Synthesis and Photocatalytic Activities of Ionic Liquid Assisted Preparation of TiO₂ Nanoparticles

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The well-crystallized anatase nanoparticles were synthesized by one-step routes under low-temperature using room temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) as an additional solvent with water. The photocatalytic properties of TiO₂ nanoparticles were evaluated by photocatalytic degradation experiments of methyl orange. The TiO₂-ionic liquid nanoparticles still hold a high photocatalytic activity after the catalyst was recycled 9 times. The TiO₂ nanoparticles show a higher photocatalytic activity than the TiO₂ with pure water and commercial TiO₂ (P25), which may be related to the high crystallinity, the pure anatase phase, small size and the enhanced absorbability associated with the existence of [BMIM][BF₄].

Key Words: Ionic liquids, TiO₂, Nanoparticles, Photocatalysis.

INTRODUCTION

Photocatalysis process is believed to be capable of removing organic pollutants into CO₂, H₂O and harmless intermediate organic compounds in water by advanced oxidation techniques¹⁻³. The principle of photocatalytic reaction is implemented by the excitation of electrons from the valence band to the conduction band of the semiconductor upon light irradiation, by which the excited electrons and holes can be used in reduction and oxidation reactions, respectively. Over the past few decades environmental purification using TiO₂ as a photocatalyst has attracted a great deal of attention because of its high activity, chemical stability, robustness photodegradation, low toxicity, low pollution load and available at low cost. However, the photo-generated holes are easy to recombine with the photo-induced electrons and thus greatly reduced the photocatalytic efficiency of TiO₂⁴⁻⁶. It remarkably, anatase titania obtains much more attention than the others because it is a highly efficient photocatalyst^{7,8}. Traditional methods like sol-gel, hydrothermal processes, chemical/physical vapour deposition and electrodeposition have been extensively reported, but most of them involve high temperature annealing to improve the crystallinity, which can cause the decrease of specific surface area. Recent studies have shown that particle size, morphology, crystallinity, phase purity and surface area have been shown to exert a significant influence on the photocatalytic activity of TiO₂⁹⁻¹¹. Hence, more attentions have been focused on the low temperature preparation of nano-crystalline titania.

Recently, attempts have been made to fuse two broad areas of research, the nanoparticles and the ionic liquids (ILs) are an exceptional type of solvent consisting virtually only of ions. Ionic liquids have practically no vapour pressure and possess tunable solvent properties^{12,13}. Now, the investigation indicated ionic liquids for the preparation of hybrid nanomaterials has novel properties¹⁴⁻¹⁶. Many common ionic liquids consist of nitrogen-containing organic cations and inorganic anions. Their chemical and physical properties can be tuned to a range of potential applications by varying the nature of cations and anions. Furthermore, the desired structures are easily synthesized and controlled. In particular, imidazolium-based are favourable because of their air, water and electrochemical stability and wide liquid range. Recently they are increasingly finding applications in nanoscience¹⁴. The potential application of ionic liquids in the synthesis of metallic architectures^{17,18} and metal compounds¹⁹ is particularly interesting because their electrostatic and coordination effects should influence and may even facilitate this synthesis. Ionic liquids seems to be ideal for the stabilization of metal nanoparticles. The intrinsic ionic charge, high polarity, high dielectric constant and supra-molecular network of ionic liquids provide an electrostatic protection according to the Derjaguin-Landau-Verwey-Overbeek theory in the form of a protective shell of metal nanoparticles.

In this study, we used an ionic liquid as a template in sol-gel low hydro-treatment methods to synthesize highly active titania photocatalyst. This approach involves the use of room

temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM] [BF₄]) as an additional solvent with water. The low vapour pressure of the ionic liquid could prevent reduction of surface area. Moreover, crystallinity of titania particle can be controlled in the water containing ionic liquid is owing to reduce the rate of hydrolysis reaction of the titanium alkoxide precursor.

EXPERIMENTAL

Tetrabutyltitanate, 1-methylimidazole, 1-bromobutane, sodium fluoborate were purchased from the Shanghai Chemical Reagent Corporation. The commercial TiO₂ (P25) purchased from Degussa Corporation. All reagents were used as received without further purification. The water used was purified through a Millipore system.

Synthesis of ionic liquid: The ionic liquid of 1-butyl-3-methylimidazoliumtetrafluoroborate ([BMIM] [BF₄]) was synthesized using reported method²⁰. The compound was analyzed by ¹H NMR, ¹³C NMR and FT-IR spectroscopy and the spectral data tally with the structure.

¹H NMR (300 MHz, acetone-d₆): δ 9.51 (s, 1H, CH), 7.89 (s, 1H, CH), 7.83 (s, 1H, CH), 4.42 (t, 2H, CH₂), 4.09 (s, 3H, CH₃), 1.92 (m, 2H, CH₂), 1.38 (m, 2H, CH₂), 0.93 (t, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 137.44, 124.34, 122.98, 49.72, 36.53, 32.48, 19.62, 13.37. IR (cm⁻¹): 3144.76, 3071.25, 2960.55, 2935.58, 2873.65, 1571.90, 1465.51, 1382.92, 1337.38, 1170.21, 1062.29, 754.75.

Synthesis of TiO₂ nanoparticles: 1.6 mL of tetrabutyl-titanate was added dropwise to the mixture with 7 mL [BMIM] [BF₄] and 7 mL water under rigorous stirring. White precipitates of hydrous oxides were produced instantly and the mixture was stirred for 2 h at room temperature. The mixture was then transferred to a Teflon-lined stainless steel autoclave and heated at 100 °C for 24 h. After cooling, the product (TiO₂-IL) was filtered, washed with deionized water several times and dried in air. For comparison, another TiO₂ sample (TiO₂-W) was prepared in pure water under the same conditions.

Photocatalytic activities: The photocatalytic activity of TiO₂ was studied by measuring the photodegradation rates of methyl orange. Methyl orange was selected as a model pollutant because it is a common contaminant in industrial waste water and it has good resistance to light degradation. In general, for each test, TiO₂ nanoparticles were dispersed in about 20 mL of methyl orange solution under vigorous stirring. The mixture was further stirred in the dark for 60 min to reach the adsorption equilibrium prior to the photocatalytic test. The mixture was irradiated by a 250 W high pressure Hg lamp and solar radiation to result in the degradation of methyl orange. During the reaction, the mixture was magnetically stirred in a water bath at 25 °C. After definite time intervals, 2.2 mL of sample solution was withdrawn and centrifuged. The residual concentration of methyl orange in each sample was measured by a UV-VIS spectrophotometer at the characteristic absorption band of methyl orange (460 nm). The maximal absorbency of methyl orange solution abides by Lambert-Beer law, so decolourization ratio, (C₀-C)/C₀, can be simply calculated from equation (A₀-A)/A₀.

Characterization of TiO₂ nanoparticles: TEM analysis was conducted on a Philips Tecnai-12 field emission trans-

mission electron microscope at 120 KV. The high-resolution TEM images were obtained by a Philips model JEM-2100F electron microscope at 200 KV. EDX analysis was performed on an energy dispersive X-ray spectrometer attached to the TEM of the JEOL model JEM-2100F. XRD measurement was carried out on PANALYTICAL/X'PERT PROMPD diffractometer at 40 kV with CuK_α radiation (λ = 0.1542 NM). The UV-VIS absorption spectra were analyzed by a TU-1810 SPC spectrophotometer. FTIR spectra were recorded on a IRAffinity-1 spectrometer. Measurements were performed with pressed pellets which were made using KBr powder as diluent. The irradiation source of photocatalytic reactions was a 250 W high pressure mercury lamp.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the TiO₂ nanoparticles prepared under different conditions. The anatase phase was produced in TiO₂ nanoparticles prepared from the mixture solvent of ionic liquid and water (Fig. 1a). However, it is clear that titania prepared from pure water contains Brookite phase at 2θ = 31° (Fig. 1b) besides the anatase phase. The XRD patterns of Titan show broad peaks, indicating small crystallite size. This result indicates that when the ionic liquid was added to the system Brookite phase almost disappears. This can be attributed to [BMIM] [BF₄] as an additional solvent with water. Because low vapour pressure of the ionic liquid could assist in preventing reduction of surface area and crystallinity of titania particle can be controlled in the water containing ionic liquid is owing to reduce the rate of hydrolysis reaction of the titanium alkoxide precursor.

Fig. 1. XRD diffraction patterns of TiO₂-IL (a), TiO₂-W (b)

Fig. 2 illustrates the TEM images of TiO₂ nanoparticles prepared from different solvent. Nanostructured TiO₂ of ionic liquid assisted preparation (Fig. 2 a, c) was *ca.* 10 nm. It is clearly seen that most of the TiO₂ nanoparticles are highly crystalline in shape, as shown by clear lattice fringes in the HRTEM images (Fig. 2d). TiO₂ nanoparticles with lattice fringes of δ = 0.351 nm are well matched with the crystallographic plane of anatase TiO₂ (101) (Fig. 2d). The diffraction

pattern of selected area electron diffraction (SAED) (inset) for the sample also clearly indicates a highly crystalline structure. However, the nanoparticles prepared from pure water (Fig. 2b) are distorted, aggregate and lower crystalline. The EDX measurements confirmed the presence of the Ti, O. The EDX was also used to calculate the atomic proportions of the elements present in nanocomposite. The atomic ratio of the TiO₂ is close between the experimental and the expected theoretical values.

Fig. 2. TEM images of TiO₂-IL (a,c), TiO₂-W (b) and HRTEM images of TiO₂-IL (d)

The FTIR spectra of the samples are shown in Fig. 3. In order to understand these spectra, the FTIR spectrum of [BMIM][BF₄] (Fig. 3a) is used as reference. The TiO₂-IL samples (Fig. 3b) show the main absorption bands of [BMIm][BF₄] at about 3390, 1617 and 1066 cm⁻¹. Comparing with the peak at 1643 cm⁻¹ and 1077 of pure ionic liquid, there is an obvious peak shift to low wavenumber for TiO₂-IL. The significant peak shift of TiO₂-IL nanoparticles is the evidence of the interaction between TiO₂ and ionic liquid. This fact indicates that ionic liquid molecules are tied to the surface of the TiO₂ nanoparticles.

Fig. 3. FT-IR spectra of ionic liquid (a) and TiO₂-IL (b)

Photocatalytic activity: Fig. 4 shows the variation of methyl orange concentration with time in the presence of TiO₂-IL nanoparticles under the irradiation of the high pressure Hg lamp. The linear relationships of $\ln(A_0/A)$ versus time as indicated in Fig. 5 revealed that the photocatalytic degradation reaction followed the pseudo-first-order kinetics $\ln(A_0/A) = kt + C$, where A is the absorbency, A_0 denotes the initial absorbency, the slope k is the apparent reaction rate constants. The apparent photocatalytic degradation rate constant was calculated to be 3.18 h⁻¹. However, compared with the TiO₂ nanoparticles sample prepared by Chen's group²¹, our sample showed a higher apparent photocatalytic degradation rate constant.

Fig. 4. First-order kinetics of methyl orange

Fig. 5. Photocatalytic degradation of methyl orange

For comparison, Degussa P25, a commercially available TiO₂ was also tested as a reference catalyst for photocatalytic decomposition of methyl orange. Fig. 5 shows a plot of decomposition versus irradiation time for photocatalytic decomposition of methyl orange for TiO₂-IL and Degussa P-25 TiO₂. After UV irradiation from a 250 W high pressure Hg lamp for 120 min, about 99.57 % of the methyl orange is degraded using the TiO₂-IL nanoparticles as a photocatalyst.

In contrast, under the same irradiation conditions, only about 85.17 % are degraded using the commercial photocatalyst (P25). It indicates that the TiO₂-IL nanoparticles are a highly efficient photocatalyst, even superior to the commercial P25. The excellent photocatalytic performance of TiO₂-IL may be ascribed to the highly crystalline, small size and the enhanced absorbability associated with the existence of [BMIM][BF₄] on the nanoparticle surface.

To test the recyclability of the TiO₂-IL nanoparticles, the catalyst was recycled 9 times, as shown in Table-1. It is noteworthy that the reuse of the catalyst does not require synthesis. The catalytic system worked extremely well each time for nine consecutive runs with almost 81.25 % conversion in 180 min, after separation of the product. It is noted that the TiO₂-IL nanoparticles still hold a high photocatalytic activity although there is a slightly lower activity after cycling.

TABLE-1
RECYCLING RESULTS OF THE METHYL
ORANGE CATALYZED BY TiO₂-IL

Run	Time (min)	Decomposition rate (%)
1	60	86.92
2	60	89.15
3	60	68.76
4	60	33.27
5	120	88.35
6	120	76.35
7	150	88.31
8	150	56.79
9	180	81.52

In order to examine the photocatalytic activity under natural lighting, solar light was as light source. After 210 min solar light illumination, the methyl orange concentration (%) in solution was near zero and the decomposition rate of methyl orange was *ca.* 99.54 %. It showed TiO₂-IL can also be reduction of the recombination of photo-generated carriers under solar light.

Conclusion

In conclusion, the anatase TiO₂-IL nanoparticles with highly crystalline, small size have been synthesized using a water miscible room temperature ionic liquid [BMIM][BF₄] as an effective additional solvent by hydro-treatment methods at low temperature. The photocatalytic activities of the TiO₂-IL nanoparticles have been studied by monitoring the degradation of methyl orange. Upon modifying TiO₂ with the ionic liquid of [BMIM][BF₄] the rate of photocatalytic destruction

of methyl orange is increased in comparison to the TiO₂ from pure water and Degussa P25, a commercially available TiO₂, respectively. The TiO₂-IL nanoparticles still hold a high photocatalytic activity after the catalyst was recycled 9 times. Moreover, under solar light illumination, TiO₂-IL nanoparticles exhibited higher photocatalytic activities significantly, which is helpful to environmental remediation.

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