이온성 액체를 이용한 나노 구조 TiO₂의 합성과 응용

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Synthesis of Nano-Structured TiO₂ using Ionic Liquids as an Effective Template

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Introduction

Currently, titanium dioxide (TiO_2, titania) has received wide spread attention due to its numerous applications in, for example, photocatalysis and catalyst support [1]. An important aspect in the preparation of TiO_2 material for several applications is the development of TiO_2 powders with small grain size, high surface area, controlled porosity and tailor-designed pore size distribution in an attempt to enhance catalytic activity and process efficiency. Recently, several studies on the preparation of mesoporous TiO_2 materials with high surface area using a surfactant template have been reported elsewhere [2,3].

Ionic liquids (ILs) are an exceptional type of solvent consisting practically only of ions. It was reported that 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 [4]. IL has little vapor pressure and possesses tunable properties [5]. IL as a template in sol-gel methods can be used to synthesize highly porous TiO_2 particles. This approach involves the use of water immiscible room temperature ionic liquid (WIRTIL) as an additional solvent with alcohol solvents. Moreover, the WIRTIL can be used successfully as a self-assembling template like long chain surfactants. In this work, anatase-containing nanostructured TiO_2 particles with high surface area was prepared using WIRTIL and characterized by XRD, N_2 physisorption, IR, EDX and TEM.

Experimental

Titanium tetraisopropoxide (TTIP, 97%, Aldrich) was initially mixed with isopropanol (99%, Fisher) at a molar ratio of $C_3H_7OH/TTIP = 30$. IL (1-butyl-3-methylimidazolium hexafluorophosphate, $[bmim][PF_6]$) was added into the mixture at a molar ratio of IL/TTIP = 3. Hydrolysis and condensation

were conducted at room temperature, by adding the mixed solution slowly into deionized water up to a molar ratio of $H_2O/TTIP = 100$ and stirred for 30 min. The product was recovered by filtration, washed thoroughly with deionized water and dried at 100 ^{o}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 ^{o}C. The final products were treated by heating at various temperatures for 2 h. The C-H stretching vibrational IR spectra of the IL around 2900 cm^{-1} disappeared after solvent extraction. This means that most of the IL and other organics were removed by extraction. The energy dispersive X-ray (EDX) measurement also showed the presence of only Ti and O elements in the samples.

Results and Discussion

Powder X-ray diffraction (XRD) patterns of prepared sample are shown in Fig. 1. All the peaks in the pattern are assigned to anatase TiO_2. The small-angle diffraction pattern shows one single peak, which indicates disordered mesostructure without long-range order in the pore arrangement. The N_2 isotherms of prepared sample are illustrated in Fig. 2. This isotherm pattern exhibits type IV-like, which is a characteristic of mesoporous materials based on the IUPAC classification [6]. A sharp inflection of adsorbed volume at $P/P_o = 0.45$ (hysteresis loop) and a relatively steep desorption branch indicate a distribution of various sized cavities but with the same entrance diameter [7]. This means the existence of mesoporosity with similar sized entrances in the material, being in agreemenet with the small-angle diffraction peak in Fig. 1. The BJH pore size distribution based on the adsorption branch of isotherm is relative narrow with an average pore diameter of 4.5 nm. The narrow pore size
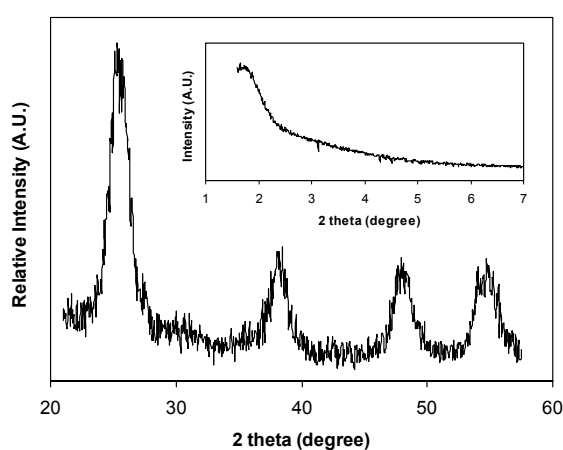
Figure 1. XRD patterns of TiO_2 particles. Insert is the small-angle diffraction pattern.
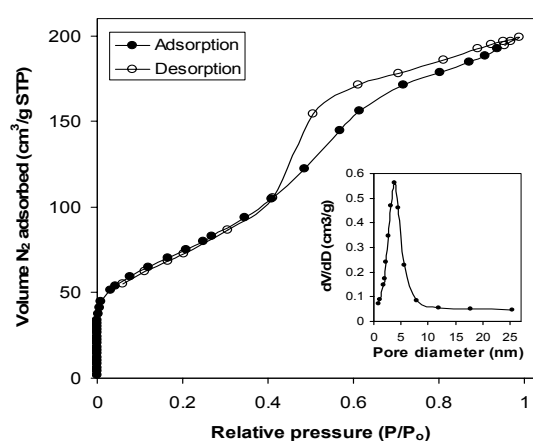
Figure 2. N_2 adsorption-desorption isotherms and pore size distribution (inserted) of TiO_2 sample.

distribution indicates good homogeneity of the pores. The BET surface area and specific pore volume of the material are about 273 m^2/g and 0.308 cm^3/g, respectively. The TEM image of TiO2 particles calcined at 100 ^oC as shown in Fig. 3 exhibits a disordered wormhole-like pore structure which is consistent with the small–angle XRD result. The pore size estimated by TEM analysis is in agreement with N_2 adsorption data as well.

The surface area of samples decreased gradually with IL addition up to IL/TTIP ratio of 3. Crystalline anatase peaks were observed from the samples with IL/TTIP ratio above 3. This means that at least three mols of IL per each mol of titanium alkoxide precursor are necessary to form crystalline TiO_2 particles at this temperature (100^oC). Due to the high vapor pressure of the organic solvents used in conventional sol-gel methods, solvent evaporation causes gel shrinkage and reduces the pore volume and surface area [4]. The pore volume and BET surface area of the TiO_2 particles prepared with IL decreased from 0.296 to 0.207 cm^3/g and from 282 to 47.9 m^2/g, respectively, upon heat treatment from 100 to 800 °C as presented in Fig. 4. On the other hand, those of control TiO_2 particles decreased rapidly from 0.707 to 0.046 cm^3/g and from 570 to 3.76 m^2/g, respectively. The pore volume and surface area of control TiO_2 particles after calcination at around 700°C were small enough to cause nucleation of rutile due to increase in contact points between anatase and rutile. However, the TiO_2 particles prepared with IL still kept highly porous structure at that temperature, which suppressed the phase transformation. The crystallite size of the TiO_2 particles prepared with IL was less than 20 nm even at 800 °C heat treatment. Indeed, the surface area of TiO_2 particles prepared without IL is only 112 m^2/g after calcination at 400 ^oC. This treated sample possesses comparable anatase crystallinity with the sample prepared with IL at 100 ^oC.
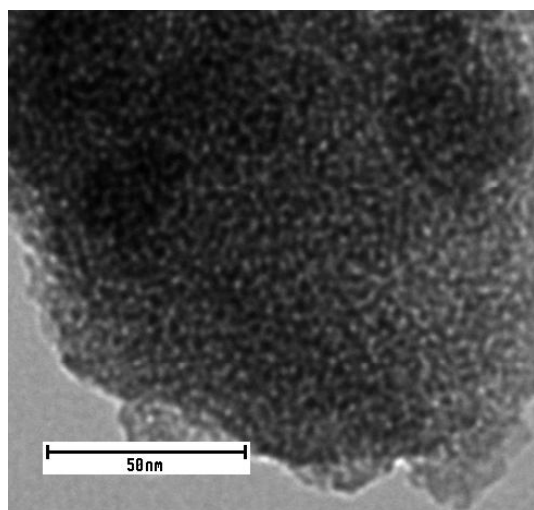

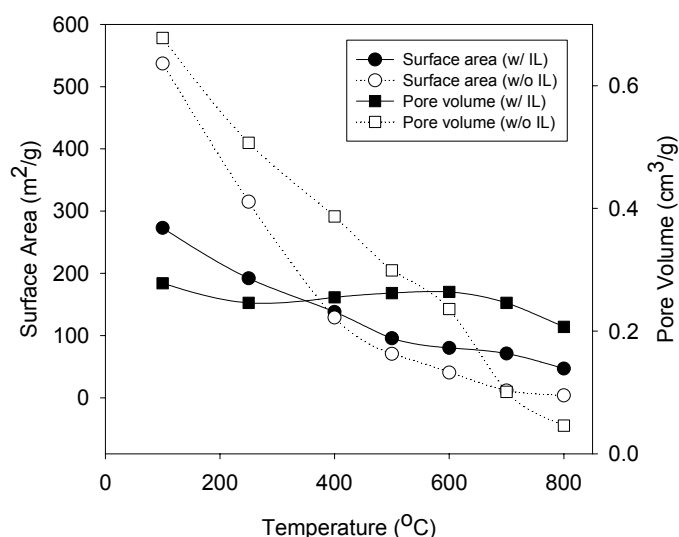Figure 3. TEM image of TiO$_2$ particles calcined at 100^oC.

Figure 4. Effect of post-treatment temperature on the surface area and pore volume over samples prepared with and without ionic liquid.

A possible mechanism for the formation of this nanostructured TiO_2 particle might be an effective aggregation of the TiO_2 particles with a self-assembled IL in the sol. The IL can play an important role in achieving longer ageing time for the formation of a stable sol-gel network with ordered array of Ti and O, not accompanying shrinkage and collapse of the gel network. Considering the special structure of IL, water molecules in IL preferentially interact with $[PF_6^-]$ strongly through hydrogen bond whereas the imidazolium ring does not interact with water [8]. Accordingly, the cation of IL, $[bmim^+]$, should be arrayed into opposite direction to $[PF_6^-]$ 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, without the formation of ordered micelles by hydrophilic and hydrophobic molecular chains, 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.

Conclusion

Anatase-containing nanostructured TiO_2 particles with high surface area and narrow nanopore structure have been synthesized at low temperature using a water immiscible room temperature ionic liquid. The mechanism for the formation of this structure is both hydrogen bond of $[PF_6^-]$ and π-π interaction of imidazolium rings. We expect that this new methodology can be used as catalyst and support in several applications of nanotechnology and environmental remediation.

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