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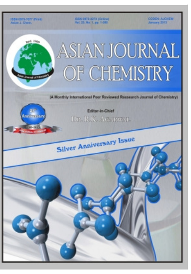

Synthesis and Photocatalytic Activities of Ionic Liquid Assisted Preparation of TiO_2 Nanoparticles

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The well-crystallized anatasetitania nanoparticles were synthesized by one-step routes under low-temperature using room temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) as an additional solvent with water. The photocatalytic properties of TiO_2 nanoparticles were evaluated by photocatalytic degradation experiments of methyl orange. The TiO_2-ionic liquid nanoparticles still hold a high photocatalytic activity after the catalyst was recycled 9 times. The TiO_2 nanoparticles show a higher photocatalytic activity than the TiO_2 with pure water and commercial TiO_2 (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][BF_4].

Key Words: Ionic liquids, TiO_2, Nanoparticles, Photocatalysis.

INTRODUCTION

Photocatalysis process is believed to be capable of removing organic pollutants into CO_2, H_2O and harmless intermediate organic compounds in water by advanced oxidation techniques[1-3]. 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 TiO_2 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 TiO_2[4-6]. It remarkably,anatasetitania obtains much more attention than the others because it is a highly efficient photocatalyst[7,8]. Traditional methods like soil-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 photoctalytic activity of TiO_2[9-11]. Hence, more attentions have been focused on the low temperature preparation of nanocrystalline 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 properties[14-16]. 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 nanoscience[14]. The potential application of ionic liquids in the synthesis of metallic architectures[17,18] and metal compounds[19] is particularly interesting because their electrostaticand 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 supramolecular network of ionic liquids provide an electrostatic protection according to the Derjaugin-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] [BF_4]) 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 TiO_2 (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] [BF_4]) was synthesized using reported method[20]. The compound was analyzed by ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy and the spectral data tally with the structure.

^{1}H NMR (300 MHz, acetone-d_6): δ 9.51 (s, 1H, CH), 7.89 (s, 1H, CH), 7.83 (s, 1H, CH), 4.42 (t, 2H, CH_2), 4.09 (s, 3H, CH_3), 1.92 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 0.93 (t, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 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 TiO_2 nanoparticles: 1.6 mL of tetrabutyltitanate was added dropwise to the mixture with 7 mL [BMIM] [BF_4] 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 ºC for 24 h. After cooling, the product (TiO_2-IL) was filtered, washed with deionized water several times and dried in air. For comparison, another TiO_2 sample (TiO_2-W) was prepared in pure water under the same conditions.

Photocatalytic activities: The photocatalytic activity of TiO_2 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, TiO_2 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 equilibriumprior 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 ºC. 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, $(C_0\text{-}C)/C_0$, can be simply calculated from equation $(A_0\text{-}A)/A_0$.

Characterization of TiO_2 nanoparticles: TEM analysis was conducted on a Philips Tecnai-12 field emission transmission 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 aIRAffinity-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 TiO_2 nanoparticles prepared under different conditions. The anatase phase was produced in TiO_2 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 = 31º (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] [BF_4] 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.

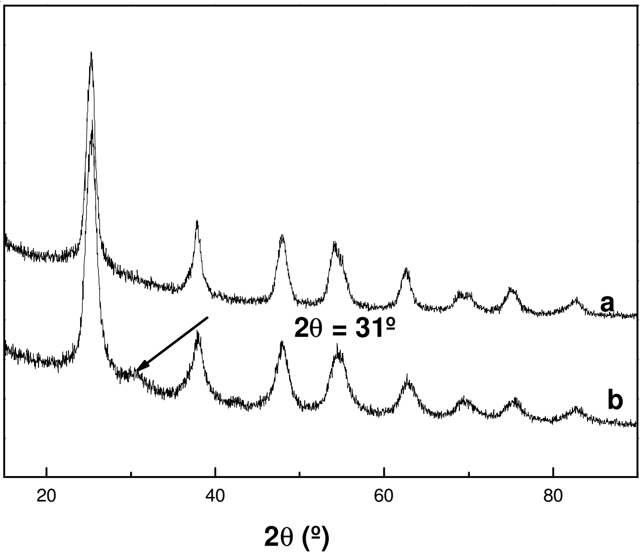

Fig. 1. XRD diffraction patterns of TiO_2-IL (a), TiO_2-W (b)

Fig. 2 illustrates the TEM images of TiO_2 nanoparticles prepared from different solvent. Nanostructured TiO_2 of ionic liquid assisted preparation (Fig. 2 a, c) was *ca.* 10 nm. It is clearly seen that most of the TiO_2 nanoparticles are highly crystalline in shape, as shown by clear lattice fringes in the HRTEM images (Fig. 2d). TiO_2 nanoparticles with lattice fringes of δ = 0.351 nm are well matched with the crystallographic plane of anatase TiO_2 (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 TiO_2 is close between the experimental and the expected theoretical values.

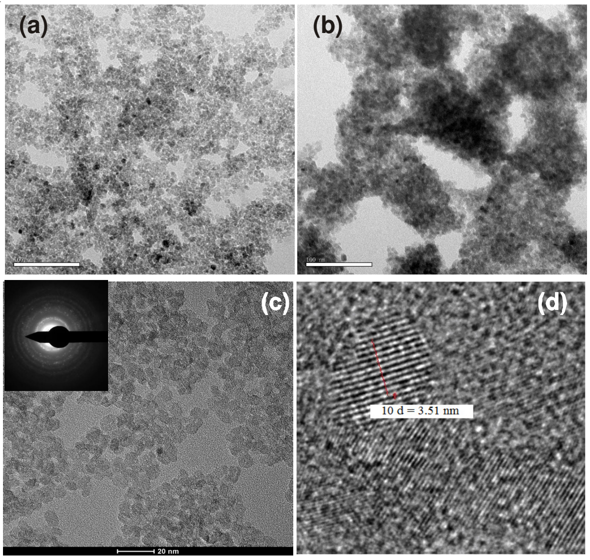

Fig. 2. TEM images of TiO_2-IL (a,c), TiO_2-W (b) and HRTEM images of TiO2-IL (d)

The FTIR spectra of the samples are shown in Fig. 3. In order to understand these spectra, the FTIR spectrum of [BMIM][BF_4] (Fig. 3a) is used as reference. The TiO_2-IL samples (Fig. 3b) show the main absorption bands of [BMIm][BF_4] 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 TiO_2-IL. The significant peak shift of TiO_2-IL nanoparticles is the evidence of the interaction between TiO_2 and ionic liquid. This fact indicates that ionic liquid molecules are tied to the surface of the TiO_2 nanoparticles.

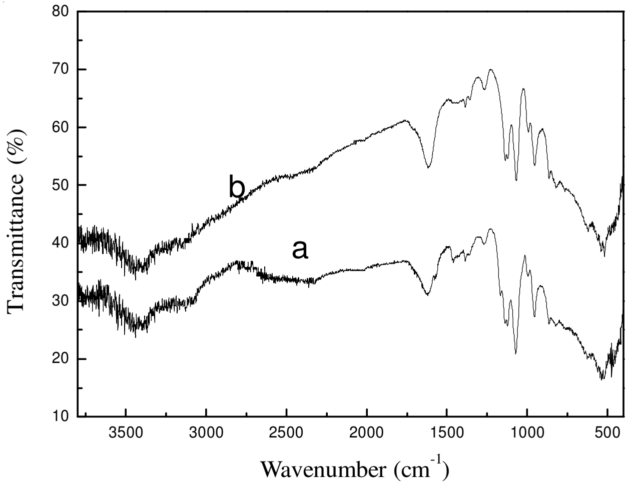

Fig. 3. FT-IR spectra of ionic liquid (a) and TiO_2-IL (b)

Photocatalytic activity: Fig. 4 shows the variation of methyl orange concentration with time in the presence of TiO_2-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 TiO_2 nanoparticles sample prepared by Chen's group[21], our sample showed a higher apparent photocatalytic degradation rate constant.

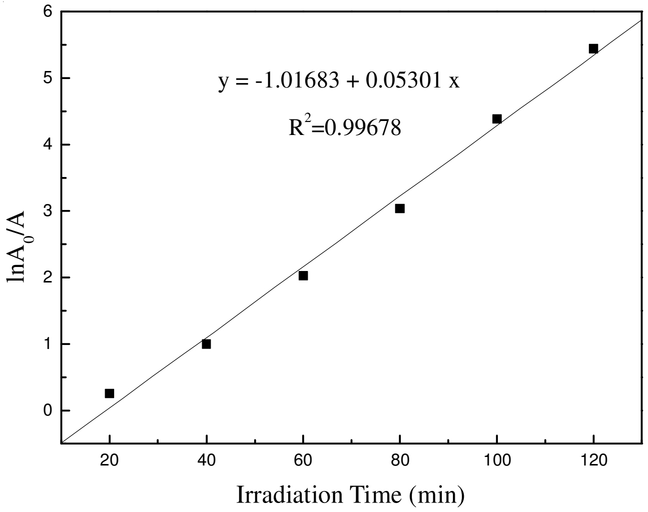

Fig. 4. First-order kinetics of methyl orange

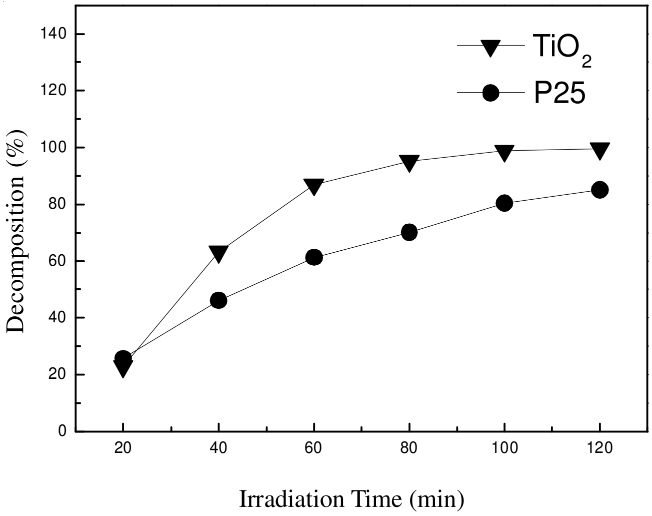

Fig. 5. Photocatalytic degradation of methyl orange

For comparison, Degussa P25, a commercially available TiO_2 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 TiO_2-IL and Degussa P-25 TiO_2. 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 TiO_2-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 TiO_2-IL nanoparticles are a highly efficient photocatalyst, even superior to the commercial P25. The excellent photocatalytic performance of TiO_2-IL may be ascribed to the highly crystalline, small size and the enhanced absorbability associated with the existence of [BMIM][BF_4] on the nanoparticle surface.

To test the recyclability of the TiO_2-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 TiO_2-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 TiO_2-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 TiO_2-IL can also be reduction of the recombination of photo-generated carriers under solar light.

Conclusion

In conclusion, the anatase TiO_2-IL nanoparticles with highly crystalline, small size have been synthesized using a water miscible room temperature ionic liquid [BMIM][BF_4] as an effective additional solvent by hydro-treatment methods at low temperature. The photocatalytic activities of the TiO_2-IL nanoparticles have been studied by monitoring the degradation of methyl orange. Upon modifying TiO_2 with the ionic liquid of [BMIM][BF_4] the rate of photocatalytic destruction of methyl orange is increased in comparison to the TiO_2 from pure water and Degussa P25, a commercially available TiO_2, respectively. The TiO_2-IL nanoparticles still hold a high photocatalytic activity after the catalyst was recycled 9 times. Moreover, under solar light illumination,TiO_2-IL nanoparticles exhibited higher photocatalytic activities significantly, which is helpful to environmental remediation.

ACKNOWLEDGEMENTS

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REFERENCES

1. J. Lovas, R.D. Suenram and G.T. Fraser, *J. Chem. Phys.*, **88**, 722 (1988); M.R. Hoffmann, S.T. Martin, W. Cho and D.W. Bahnemann, *Chem. Rev.*, **95**, 56 (1995).
2. L. Diamandescu, F. Vasiliu, D. Tarabasanu-Mihaila, M. Feder, A.M. Vlaicu, C.M. Teodorescu, D. Macovei, I. Enculescu, V. Parvulescu and E. Vasile, *Mater. Chem. Phys.*, **112**, 146 (2008).
3. A. Fujishima, T.N. Rao and D.A. Tryk, *J. Photochem. Photobiol. C: Photochem. Rev.*, **1**, 1 (2000).
4. H. Yaghoubi, N. Taghavinia and E.K. Alamdari, *Surf. Coat. Technol.*, **204**, 1562 (2010).
5. C. He, Y. Xiong, J. Chen, C. Zha and X. Zhu, *J. Photochem. Photobiol. A*, **157**, 71 (2003).
6. W.Y. Ahn, S.A. Sheeley, T. Rajh and D.M. Cropek, *Appl. Catal. B: Environ.*, **74**, 103 (2007).
7. B. Kraeutler and A.J. Bard, *J. Am. Chem. Soc.*, **100**, 5985 (1978).
8. J. Lee and W. Choi, *J. Phys. Chem. B*, **109**, 7399 (2005).
9. A.O. Ibhadon, G.M. Greenway, Y. Yue, P. Falaras and D. Tsoukleris, *J. Photochem. Photobio. A: Chem.*, **197**, 321 (2008).
10. X. Yan, D. Pan, Z. Li, Y. Liu, J. Zhang, G. Xu and M. Wu, *Mater. Lett.*, **64**, 1833 (2010).
11. M.A. Khan, H.T. Jung and O.B. Yang, *J. Phys. Chem. B*, **110**, 6626 (2006).
12. P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, **39**, 3772 (2000).
13. T. Welton, *Chem. Rev.*, **99**, 2071 (1999).
14. M. Antonietti, D.B. Kuang, B. Smarsly and B.Z. Yong, *Angew. Chem. Int. Ed.*, **43**, 4988 (2004).
15. C.W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtne and S.R. Texeir, *Inorg. Chem.*, **42**, 4738 (2003).
16. R. Tatumi and H. Fujihara, *Chem. Commun.*, 83 (2005).
17. C.W. Scheeren, G. Machado, S.R. Teixeira, J. Morais, J.B. Domingos and J. Dupont, *J. Phys. Chem. B*, **110**, 13011 (2006).
18. W. Dobbs, J.M. Suisse, L. Douce and R. Welter, *Angew. Chem. Int..Ed.*, **45**, 4179 (2006).
19. A. Taubert, *Angew. Chem. Int. Ed.*, **43**, 5380 (2004).
20. D. Fang, J. Cheng, K. Gong, Q. Shi, X. Zhou and Z. Liu, *J. Fluorine Chem.*, **129**, 108 (2008).
21. H. Chuang and D. Chen, *Nanotechnology*, **20**, 105704 (2009).