

Preparation and characterization of nanoporous TiO₂ particle using ionic liquid as an effective template

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Introduction

Titanium dioxide (TiO₂ titania) has received wide spread attention due to its numerous applications in, for example, photocatalysis and catalyst support [1]. The research on TiO₂ technologies includes preparation of TiO₂ particles with controlled nanostructure and enhanced surface area, in an attempt to further enhance catalyst activity and process efficiency. So, an important aspect in the preparation of TiO₂ catalyst is the development of TiO₂ particles with high surface area, controlled porosity and tailor-designed pore size distribution. Recently, the preparation of mesoporous TiO₂ materials with high surface area was the focus of several studies. Indeed, various techniques of surfactant templating have been employed on preparing such a TiO₂ particle [2-5].

Ionic liquids (ILs) are an exceptional type of solvent consisting practically only of ions. ILs have little vapor pressure and possess tunable properties [6-7]. In this study, various types of room temperature ionic liquids were used as an effective template in sol-gel methods to synthesize nanostructured TiO₂ particles with high surface area. The low vapor pressure of the ILs could assist in reducing the problem of gel shrinkage during sol ageing and gel drying, which could prevent reduction of surface area [8]. Moreover, the IL can be used successfully as a self-assembling template like long chain surfactants. In this study, nanostructured TiO₂ particles with high surface area were successfully synthesized using an effective room temperature ionic liquid (RTIL).

Experimental

Titanium tetraisopropoxide (TTIP, 97%, Aldrich) was initially mixed with isopropanol (99%, Fisher) at a C₃H₇OH/TTIP molar ratio of 30. One of ionic liquids as illustrated in Table 1 was then added into the mixture at a IL/TTIP molar ratio of 3. Hydrolysis and condensation were conducted at room temperature, by adding the mixed solution slowly into deionized water up to a H₂O/TTIP molar ratio of 100 and stirred for 30 min. The product was recovered by

filtration, washed thoroughly with deionized water and dried at 100 °C for 2 h. The entrapped IL and organics were extracted by refluxing the above powder in acetonitrile (HPLC grade, Fisher) at room temperature for 12 h. The subsequent product was also recovered by filtration, washed and dried at 100°C. The final products were treated by heating at various temperatures for 2 h. The C-H stretching vibrational IR spectra of the IL at 2900 cm⁻¹ disappeared after solvent extraction. The structural properties of TiO₂ particle were determined from the nitrogen isotherms at 77 K measured in a Micromeritics ASAP 2020 apparatus. All samples were degassed with He for 4 hours at 100 °C prior to measurement. The XRD patterns were collected with a Siemens (D500) powder X-ray Diffractometer using CuK_α radiation (wavelength 1.5406 Å) to determine the crystal structure and crystallinity of the TiO₂ particles.

Table 1. List of room temperature ionic liquids

Symbol	Full name
[Bmim][PF ₆]	1-Buthyl-3-methylimidazolium hexafluorophosphate
[Bmim][BF ₄]	1-Buthyl-3-methylimidazolium tetrafluoroborate
[Bmim][CF ₃ SO ₃]	1-Buthyl-3-methylimidazolium trifluoromethanesulfonate
[Hmim][PF ₆]	1-Hexyl-3-methylimidazolium hexafluorophosphate
[Omim][PF ₆]	1-Octyl-3-methylimidazolium hexafluorophosphate

Results and Discussion

The various ionic liquids were employed in preparation of TiO₂ particle to investigate an influence on composition of ILs. The effect of anion part in the IL on the formation of crystalline phase is illustrated in Fig 1. It was observed that the TiO₂ particles prepared with IL containing [PF₆⁻] possessed relatively higher crystalline structure. It is worthy to note that these TiO₂ particles contain crystalline anatase phase, although they were only dried at low temperature.

The N₂ isotherms of obtained sample using [Bmim][PF₆] are illustrated in Fig. 2. This isotherm pattern exhibits type IV-like, which is a characteristic of mesoporous materials [9]. A sharp inflection of adsorbed volume (hysteresis loop) and a relatively steep desorption branch indicate that a distribution of various sized cavities but with the same entrance diameter [10]. The small-angle diffraction pattern (in Fig. 2) show one single peak, which also indicates disordered mesostructure without long-range order in the pore arrangement.

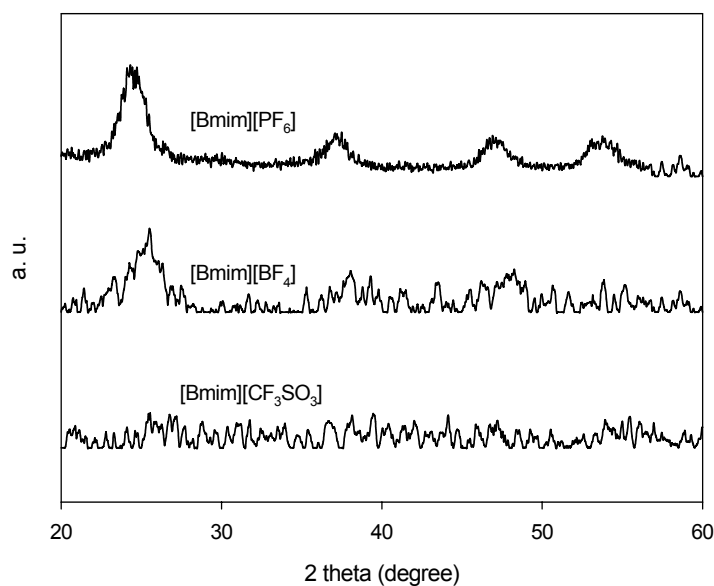


Figure 1. XRD patterns of TiO₂ particles prepared using various ionic liquids with heat treatment at 100 °C.

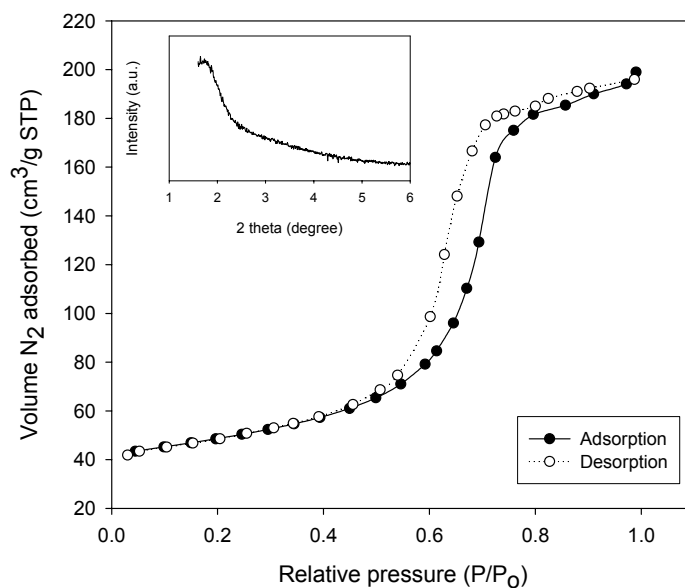


Figure 2. N₂ adsorption-desorption isotherms and XRD pattern (inserted) of sample prepared using [Bmim][PF₆] with heat treatment at 100 °C.

The mechanism for the formation of these TiO₂ particles is an effective aggregation of the TiO₂ particles with a self-assembled IL. The IL plays a significant role in the formation of a stable sol-gel network with ordered array of Ti and O, not accompanying shrinkage and collapse of the gel network. Regarding the typical structure of IL, water molecules preferentially

interact with $[\text{PF}_6^-]$ through hydrogen bond whereas the imidazolium rings barely interact with water [11-12]. Thus, the cation of IL, $[\text{Bmim}^+]$ should be arrayed into opposite direction to $[\text{PF}_6^-]$ bonded with water and then they start to pile up and stack by possibly π - π interaction or other noncovalent interactions of imidazolium rings. This indicates that IL can be used successfully as a self-assembling template like long chain surfactants. Consequently, the titanium precursor is hydrolyzed and condensed around the self-assembled IL structure combined with water at a controlled rate, resulting in the formation of highly porous crystalline TiO_2 .

The described mechanism is also supported by the result that the anion part of IL has significant influence on the structure of produced TiO_2 particle as shown in Fig. 3. The TiO_2 particles prepared with IL containing $[\text{PF}_6^-]$ showed the highest structural stability by heat treatment. Moreover, this sample possessed the highest surface area among the samples with comparable crystallinity as shown in Fig 4. This is mainly attributed to the formation of homogeneous distribution of the pores in the matrix by effective templating of IL. The strength of the hydrogen bonds increases in the order $[\text{PF}_6^-] < [\text{BF}_4^-] < [\text{CF}_3\text{SO}_3^-]$. The stronger hydrogen bonds can prevent the formation of π - π stacks of imidazolium rings leading a self-assembling of ILs and enhancing hydrolysis in the presence of excessive amount of water. Thus, balanced strength between hydrogen bond and noncovalent interactions is essential to enhance the templating effect of IL. Indeed, little templating role of IL with $[\text{CF}_3\text{SO}_3^-]$ was observed.

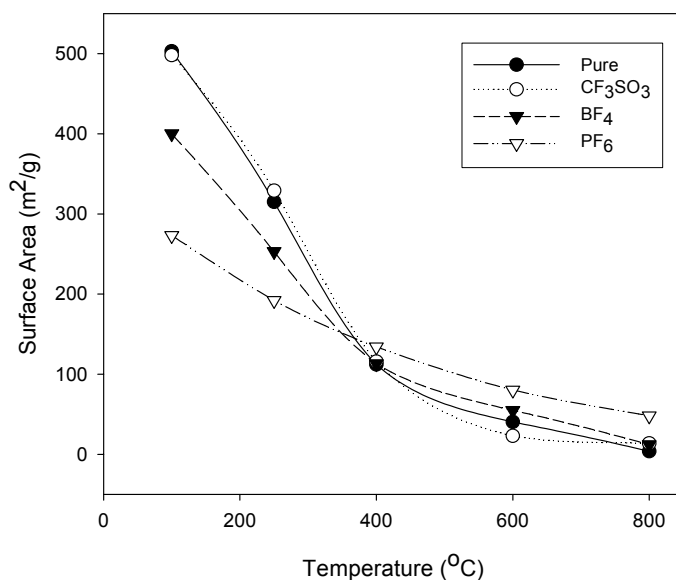


Figure 3. The effect of anion parts in ionic liquid with $[\text{Bmim}^+]$ on surface area of TiO_2 particles obtained with heat treatment at various temperatures.

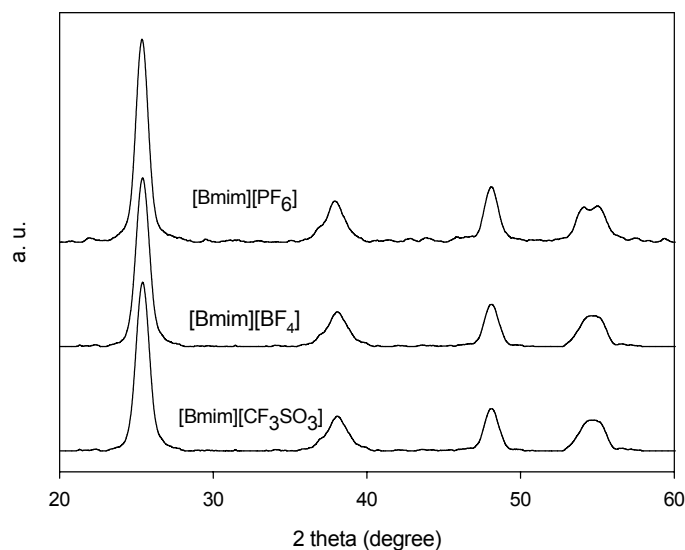


Figure 4. XRD patterns of TiO₂ particles prepared using various ionic liquids with heat treatment at 400 °C.

The effect of cation parts in IL on the pore structure of TiO₂ particle is illustrated in Table 1. The higher pore size and volume were obtained with larger cation part of ionic liquid. The result is directly attributed to the large size of cation stack producing porous structure of TiO₂ particle. Moreover, the relatively stable structure of TiO₂ prepared with [Bmim] [PF₆] with heat treatment was observed. The result is mainly attributed to the fact that the π - π interaction or other noncovalent interactions of imidazolium rings over [Omim] [PF₆] is diminished due to its longer alkyl chain length.

Table 2. The effect of cation parts in ionic liquid with [PF₆] on pore size and volume of TiO₂ particles obtained with heat treatment at various temperatures.

Cation part	[Bmim]				[Hmim]				[Omim]			
Temperature (°C)	100	400	600	800	100	400	600	800	100	400	600	800
BET surface area (m ² /g)	273	134	80	48	196	147	100	30	158	152	86	24
BJH pore volume (cm ³ /g)	0.32	0.27	0.25	0.22	0.47	0.6	0.54	0.17	0.33	0.68	0.26	0.19

Conclusion

Nanostructured TiO₂ particles with high surface area were successfully synthesized with room temperature ionic liquid by sol-gel method. The result shows that this approach leads to the formation of sponge-like mesoporous TiO₂ particles with anatase phase even low temperature. The product has a disordered nanostructure with comparable sized entrances. The mechanism for the formation of this structure is an effective aggregation of the TiO₂ particles with a self-assembled ionic liquid. Especially, an anion part of ionic liquid was crucial due to its strength of hydrogen bond with water. Among the anions used in this study, it was found that [PF₆⁻] possessed balanced interactions to form a desirable pore structure. In addition, a cation part of ionic liquid gave an influence on determining the pore size and volume of TiO₂ particles. Thus, [Bmim][PF₆] was identified as an effective self-assembling template in this new methodology.

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