from the F mode in the initial temperature, which was set to a desired temperature for 10 min before MW irradiation.

Figure 2 illustrates the observed temperature profiles for the three MW irradiation modes at five molar ratios of $H_2O$/TIP. The final temperature for each mode was approximately 160 °C and in the F mode the temperature increased much faster to 160 °C during the initial 10 min. To heat water above temperatures of 100 °C is difficult under MW irradiation at ambient conditions. Hence, the rapid increase in temperature during the initial 10 min in the F mode was due to the superheating effect of IL under MW irradiation.

Figure 3 demonstrates temperature profiles of the reaction system with different IL concentrations. A 1.0 mol concentration of IL obtained the highest temperature increase. When the IL concentration was above or below 1.0 mol, the temperature decreased.

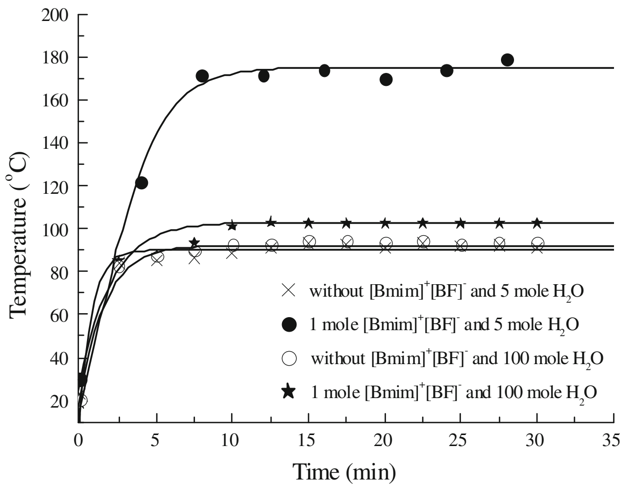

**Fig. 1** Temperature profiles of $TiO_2$ samples prepared with and without IL at two different molar ratios of $H_2O$/TIP

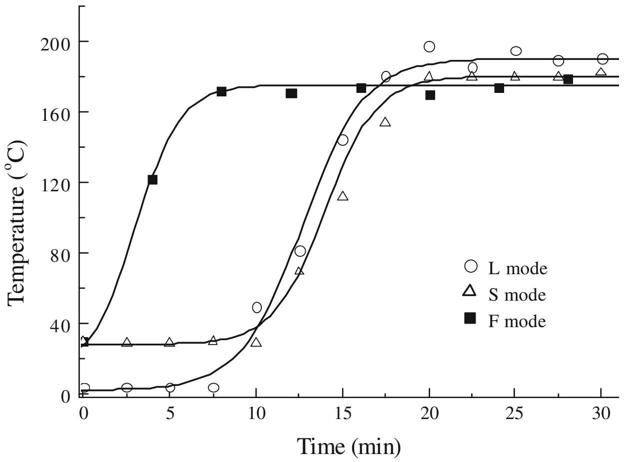

**Fig. 2** Temperature profiles of the reaction system for three MW irradiation modes containing 1 mol of $[Bmim]^+[BF_4]^-$ and five molar ratios of $H_2O$/TIP

In IL/water mixture system, IL exists as free anions and cations in diluted solution regions, but tight ionic pairs form with an increasing IL concentration [20] and affect the conductivity of system [21]. The conductivity of the IL/water mixture system depends on the IL concentration [22]. Figure 4 demonstrates that the conductivity of the IL solution increases sharply at one molar ratio of IL/TIP to a steady value in our experimental condition.

When the ionothermal reaction was conducted under MW irradiation, the reaction mixture could be heated up by two different mechanisms: the ion conduction mechanism and the dipolar polarization mechanism. In ion conduction mechanism, MW irradiation moves the ions through the solution, increases collisions and thus converts kinetic energy into heat. In dipolar polarization mechanism, when the polar molecules are exposed to MW frequencies, the molecular dipoles align in the applied electric field. When the applied field oscillates, the dipole field will follow these oscillations and the energy is lost in the form of heat through molecular friction [19].

From the conductivity results of our study, we can say that when the MW irradiation was conducted below the one molar ratio of IL/TIP, ion conduction mechanism operates due to the existence of free anions and cations of IL. However, in the experimental condition above the one molar ratio of IL/TIP, because the excess IL exists as tight ion pair, the mobility and collision of the ions could be declined due to the presence of these tight ion pairs. On the other hand, each tight ion pair of IL can be considered as a polar molecule due to no coincidence of the asymmetric charge centers. The dipolar polarization mechanism will then dominate. With a much stronger heating effect than the dipolar polarization, the ion conduction mechanism is able to cause a marked increase in heating rate and attain

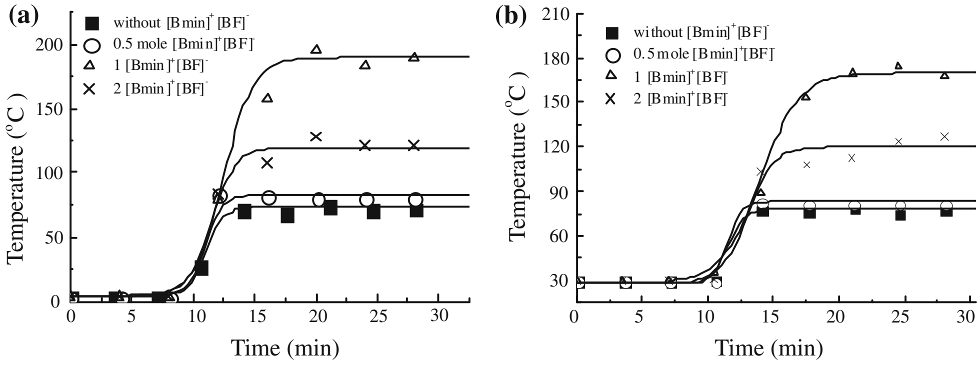

**Fig. 3** Temperature plots of the reaction system with different IL contents at five molar ratios of $H_2O$/TIP. **a** L mode, **b** S mode

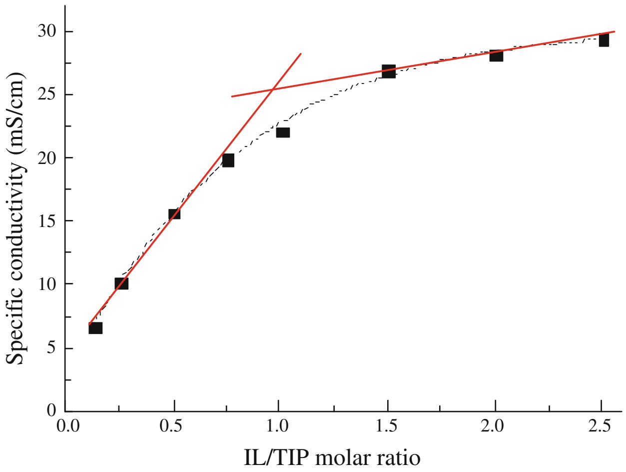

**Fig. 4** The conductivity of the IL solution at different molar ratios of IL/TIP (the molar ratio of $H_2O$/TIP and IPA/TIP was fixed at 5 and 3, respectively)

higher reaction system temperatures [19]. Hence we can obtain the highest reaction temperature at the case of one molar ratio of IL/TIP (Fig. 3).

Figure 5 illustrates XRD curves of samples prepared at different concentrations of $[Bmim]^+[BF_4]^-$ at five molar ratios of $H_2O$/TIP for each mode. Table 2 lists measured anatase crystallinity of $TiO_2$ from the XRD data of Fig. 5. The highest anatase crystallinity of $TiO_2$ was obtained at the lowest initial reaction temperature (L mode, Table 2). Hence, the difference in anatase crystallinity of the final $TiO_2$ products for the three MW irradiation modes may be due to the reaction temperature effect of the initial 10 min on the structure of $TiO_2$ and its anatase crystallization behavior.

For a long time, XPS was used to examine the structural composition of $TiO_2$ [23]. In XPS analysis of $TiO_2$, the bonding energy of Ti and O was measured 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 the titanium compound [24]. Table 3 demonstrates that the XPS data and the calculated amounts of the hydroxylated titanium compound of the reaction products were from the initial 10 min for each mode and that the F mode obtained a lower amount of hydroxylated titanium.

In general, hydrolysis of titanium precursors can form hydroxylated titanium compounds and high initial reaction temperatures can enhance the condensation of hydrolysis products. Hence, the F mode formed a higher amount of condensation products during the initial 10 min (Table 3).

Hydroxylated titanium compounds were a key intermediate for forming anatase $TiO_2$ in ionothermal synthesis of nanostructured $TiO_2$ [25]. In S or L mode, a higher proportion of hydroxylated titanium compounds derived from hydrolysis of titanium precursors. On the other hand, ILs can induce water dissolution of higher molecular weight condensation products in the ionothermal synthesis system and also result in a hydroxylated titanium compound. In this reaction system, this type of hydroxylated titanium compound mainly occurred in the F mode. The IL acted as a steric stabilizer after the formation of hydroxylated titanium compounds. Thereafter, the self organization ability of the IL would drive anatase crystallization through the dehydration of the Ti–OH group in the hydroxylated titanium compound. When IL drives anatase crystallization, the hydroxylated titanium compound from IL-induced water dissolution of the condensation product has a lower anatase crystallinity at the same thermal annealing condition [18]. It could explain the lower anatase crystallinity in the F mode (Table 2). In addition, due to a lower initial reaction temperature, a high anatase crystallinity was observed at 100 molar ratios of $H_2O$/TIP (Table 1).

Table 2 demonstrates that an IL concentration of 1.0 mol led to higher anatase crystallinity. Furthermore, a 1.0 mol concentration of IL resulted in the highest temperature increase (Fig. 3). This temperature effect on

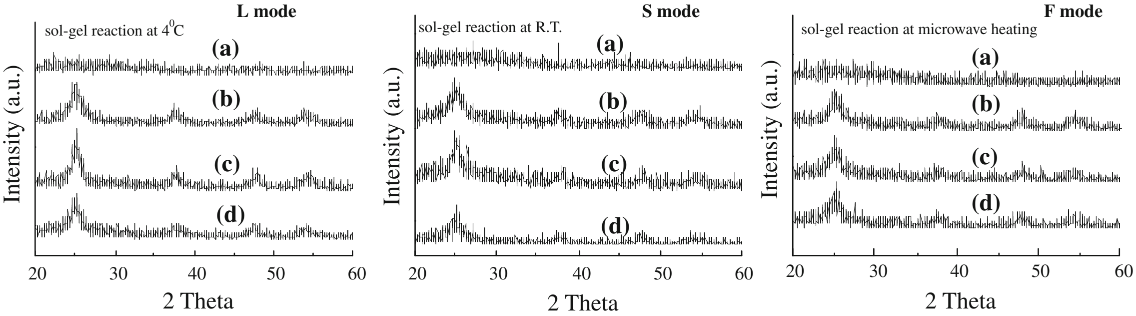

**Fig. 5** XRD curves of $TiO_2$ samples prepared at different IL concentrations and five molar ratios of $H_2O$/TIP for three MW irradiation modes. (*A*) no IL (*B*) 0.5 molar ratio of $[Bmim]^+[BF_4]^-$/TIP, (*C*) one molar ratio of $[Bmim]^+[BF_4]^-$/TIP, and (*D*) two molar ratios of $[Bmim]^+[BF_4]^-$/TIP

**Table 2** Anatase crystallinity of samples prepared with different IL concentrations at five molar ratios of $H_2O$/TIP for three MW irradiation modes

| $[Bmim]^+[BF4]^-$ (mol) | Anatase crystallinity (%) | | |
|---|---|---|---|
| | L mode | S mode | F mode |
| 0 | Amorphous | Amorphous | Amorphous |
| 0.5 | 72 | 45 | 25 |
| 1 | 83 | 49 | 36 |
| 2 | 43 | 33 | 34 |

**Table 3** Fitting results from XPS curves of $TiO_2$ samples obtained from the initial 10 min for each mode

| Mode | Water/TIP molar ratio | IL/TIP molar ratio | O1s (Ti–O–Ti) area ratio (%) | O1s (Ti–OH) area ratio (%) |
|---|---|---|---|---|
| L | 5 | 0 | 77 | 23 |
| | | 1 | 73 | 27 |
| | | 2 | 76 | 24 |
| S | 5 | 0 | 79 | 21 |
| | | 1 | 75 | 25 |
| | | 2 | 77 | 23 |
| F | 5 | 0 | 85 | 15 |
| | | 1 | 76.5 | 23.5 |
| | | 2 | 77.5 | 22.5 |

anatase crystallization differs from the initial temperature effect described above on anatase crystallization behavior. In contrast to the initial temperature effect on a hydrolysis–condensation reaction, this temperature effect was a thermal annealing effect. Hence, higher annealing temperatures result in higher anatase crystallinity [25].

In summary, diverse effects of MW heating on anatase crystallization were found in ionothermal synthesis of nanostructured $TiO_2$ under IL/MW condition and depend on initial water concentration, MW irradiation time, and IL concentration.

## Conclusion

Diverse effects of MW heating on anatase crystallization in ionothermal synthesis of nanostructured $TiO_2$ were studied. These effects depended on MW irradiation time, initial water concentration, and IL concentration. The results indicated that higher anatase crystallinity was obtained at higher water amounts, irrespective of IL concentration. However, at lower water amounts and lower initial temperature, a higher anatase crystallinity occurred only when MW heating was applied after the mixtures reacted for certain duration and at a specific IL concentration. This was due to different MW heating effects on the hydrolysis/condensation and post-treatment stage and the heating characteristics of IL/water mixtures under MW irradiation.

## References

1. Leadbeater NE, Torenius HM, Tye H (2004) Comb Chem High Throughput Screen 7:511
2. Bilecka I, Niederberger M (2010) Nanoscale 2:1358
3. Harta JN, Cervinia R, Chenga YB, Simona GP, Spiccia L (2004) Sol Energ Mat Sol C 84:135
4. Periyat P, Leyland ND, McCormack E, Colreavy J, Corrc D, Pillai SC (2010) J Mater Chem 20:3650
5. Komarneni S, Rajha RK, Katsuki H (1999) Mater Chem Phys 61:50
6. Ma Z, Yu J, Dai S (2010) Adv Mater 22:261
7. Yoo K, Choi H, Dionysiou DD (2004) Chem Commun 2000
8. Taubert A (2005) Acta Chim Slov 52:183
9. Antonietti M, Kuang D, Smarsly B, Zhou Y (2004) Angew Chem Int Ed 43:4988
10. Zhou Y (2005) Curr Nanosci 1:35
11. Taubert A, Li Z (2007) Dalton Trans 7:723
12. Li Z, Jia Z, Luan Y, Mud T (2008) Curr Opin Solid State Mater Sci 12:1

13. Hoffmann J, Nüchter M, Ondruschk B, Wasserscheid P (2003) Green Chem 5:296
14. Martínez-Palou R (2010) Mol Divers 14:3
15. Morris RE (2008) Angew Chem Int Ed 47:442
16. Ding K, Miao Z, Liu Z, Zhang Z, Han B, An G, Miao S, Xie Y (2007) J Am Chem Soc 129:6362
17. Dong W, Li M, Liu C, Lin F, Liu Z (2008) J Colloid Interface Sci 319:115
18. Liu YH, Chang MC, Shao H, Huang MS, Yang AC (2010) J Mater Sci 45:369. doi:10.1007/s10853-009-3945-2
19. Dallinger D, Kappe CO (2007) Chem Rev 107:2563
20. Liu W, Zhao T, Zhang Y, Wang H, Yu M (2006) J Solut Chem 35:1337
21. Vila J, Gines P, Rilo E, Cabeza O, Varela LM (2006) Fluid Phase Equilib 247:32
22. Jarosik A, Krajewski SR, Lewandowski A, Radzimski P (2006) J Mol Liq 123:43
23. Yu J, Wang G, Chemg B, Zhou M (2007) Appl Catal B Environ 69:171
24. Pouilleau J, Devilliers D, Groult H (1997) J Mater Res 32:5645
25. Liu YH, Lin CW, Chang MC, Shao H, Yang ACM (2008) J Mater Sci 43:5005. doi:10.1007/s10853-008-2740-9