J Mater Sci (2008) 43:5005–5013
DOI 10.1007/s10853-008-2740-9

The hydrothermal analogy role of ionic liquid in transforming amorphous TiO_2 to anatase TiO_2: elucidating effects of ionic liquids and heating method

**Yen Hiu Liu · Chih Wei Lin · Min Chao Chang ·
Hsin Shao · Arnold Chang-Mou Yang**

Received: 7 January 2008 / Accepted: 16 May 2008 / Published online: 30 May 2008

Abstract In this study, the specific coexistence of water and ionic liquid being the lower temperature thermal annealing condition for anatase crystallization of amorphous titania at ambient pressure was found. The test ionic liquids were 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrafluoroborate. After deep investigation, we found that there existed an analogy between our lower temperature thermal annealing treatment system (LTTAT) and hydrothermal treatment system. In LTTAT system, the ionic liquid played an important role in driving surface crystallization of amorphous TiO_2 to the anatase phase by retaining a suitable amount of water through a dissolution–crystallization mechanism. We could observe higher hydroxyl group ratio of hydroxylated titanium compound from X-ray photoelectron spectroscopy (XPS) data during initial thermal annealing period. The self-assembly ability of ionic liquid then lead to kinetical dehydration and crystallization of hydroxylated titanium compound around it during the following annealing process. Based upon this proposition, the effects of different types of ionic liquid and its amount, temperature effect, and heating method on anatase crystallinity, characterized by X-ray diffraction (XRD), were investigated. It was found that different temperatures and microwave heating effect were observed for different types of ionic liquid. From these observations, it was pointed out that we could get better anatase crystallinity and good photodegradation performance by using the system containing ionic liquid having higher water-adsorbing ability and microwave heating annealing.

Introduction

TiO_2 is polymorphic with three crystalline structures: anatase, rutile, and brookite. It is well known that anatase TiO_2 is very useful due to its high photoactivity and suitable for making high efficiency photocatalyst for air and water purification, solar cell, opto-electronic and medical applications. Extensive research efforts have been devoted to study the preparation and characterization of anatase nanocrystalline TiO_2.

TiO_2 can be synthesized from hydrolysis and condensation of titanium precursor by sol-gel method. The initial reaction product of this sol-gel reaction is generally amorphous. For achieving crystalline anatase TiO_2 from amorphous product, high temperature calcination or hydrothermal treatment was required. In latter case, for example, Burnside et al [1] reported that anatase TiO_2 could be obtained from self-organization of TiO_2 particles in a basic condition under hydrothermal condition.

In recent years, room temperature ionic liquid has received extensive attention for both academic research and industrial applications [2]. Ionic liquid is considered as a

Y. H. Liu · C. W. Lin · A. C.-M. Yang
Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan

Y. H. Liu
e-mail: d947531@oz.nthu.edu.tw

C. W. Lin
e-mail: d937538@oz.nthu.edu.tw

A. C.-M. Yang
e-mail: acyang@mse.nthu.edu.tw

M. C. Chang (✉) · H. Shao
Energy and Environmental Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan
e-mail: minchaochang@itri.org.tw

H. Shao
e-mail: HsinShao@itri.org.tw

green solvent due to its low melting points below 100 °C and negligible vapor pressure even at elevated temperature. It is considered to be a good solvent for organic, inorganic, and polymeric material. Particularly, owing to its pronounced self-organization ability, application as reaction media for synthesis of highly organized nanostructural material had been studied by many authors [3, 4]. For example, Jiang et al [5] reported that mixture of ionic liquid and water could be used as the medium for morphogenesis and crystallization of Bi_2S_3 nanostructures. As for titanium dioxide, Zhou and Antonietti [6] synthesized TiO_2 nanocrystals by addition of $TiCl_4$/ionic liquid mixture to water. Nakashima and Kimizuka [7] reported the preparation of hollow TiO_2 microspheres by means of interfacial sol-gel interaction method with the ionic liquid added with toluene solution of titanium tetrabutoxide. The group of Dr. Dionysiou D systematically studied the preparation and characterization of mesoporous TiO_2 by sol-gel method with reaction of titanium tetraisopropoxide and water in the presence of ionic liquid [8, 9, 10].

In recent chemical reaction study, microwave heating was widely employed for synthesizing organic compound or inorganic materials [11]. The microwave heating effect is considered to be a thermal effect due to absorbing microwave energy by polar molecule in the system. In microwave processing of material, Hartel et al [12] found that crystallization of sol-gel white precipitate formed from hydrolysis of titanium precursor to anatase TiO_2 could be achieved with a shorter time.

In discussing the role of ionic liquid for sol-gel system containing ionic liquid, Dionysiou D et al pointed out that it could control the rate of hydrolysis conditions of sol-gel reaction and had a conclusion that the interaction between water and the anion part of the ionic liquid is the essential factor for the observed TiO_2 crystallinity rather than the amount of water and TiO_2 particles prepared with 1-butyl-3-methylimidazolium hexafluorophosphate ($[BuMIm]^+[PF_6]^-$) had higher crystalline structure [8, 9, 10]. Antonietti et al [3] pointed out that ionic liquid played the role of a classic surfactant in water-rich media during sol-gel synthesis of inorganic nanomaterials containing ionic liquid. In another paper, Choi et al [13] suggested that the capping effect of $[BuMIm]^+[PF_6]^-$ ionic liquid induced controlling hydrolysis of titanium alkoxide precursor in sol-gel reaction. On the other hand, in studying preparation of nanostructure anatase TiO_2 monoliths using 1-butyl-3-methylimidazolium tetrafluoroborate ($[BuMIm]^+[BF_4]^-$), Liu et al [14] thought that $[BuMIm]^+[BF_4]^-$ could enhance the polycondensation and crystallization rate in forming anatase crystal.

From above discussions, we could see that the detailed reaction mechanism of forming TiO_2 nanostructures by sol-gel method in the presence of ionic liquid remains unclear. For getting clarified, the two things must be considered: which stage (synthesis stage or crystallization stage) was the stage mainly affected by ionic liquid and what is the actual role of ionic liquid. Herein we firstly considered crystallization stage. Hence the purpose of this study was to investigate the role of ionic liquid during transformation of amorphous TiO_2 prepared by sol-gel reaction to anatase nanocrystalline TiO_2 in LTTAT system. We also studied different heating methods (microwave treatment and conventional thermal treatment) on the crystallization behavior during this transformation.

Experimental

Synthesis of titanium dioxide by sol-gel method

TiO_2 was synthesized via a sol-gel reaction with de-ionized water and pre-dissolved titanium tetraisopropoxide (Aldrich) in isopropanol (J. T. Barker,). During the reaction at room temperature, de-ionized water was slowly added into a constantly stirred mixture of dissolved tetraisopropoxide in isopropanol. In a typical experiment, 0.3 g (1 mmol) of titanium tetraisopropoxide was blended with 1.935 g (32.25 mmol) of isopropanol by stirring using a spin bar for approximately 10 min. Then, 1.935 g (107 mmol) of de-ionized water was slowly added into the above solution. The entire reaction typically took 30 min. The reaction product of the sol-gel reaction was collected by filtration of the above solution with a filter paper. The precipitate was washed with 75 mL of de-ionized water and then dried by freeze dry in a freeze-dryer (FTS system) at –50 °C under a 0.05 torr vacuum for 2 h (freeze-dried precipitate). The final product was a white powder.

Thermal annealing treatments with or without ionic liquid/water

Conventional thermal annealing adopted in this study was conducted by heating at 100 °C for 2 h. To examine the role of ionic liquid during this thermal annealing, experiments were conducted by mixing freeze-dried precipitate with various amounts of the ionic liquid in pure state or in a mixture of water and ionic liquid before being annealed. The ionic liquid used in this study included hydrophobic $[BuMIm]^+[PF_6]^-$ and hydrophilic $[BuMIm]^+[BF_4]^-$. The resulting powder was then washed with de-ionized water and acetonitrile mixture, freeze-dried, and characterized by XRD.

Microwave treatment

The microwave reactor was modified from household microwave oven (Sampo MOB-201R, frequency 2.45 GHz, maximum power 800 W). It can either be fitted with standard glassware (non-reflux condition) or a reflux condenser (reflux temperature was 5 °C) for operation at atmospheric pressure. The reflux apparatus consists of a reaction vessel (10 mL round bottom flask) and a water reflux condenser. The temperature of the reaction system during irradiation was monitored online by use of a thermocouple connected with a computer.

Characterization methods

The chemical structure bonding of the TiO_2 samples was studied using X-ray photoelectron spectroscopy (XPS) measurements on the PHI 1600/3057 (Physical Electronics) with Mg Kα source. The crystalline phase was investigated by using X-ray diffraction method (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 average crystal sizes (D) were calculated from the most intense diffraction peak (101) using the Scherrer formula, $D = 0.89\lambda/(\beta \cos \theta)$ 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 crystallinity of TiO_2 sample was estimated by comparing its intensity of the anatase peak of (101) planes with that of sample annealed at 600 °C. The latter annealed sample was assumed to be wholly crystalline.

Photocatalytic performance test

Photocatalytic performance of sample after annealing was evaluated for degradation of methylene blue in water and compared with that of Degussa P-25. The concentration of TiO_2 aqueous suspension in the reactor system was 1000 mg/L. The concentration of methylene blue was 5 mg/L. The UV radiation was performed from four black lamps of 4 W power and wavelength of 365 nm with light intensity of 6 mW/cm^2. Methylene blue was chemical reagent grade. The photodegradation was monitored by the absorbance of the methylene blue at 655 nm. It was measured by using Hitachi u-2000 UV-vis spectrometer.

Results and discussion

In our preliminary study, we found that ionic liquid plays a role in driving a post-condensation crystallization of amorphous TiO_2 to anatase phase during ensuing drying at 100 °C and 1 atm [15]. In that study, the freeze-dried sol-gel titania powder showed featureless X-ray diffraction curve, the TiO_2 particle was predominantly amorphous. Titania powder was still amorphous and did not crystallize to anatase by annealing treatment with H_2O and $[BuMIm]^+[PF_6]^-$, respectively, at 100 °C for 2 h. However anatase peak was observed by annealing treatment with mixture of $[BuMIm]^+[PF_6]^-$ and water. It was also found when TiO_2 annealing experiments were conducted with mixture of $[BuMIm]^+[PF_6]^-$and isopropyl alcohol, or mixture of $[BuMIm]^+[PF_6]^-$ and N-methylpyrrolidone, respectively. Anatase peak was not observed at 100 °C for 2 h in each case. These results pointed out that the specific coexistence of water and ionic liquid was essential factor for anatase crystallization of amorphous titania during thermal annealing at 100 °C for 2 h.

Recently, many effects were focused to study the physicochemical behavior of water dissolved in room temperature dialkylimidazolium type ionic liquid, e.g.: $[BuMIm]^+[PF6]^-$ and $[BuMIm]^+[BF_4]^-$ [16, 17]. Based upon their finding, the physicochemical characteristic of mixture of ionic liquid and water and the key role of the ionic liquid in this mixture during crystallization of amorphous titania in our LTTAT system would be explored in this study.

An analogy discussion for hydrothermal treatment system and LTTAT system

For a long time, hydrothermal method is considered as one of the methods for producing crystalline metal oxide powder. In this method, the reaction is carried out with aqueous or organo-aqueous media and reaction temperature can be in the range of 100–300 °C and reaction pressure is well above 1 atm in closed systems. It is suggested that adsorbed water around starting material in autoclave is considered as the key role for the crystallization of the amorphous material. For example, in studying nucleation and crystal growth of kanemite powder prepared from silicalite 1 precursor by hydrothermal method, Salou et al [18] found out that amorphous product was obtained at temperature above 100 °C in open system but crystallization could only be seen with sealed glass ampoules. Due to the fact that adsorbed water is easy to evaporate away at temperature above100 °C in an open system, they considered that the water adsorbed in the starting powder plays an important role during crystallization in sealed glass ampoules.

The anatase crystallization of TiO_2 from amorphous titania by hydrothermal method had also been studied by Yanagisawa et al [19]. They had a conclusion that formation of fine anatase titania crystal was accelerated by the adsorbed water molecule in the autoclave. The adsorbed water around the amorphous TiO_2 particle accelerates the nucleation of anatase crystals. Hence a proposition that the role of water for crystallization of amorphous titania annealed at 100 °C for 2 h in LTTAT system could be similar to that of the adsorbed water in hydrothermal treatment system. An analogy was deduced between hydrothermal treatment system and our LTTAT system [15]. The difference between hydrothermal treatment system and LTTAT system was the latter system being operated at ambient condition. The function of ionic liquid in LTTAT system was considered to be by retaining water through hydrogen bonding interaction with water molecule around amorphous titania and then induced surface crystallization of amorphous titania through dissolution–crystallization mechanism to anatase phase during thermal annealing at 100 °C. In this case, the ionic liquid served as a structure ordering agent [3].

This proposition could be further proved by the following X-ray photoelectron spectroscopy (XPS) data. XPS has been used to examine the structural composition of TiO_2 [20]. In XPS analysis, the bonding energy of Ti and O was measured and the change in the bond type could be characterized by observing the shift in binding energy. In this study, chemical bonding types of the freeze-dried TiO_2 powder without or with 20% ionic liquid ($[BuMIm]^+[PF_6]^-$and $[BuMIm]^+[BF_4]^-$) and 300% water were determined by XPS. Figure 1 show typical XPS photopeaks for O1s bonds energy. The O1s regions are fitted into three peaks; the main peaks are 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 hydroxide. The other minor peak belongs to the adsorbed water [21]. Figure 2 demonstrated that the time profile of hydroxyl group content and anatase crystallinity during thermal annealing of sample in the presence of ionic liquid. It could be seen from Fig. 2 that we could observe maximum hydroxyl group ratio in XPS data and the hydroxyl group content of titanium hydroxide became decreasing after crystallization. The appearance of maximum peak was resulted from initial surface water dissolution of the condensation product with Ti–O–Ti structure to form hydroxylated titanium compound. Table 1 lists the results of curve fitting data for the O1s of TiO_2 samples with/without addition of ionic liquid and water annealed at 100 °C for 2 h. The results shown in Table 1 indicated that the hydroxyl group ratio of freeze-dried sample was higher

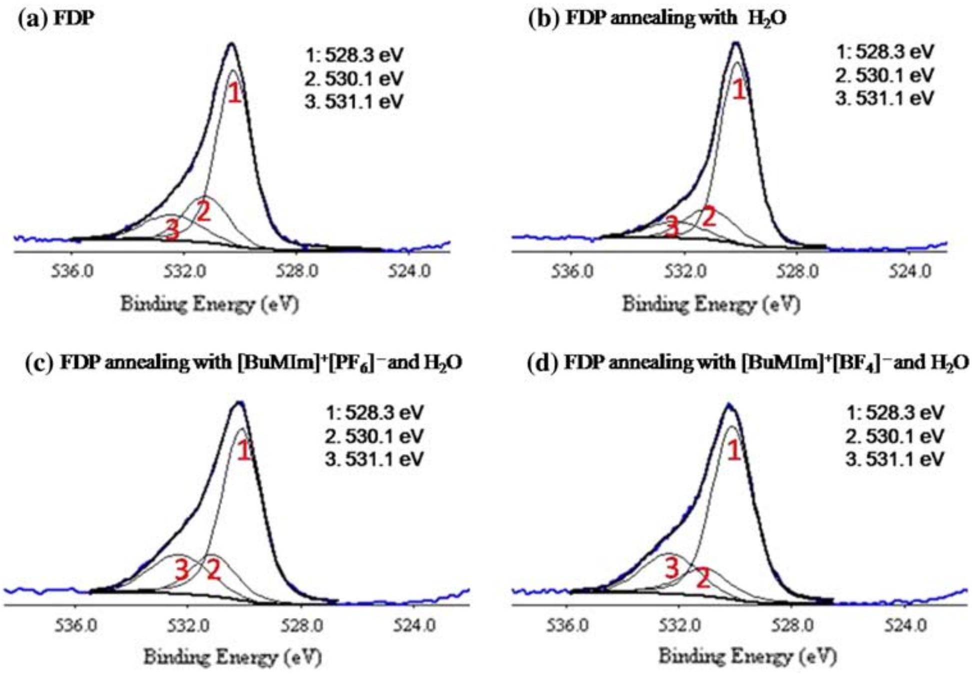

Fig. 1 The XPS curves for different TiO_2 samples (**a**) freeze-dried powder (FDP), (**b**) freeze-dried powder annealed with 300% de-ionized water at 100 °C for 2 h, (**c**) freeze-dried powder annealed with 20% $[BuMIm]^+[PF_6]^-$ and 300% water at 100 °C for 2 h, and (**d**) freeze-dried powder annealed with 20% $[BuMIm]^+[BF_4]^-$ and 300% water at 100 °C for 2 h

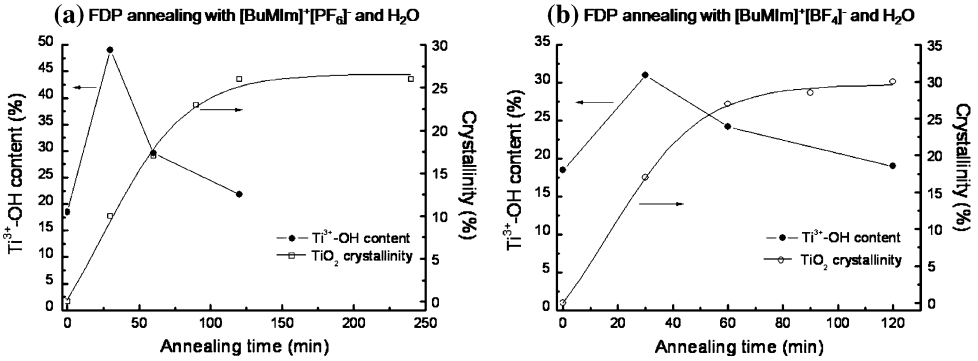

Fig. 2 The time profile of hydroloxyl group content and anatase crystallinity during thermal annealing of FDP sample (**a**) freeze-dried powder annealed with 20% $[BuMIm]^+[PF_6]^-$ and 300% water at 100 °C for 2 h, and (**b**) freeze-dried powder annealed with 20% $[BuMIm]^+[BF_4]^-$ and 300% water at 100 °C for 2 h

Table 1 The fitting results of XPS curves of different TiO_2 samples after thermal annealing at 100 °C for 2 h

Sample codes	O1s (Ti–O) area ratio (%)	O1s (Ti–O) FWHM (eV)	O1s (OH^-) area ratio (%)	O1s (OH^-) FWHM (eV)
FDP	76.3	1.6	23.7	1.4
FDP + H_2O	81.5	1.4	18.5	2.1
FDP + H_2O + $[BuMIm]^+[PF_6]^-$	78.2	1.6	21.8	1.9
FDP + H_2O + $[BuMIm]^+[BF_4]^-$	81.0	1.7	19.0	2.0

Table 2 The found anatase crystallinity of TiO_2 sample with 20% $[BuMIm]^+[PF_6]^-$ and 300% water at different annealing time

Annealing time (min)	Crystallinity (%)
15	0
60	17
120	26

than that of thermal-dried sample annealed with 300% water at 100 °C. The hydroxyl group ratio was 21.8% and 19% when the TiO_2 samples were annealed in the presence of $[BuMIm]^+[PF_6]^-$ or $[BuMIm]^+[BF_4]^-$ at the same condition respectively.

In general, the initial reaction product of sol-gel reaction is the mixture of hydrolysis product (hydroxylated titanium) and condensation product with Ti–O–Ti structure (oxide compound). The content of hydrolysis product is dependent upon the degree of being condensated [22]. Thermal annealing of freeze-dried sample without ionic liquid at 100 °C would only lead to random dehydration of hydrolysis product to form amorphous condensation product. However the self-assembly ability of ionic liquid would lead to kinetical dehydration and crystallization of hydroxylated titanium compound around it [23]. The degree of such dehydration and crystallization process is dependent upon applied annealing time. The anatase crystallinity for TiO_2 samples with 20% ionic liquid and 300% water at different annealing time are also shown in Table 2. It was found that the higher anatase crystallinity was observed for longer annealing time.

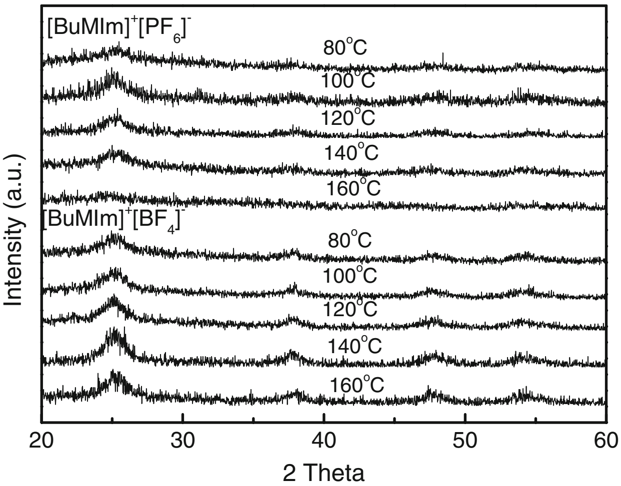

Fig. 3 The XRD curves for TiO_2 sample with 20% ionic liquid and 300% water annealing at different temperature and ionic liquid

Table 3 The anatase crystallinity of TiO_2 sample calculated from XRD curves in Fig. 3

Ionic liquid	Crystallinity (%)				
	80 °C	100 °C	120 °C	140 °C	160 °C
$[BuMIm]^+[PF_6]^-$	15	26	18	11	8.5
$[BuMIm]^+[BF_4]^-$	24	27	30	39	29

The effect of different ionic liquid and temperature in LTTAT system

The XRD curves for freeze-dried TiO_2 powder containing 20% ionic liquid and 300% water with $[BuMIm]^+[PF_6]^-$ and $[BuMIm]^+[BF_4]^-$ annealed at different temperatures for 2 h is shown in Fig. 3. The anatase crystallinity of TiO_2 samples calculated from XRD curves is also listed in Table 3. The crystallite size was around 3∼4 nm. The results obtained from Fig. 3 and Table 3 indicated different temperature effect on anatase crystallization of freeze-dried amorphous TiO_2 powder with different ionic liquid. It can be seen that higher anatase crystallinity was obtained for $[BuMIm]^+[BF_4]^-$, especially annealing temperature above 100 °C. These results were different from that of Dionysiou et al work. They observed the TiO_2 particles prepared with ionic liquid containing $[PF_6]^-$ had higher anatase crystalline structure [8]. In studying physicochemical properties of aqueous solution with two 1,3-dialkylimidazolium based ionic liquid, ($[BuMIm]^+[BF_4]^-$) and ($[BuMIm]^+[PF_6]^-$), Tran et al [24] found out that the strength of hydrogen bonding between anion and water molecules was greater for $[BuMIm]^+[BF_4]^-$and demonstrated that $[BuMIm]^+[BF_4]^-$ can absorb up to 0.32 M of water, whereas $[BuMIm]^+[PF_6]^-$ can only absorb 8.3×10^{-2} M of water in studying absorption of water by near-infrared spectrometry. Our interesting results having higher anatase crystallinity for $[BuMIm]^+[BF_4]^-$system may be resulted from higher content of adsorbed water molecule and better stability of ionic liquid/water hydrogen-bonded complex for $[BuMIm]^+[BF_4]^-$. In this case, it could provide more beneficial for inducing dissolution-crystallization process of amorphous titania to anatase phase during thermal annealing.

As for temperature effect, it was found that there exists a remarkable difference for these two ionic liquids. When the temperature was above 100 °C, we could see that anatase crystallinity was increasing with increasing temperature for $[BuMIm]^+[BF_4]^-$case except highest temperature 160 °C and decreasing with increasing temperature for $[BuMIm]^+[PF_6]^-$ case. This is also due to the difference in temperature stability of ionic liquid/water hydrogen-bonded complex for these two ionic liquids. In studying the interactions between water molecules and ionic liquids, Wang et al [25] found out that BF_4^- anion in $[BuMIm]^+[BF_4]^-$ could form stable complex with water molecules while PF_6^- anion in $[BuMIm]^+[PF_6]^-$ could not form a stable complex. Hence the adsorbed water could be easily heated away and then lower anatase crystallinity was observed at annealing temperature above100 °C with $[BuMIm]^+[PF_6]^-$. On the other hand, due to the formation of the stable hydrogen-bonded complex between anion and water in $[BuMIm]^+[BF_4]^-$, the adsorbed water was not easy to evaporate away and kinetically led to higher surface dissolution and crystallization rate of TiO_2 samples when annealing at moderately high temperature. However the hydrogen-bonded complex could be broken when temperature is too high. This is why we could observe lower anatase crystallinity at 160 °C.

The effect of ionic liquid content in LTTAT system

The XRD curve for the freeze-dried TiO_2 samples with different $[BuMIm]^+[PF_6]^-$ content and 300% water is shown in Fig. 4. Table 4 lists the calculated anatase crystallinity from XRD data. It was shown that a minimum ionic liquid content around 7.5% was required for the formation of anatase TiO_2 nanocrystal under 100 °C annealing for 2 h. The anatase crystallinity increases with ionic liquid content, from 14% at 7.5% ionic liquid to a maximum of 26% at 20% ionic liquid, and then decreases slowly to 24% for 50% ionic liquid. Liu et al [26] studied water concentration effect on physical properties of aqueous solution containing $[BuMIm]^+[BF_4]^-$. They proposed a model to describe structure change upon addition of water. In water-rich condition, ionic liquid molecule ionizes to form anion and cation. However in ionic liquid-rich condition, ionic liquid exists as tight ion pair. Hence the maximum shown in Table 4 could be resulted from limiting water solubility in ionic liquid having tight ion pair structure and the amount of adsorbed water became less at higher ionic liquid content for $[BuMIm]^+[PF_6]^-$. That is to say, ionic liquid concentration is a limiting factor during crystallization of amorphous TiO_2 samples of our LTTAT system and this conclusion indirectly supports the finding that the amount of water was not an essential factor in Dionysiou et al paper [8, 9].

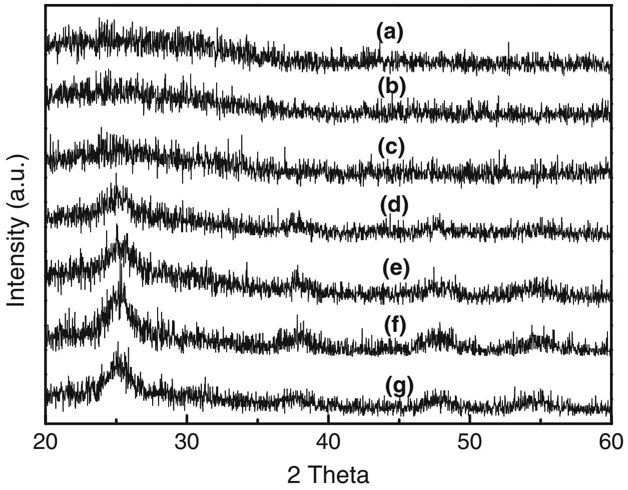

Fig. 4 The XRD curves for the TiO_2 sample for different $[BuMIm]^+[PF_6]^-$ ionic liquid content with 300% water. (a) 0% (b) 2.5% (c) 5% (d) 7.5% (e) 10% (f) 20% (g) 50%

Table 4 The anatase crystallinity of TiO_2 sample calculated from XRD curves in Fig. 4. (ionic liquid: $[BuMIm]^+[PF_6]^-$)

Ionic liquid content (%)	Crystallinity (%)
0	–
2.5	–
5	–
7.5	14
10	17
20	26
50	24

Microwave heating effect in LTTAT system

In a good review article about microwave assisted synthesis of nanoporous materials. Tompsett et al [27] pointed out the specific features of using microwave heating: (1) high heating rate, instantaneous and selective (2) more uniform heating (3) reaction mixture might be superheated in a specific region for a short period of time and lead to the breaking of hydrogen bond between species. (4) enhancement of nucleation rate due to increasing the rate of gel dissolution. Microwave energy can also be coupled with hydrothermal method [28]. Microwave hydrothermal method has been used for treatment of colloidal TiO_2

suspensions [29] or synthesis of nanocrystalline TiO_2 [30]. Wilson et al found out that microwave hydrothermal treatment of TiO_2 colloids gave higher anatase crystallinity with less time. Murugan et al synthesized nanocrystalline anatase TiO_2 using urea and $TiOCl_2$ by microwave hydrothermal method.

Owing to an analogy between our LTTAT system and hydrothermal system, it is worth to investigate the microwave heating effect on anatase crystallinity in our LTTAT system. In fact, ionic liquid is also a good medium for absorbing microwave energy. Some workers reported combining ionic liquid with microwave irradiation to prepare inorganic material. For example, Xu et al [31] studied microwave–ionic liquid method for synthesis of aluminophosphate molecular sieves. They found that crystal nucleation and crystal growth are faster than conventional hydrothermal method and considered that it is due to higher reactants digestion or dissolution rate as a consequence of rapid microwave heating rate.

The XRD curves for TiO_2 samples containing different ionic liquid content and 300% water at 2 h microwave annealing with two ionic liquids in our LTTAT system are shown in Fig. 5. The anatase crystallinity of TiO_2 sample calculated from Fig. 5 is listed in Table 5. It was found that anatase crystallinity of TiO_2 was significantly increased with higher ionic liquid content for $[BuMIm]^+[BF_4]^-$case. However, comparison of anatase crystallinity data in Table 5 to that of TiO_2 sample at 100 °C thermal annealing shown in Table 4, it was surprising to find out that the anatase crystallinity of TiO_2 sample containing $[BuMIm]^+[PF_6]^-$ became lower and almost same for two ionic liquid content. Lower anatase crystallinity in $[BuMIm]^+[PF_6]^-$ case is probably due to water evaporation resulted from the breaking of hydrogen bond in low stability water-hydrogen-bonded complex as a sequence of microwave local superheating. This viewpoint could further be identified by microwave annealing results under reflux or non-reflux condition, as shown in Fig. 6 and Table 6. The XRD curves for TiO_2 samples containing 20% $[BuMIm]^+[PF_6]^-$ and 300% water with thermal annealing at 100 °C for 2 h and microwave annealing for 1 h under these reflux or non-reflux conditions are shown

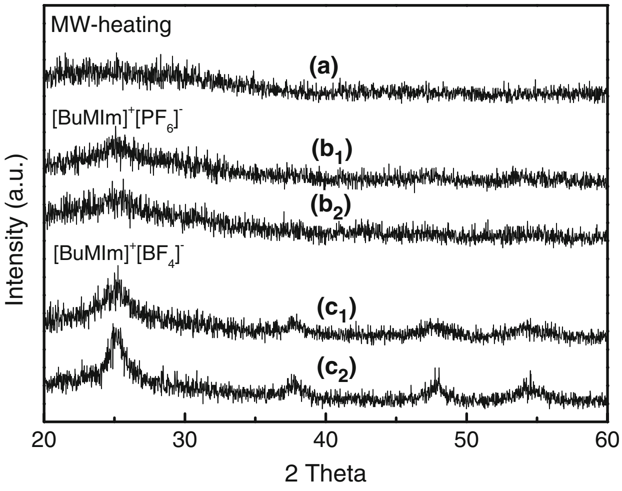

Fig. 5 The XRD curves for TiO_2 samples containing different ionic liquid content and 300% water with 2 hours microwave annealing (ionic content (IL/TiO_2) (a) 0% (b_1) 20% (b_2) 50% (c_1) 20% (c_2) 50%

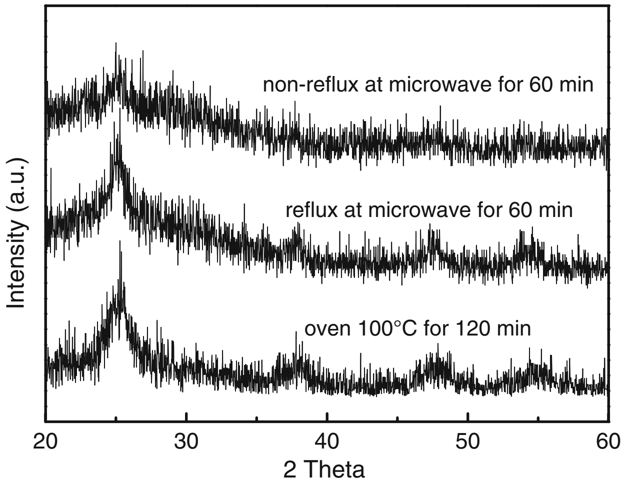

Fig. 6 The XRD curves for TiO_2 sample with 20% ionic liquid and 300% water by thermal annealing at 100 °C (2 h) and microwave annealing with (60 min) and without (60 min) reflux

Table 5 The crystallinity of TiO_2 containing different ionic liquid content and 300% water with 2 h microwave annealing for ionic liquids

Ionic liquid	Ionic liquid content (%)	Crystallinity (%)
$[BuMIm]^+[PF_6]^-$	20	16
	50	18
$[BuMIm]^+[BF_4]^-$	20	25
	50	35

Table 6 The crystallinity for TiO_2 sample with 20% ionic liquid and 300% by thermal annealing with and without reflux (ionic liquid: $[BuMIm]^+[PF_6]^-$)

Annealing method	Crystallinity (%)
1. Microwave heating	
Non-reflux	12
Reflux	25
2. Conventional thermal heating (non-reflux)	26

in Fig. 6. In reflux condition, the reaction site temperature would be around 100 °C. However the reaction site temperature would be excess 100 °C due to microwave local superheating in non-reflux condition. Table 6 listed anatase crystallinity evaluated from XRD data in Fig. 6. The results in Table 6 demonstrated that the anatase crystallinity of TiO_2 sample was almost the same for thermal annealing at 100 °C and microwave annealing under reflux condition. However the anatase crystallinity of TiO_2 sample was lower value under non-reflux condition. The lower anatase crystallinity in non-reflux case is probably due to the breaking of hydrogen bond in low stability water-hydrogen-bonded complex and then evaporation out of water as a sequence of microwave local superheating.

From above discussions, it can be seen that the effect of microwave annealing on transforming amorphous titania to anatase TiO_2 was not always same for different ionic liquids in LTTAT system. It was also found that different temperature effects for different types of ionic liquid. Hence in order to get higher anatase crystallinity, we must conduct microwave heating annealing experiment using ionic liquid having high water-adsorbing ability and strong stability of water-ionic liquid hydrogen-bonded complex.

Photocatalytic performance of sample treated with ionic liquid

Figure 7 shows the photodegradation of methylene blue in aqueous suspension containing TiO_2 sample treated without and with ionic liquid under UV radiation. We could see that good photodegradation performance was obtained for sample treated with $[BuMIm]^+[BF_4]^-$. The measured surface area of this TiO_2 powder was 33.5 $m^2\ g^{-1}$. In comparison with P-25 TiO_2 powder having surface area of about 50 $m^2\ g^{-1}$, it was surprised to find out that only slight difference in photodegradation performance was seen in spite of an appreciable difference in anatase crystallinity. Further study for investigation of this particular photodegradation performance of our sample was still in progress.

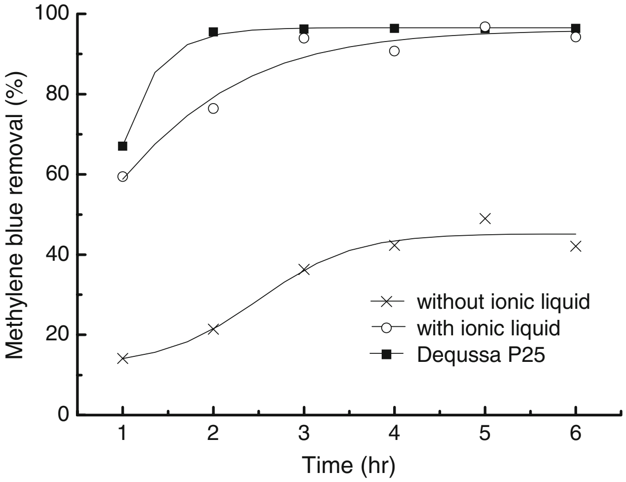

Fig. 7 The photodegradation of methylene blue in aqueous suspension containing TiO_2 sample treated without and with ionic liquid under UV irradiation

Conclusion

1. Ionic liquid could play a role in driving surface crystallization of amorphous TiO_2 to the anatase phase by retaining a suitable amount of water through a dissolution-crystallization mechanism and there existed an analogy between our thermal annealing treatment with ionic liquid/water system and hydrothermal treatment system.
2. In this study, we observed that different temperature effects and microwave heating effect were observed for different types of ionic liquid. Based upon these observations, it was pointed out that we could get better anatase crystallinity and good photodegradation performance when the system containing ionic liquid having higher water-adsorbing ability and microwave heating annealing were used simultaneously.

Acknowledgements The authors are grateful to Ministry of Economic affair (MOEA) of Taiwan for funding support. A complementary financial support from National Science Council of Taiwan is acknowledged.

References

1. Burnside SD, Shklover V, Barbě C, Comte P, Arendse F, Brooks K, Grãtzel M (1998) Chem Mater 10:2419. doi:10.1021/cm980702b
2. Chiappe C, Pieraccini D (2005) J Phys Org Chem 18:275. doi:10.1002/poc.863
3. Antonietti M, Kuang D, Smarsly B, Zhou Y (2004) Angew Chem Int Ed 43:4988. doi:10.1002/anie.200460091
4. Zhou Y (2005) Curr Nanosci 1:35. doi:10.2174/1573413052953174
5. Jiang J, Yu S, Tao W, Ge H, Zhang G (2005) Chem Mater 17:6094. doi:10.1021/cm051632t
6. Zhou Y, Antonietti M (2003) J Am Chem Soc 125:14960. doi:10.1021/ja0380998
7. Nakashima T, Kimizuka N (2003) J Am Chem Soc 125:6386. doi:10.1021/ja034954b
8. Yoo KS, Choi H, Dionysiou D (2004) Chem Commun 17:2000–2001. doi:10.1039/b406040g
9. Yoo KS, Choi H, Dionysiou D (2005) Catal Commun 6:259. doi:10.1016/j.catcom.2005.01.010
10. Yoo KS, Lee TG, Kim J (2005) Microporous Mesoporous Mater 84:211–217. doi:10.1016/j.micromeso.2005.05.029
11. Galema SA (1997) Chem Soc Rev 26:233. doi:10.1039/cs9972600233
12. Hart JN, Cervini R, Cheng YB, Simon GP, Spiccia L (2004) Sol Energy Mater Sol Cells 84:135. doi:10.1016/j.solmat.2004.02.041

13. Choi H, Kim YJ, Varma RS, Dionysiou D (2006) Chem Mater 18:5377. doi:10.1021/cm0615626
14. Liu Y, Li J, Wang M, Li Z, Liu H, Yang PHX, Li J (2005) Cryst Growth Des 5:1643. doi:10.1021/cg050017z
15. Liu YH, Lin CW, Chang MC, Shao H, Yang ACM (2007) (Europacat VIII) 26–31 August 2007 Turku / Åbo, Finland
16. Dominguez-Vidal A, Kaun N, Ayora-Cañada MJ, Lendl B (2007) J Phys Chem B 111:4446. doi:10.1021/jp068777n
17. Katayanagi A, Nishikawa K, Shimozaki H, Miki K, Westh P, Koga Y (2004) J Phys Chem B 108:19451. doi:10.1021/jp0477607
18. Salou M, Kiyozumi Y, Mizukami F, Nair P, Maeda K, Niwa S (1998) J Mater Chem 8:2125. doi:10.1039/a803085e
19. Yanagisawa K, Yamamoto Y, Feng Q, Yamasaki N (1998) J Mater Res 13:825. doi:10.1557/JMR.1998.0106
20. Yu J, Wang G, Chemg B, Zhou M (2007) Appl Catal B 69:171
21. Pouilleau J, Devilliers D, Groult H (1997) J Mater Sci 32:5645. doi:10.1023/A:1018645112465
22. Shin H, Jung HS, Hong KS, Lee JK (2005) J Solid State Chem 178:15. doi:10.1016/j.jssc.2004.09.035
23. Cooper ER, Andrews CD, Wheatley PS, Webb PB, Wormald P, Morris RE (2004) Nature 430:1012. doi:10.1038/nature02860
24. Tran CD, Paolilacedra SHD, Oliverira D (2003) Appl Spectrosc 57:152. doi:10.1366/000370203321535051
25. Wang Y, Li H, Han S (2006) J Phys Chem B 110:24646. doi:10.1021/jp064134w
26. Liu W, Zhao T, Zhang Y, Wang H, Yu M (2006) J Solut Chem 35:1337. doi:10.1007/s10953-006-9064-7
27. Tompsett GA, Conner WC, Yngvesson KS (2006) ChemPhysChem 7:296. doi:10.1002/cphc.200500449
28. Komarneni S (2003) Curr Sci 85:1730
29. Wilson GJ, Will GD, Frost RL, Montgomery SA (2002) J Mater Chem 12:1787
30. Murrugan AV, Samuel V, Ravi V (2006) Mater Lett 60:479. doi:10.1016/j.matlet.2005.09.017
31. Xu Y, Tian Z, Wang S, Hu Y, Wang L, Ma Y, Hou L, Yu J, Lin L (2006) Angew Chem Int Ed 45:3965. doi:10.1002/anie.200600054