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Ionic liquid assisted preparation of nanostructured TiO_2 particles

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Anatase-containing nanostructured TiO_2 particles with high surface area have been synthesized using a water immiscible room temperature ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) as an effective additional solvent by the sol–gel method at low temperature.

Currently, titanium dioxide photocatalysis is receiving widespread attention and it is accepted as one of the most promising technologies for the complete destruction and elimination of organic contaminants in the environment.[1] An important aspect in the preparation of TiO_2 catalysts for environmental 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 further enhance catalytic activity and process efficiency. Recently, the preparation of mesoporous TiO_2 materials with high surface area using surfactant template was the focus of several studies.[2]

In addition to grain size, the phase and the degree of crystallinity of the TiO_2 particles play an important role. If possible, it is beneficial to synthesize crystalline TiO_2 nanostructures at ambient temperature since the usual sol–gel methods performed in excessive water-containing solvent mixtures result in amorphous TiO_2 particles which do not possess photocatalytic activity and need a high temperature heat treatment for crystallization. This will save energy in the preparation steps and could also allow for a wider selection of support materials when such procedures are applied to prepare immobilized TiO_2 catalyst.

Ionic liquids (ILs) are an exceptional type of solvent consisting virtually only of ions. ILs have practically no vapor pressure and possess tunable solvent properties.[3] In this study, we used an IL as a template in sol–gel methods 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. The low vapor pressure of the IL could assist in reducing the problem of gel shrinkage during sol ageing and gel drying, which could prevent reduction of surface area.[4] Moreover, the WIRTIL containing a small amount of water can be well blended with alcohol solvents to reduce the rate of hydrolysis reaction of the titanium alkoxide precursor, which can yield more porous structures. Here we report the successful preparation of anatase-containing nanostructured TiO_2 particles with high surface area using WIRTIL.

The synthesis was carried out as follows. Titanium tetraisopropoxide (TTIP, 97%, Aldrich) as the sol–gel precursor was first mixed with isopropanol (99%, Fisher) at a C_3H_7OH/TTIP molar ratio of 30. IL (1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6]) was then added into the mixture at a [bmim][PF_6]/TTIP molar ratio of 3 and stirred for 10 min. Hydrolysis and condensation were conducted at room temperature, by adding the mixed solution slowly into deionized water up to a H_2O/TTIP molar ratio of 100. The mixed solution was stirred vigorously for 30 min. The product was recovered by filtration, washed thoroughly with deionized water and dried at 100 °C for 2 h. A light-yellowish-white powder was obtained. The entrapped IL and organics were extracted by refluxing the above powder in acetonitrile (Fisher, HPLC grade) at room temperature for 12 h. The subsequent product was also recovered by filtration, washed and dried at 100 °C. The final product was a white powder. 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.

All the peaks in the X-ray powder diffraction (XRD) pattern shown in Fig. 1 are assigned to anatase TiO_2 without any indication of the other crystalline products and they are relatively broad due to the nanosize of the crystals. It is worthy to note that the TiO_2 particles contain crystalline anatase phase, although they were only dried at low temperature. Crystallinity of 37% was approximately calculated from the mass fraction of crystal, based on the XRD peak area and base line. The crystallite size was around 5 nm and it was calculated using Scherrer's equation based on the XRD peak broadening analysis at 101. The small-angle diffraction pattern shows one single peak, which indicates a disordered mesostructure without long-range order in the pore arrangement. The N_2 isotherms of the obtained sample are illustrated in Fig. 2. This isotherm pattern exhibits type IV-like behavior, which is a characteristic of mesoporous materials based on the IUPAC classification.[5] Practically no micropores are present. 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.[6] This means the existence of mesoporosity with similar sized entrances in the material, being in agreement with the small-angle diffraction peak in Fig. 1. The pore size distribution based on the adsorption branch of the isotherm is relatively narrow with an average pore diameter of 4.5 nm. The narrow pore size distribution indicates good homogeneity of the pores. The BET surface area and pore volume of the material are about 273 $m^2 g^{-1}$ and 0.308 $cm^3 g^{-1}$, respectively. The TEM image (not shown) of this sample exhibits a disordered sponge-like pore structure which is consistent with the small-angle XRD result.

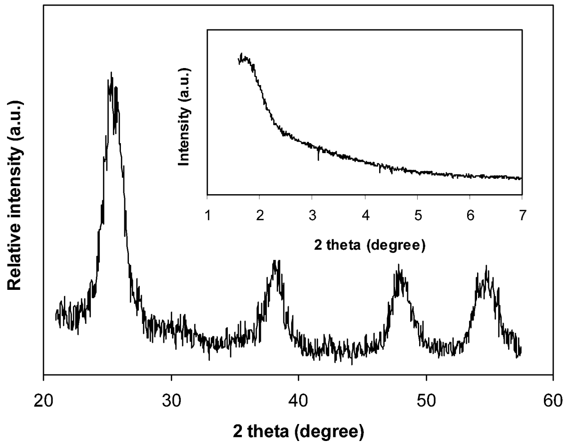

Fig. 1 XRD patterns of anatase nanostructured TiO_2 particles. Insert is the small-angle diffraction pattern of sample.

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It can be seen from Table 1 that the surface area of samples decreased gradually with IL addition up to an IL/TTIP ratio of 3. After this point, the surface area of the samples did not change significantly. Crystalline anatase peaks were observed from the samples with an 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 °C). Due to the high vapor pressure of the organic solvents used in conventional sol–gel methods, solvent evaporation causes gel shrinkage and consequently reduces the pore volume and surface area.[6] Indeed, the surface area of TiO_2 particles prepared without IL (sample 1) is only 112 $m^2 g^{-1}$ after calcination at 400 °C. This treated sample possesses anatase crystallinity comparable with the sample prepared with IL (sample 4) at 100 °C. In this modified sol–gel method, the surface area and crystallinity of the samples were hardly affected by the amount of H_2O, as shown in Table 1. This result can be attributed to the fact that the WIRTIL can be blended homogeneously with TTIP in the alcohol solvent. This solvent mixture as a template plays an essential role in building porous crystalline TiO_2 particles.

A possible mechanism for the formation of these nanostructured TiO_2 particles 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 an ordered array of Ti and O, without accompanying any 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 bonding whereas the imidazolium ring does not interact with water.[7] Accordingly, the cations of IL, $[bmim^+]$ should array in the opposite direction to $[PF_6^-]$ bonded with water, and then start to pile up and stack, possibly by π–π interactions or other noncovalent interactions between 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 condenses around the self-assembled IL structure combined with water at a controlled rate, resulting in the formation of highly porous crystalline TiO_2. The so-called reaction limit aggregation (RLA) has also been proposed recently to lead to the formation of comparable pore structure.[8]

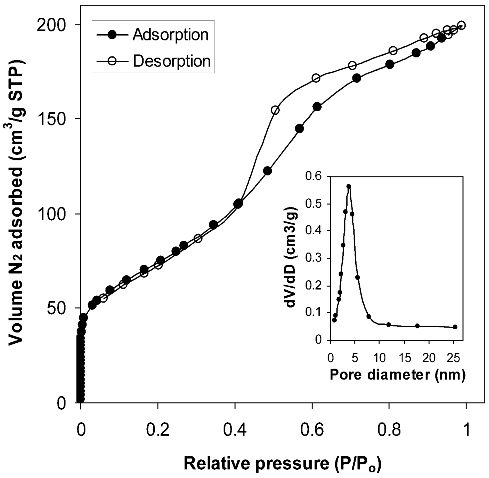

Fig. 2 Nitrogen adsorption–desorption isotherms and pore size distribution (inserted) of TiO_2 sample.

Table 1 BET surface area of TiO_2 particle with various compositions

Entry	IL/TTIP	H_2O/TTIP	BET area/$m^2 g^{-1}$
1	0	100	570 (112)[a]
2	1	100	478
3	2	100	379
4	3	100	273
5	4	100	267
6	5	100	253
7	3	10	275
8	3	25	264
9	3	50	268
10	3	75	258
11	3	150	263

[a] The value was obtained after 400 °C calcination of sample 1 that has comparable crystallinity with sample 4.

Further heat treatment aimed at improving the crystallinity of the nanoparticles showed that TiO_2 particles prepared with IL exhibited better thermal stability of their pore structure. The pore volume and BET surface area of the TiO_2 particles prepared with IL decreased from 0.296 to 0.207 $cm^3 g^{-1}$ and from 282 to 47.9 $m^2 g^{-1}$, respectively, upon heat treatment from 20 °C to 800 °C and all crystalline materials were the anatase phase. On the other hand, those of TiO_2 particles prepared without IL decreased rapidly from 0.707 to 0.046 $cm^3 g^{-1}$ and from 570 to 3.76 $m^2 g^{-1}$, and anatase was formed between 250–400 °C and completely transformed to rutile at 800 °C. Photocatalytic experiments showed that the photocatalytic activity of TiO_2 nanoparticles prepared with IL at 100 °C was comparable to that of TiO_2 prepared without IL at 300–400 °C. This means that this TiO_2 sample possesses anatase phase crystallinity. Therefore, we believe the high surface area of our sample is responsible for the formation of mesopores with crystallinity. Further investigations have to be carried out to gain further understanding of the formation mechanism, thermal stability, catalytic properties, and solid state chemistry of the prepared TiO_2 particles and to increase the crystallinity of the TiO_2 nanoparticles prepared by this method.

In conclusion, anatase-containing nanostructured TiO_2 particles with a high surface area and narrow nanopore structure have been synthesized at low temperature using a water immiscible room temperature ionic liquid. We expect that this new methodology can be used in several applications of nanotechnology and environmental remediation.

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