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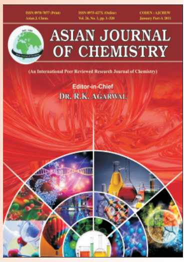

Influence of Modification Amount, Reactant Concentration and pH Value on the Photocatalytic Activity of Ionic Liquid Modified TiO_2 Under Visible Light

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Ionic liquid ([Bmim]OH, [Bmim]Br, [Bmim]BF_4) modified TiO_2 catalysts were prepared by hydrothrmal method. XRD and UV-visible spectra were used to characterize the prepared composite materials. Ionic liquid modification did not change the crystalline structure of TiO_2 particles but reduced the particle size. [Bmim]OH modified TiO_2 shows the obviously enhanced visible light absorption. The influence of ionic liquid types, modification amount, reactant concentration and pH value on the photocatalytic activity of TiO_2 catalyst under visible light were investigated.

Keywords: Ionic liquid, TiO_2, Modification, Photocatalyst, Visible light.

INTRODUCTION

Photocatalytic technology has attracted worldwide research interest for the degradation of toxic pollutants in water, air and soil. Among the various photocatalysts, TiO_2 has proven to be the promising one because of its features such as non-toxicity, high efficiency, chemical stability, low cost and environmentally friendly. It has wide applications including mineralization of toxic organic substances, water splitting and solar cell[1,2]. However, the wide band gap of titania photocatalyst makes it only active under UV irradiation. Therefore, the photocatalytic activity of TiO_2 need to be further improved for the practical applications[3,4]. In order to the efficient utilization of solar energy, it is still a big challenge to develop TiO_2 photocatalysts with highly activity under visible light.

It is reported that TiO_2 doped with transition metals could absorb visible light and exhibited high photocatalytic activity under visible light irradiation[5,6]. However, the disadvantage of metal cation dopants is that they can serve as recombination centers for photogenerated electron-hole pairs, leading to a decreased activity[7]. Recently, the substitution of non-metal atoms, such as nitrogen[8], sulfur[9], phosphorous[10], iodine[11], and boron[12], for oxygen in the lattice of TiO_2 was reported to enhance the catalytic activity of TiO_2 under visible light. But the synthesis of the nonmetal-doped TiO_2 materials is much more difficult, because the lattice exchange requires high temperature and complicated procedures. Recently, much interest has been focused on the surface modification of TiO_2 with organic dyes for the construction of dye-sensitized photocatalytic systems under visible light irradiation[13]. Since the dye molecules are generally absorbed on rather than chemically bonded to the surface of TiO_2, resulting in a gradual decrease in photocatalytic activity.

Ionic liquids (ILs) are low melting salts with negligible vapour pressure and represent a new and promising solvent class, particularly with regard to homogeneous two phase catalysis and extractions. The high potential of ionic liquids will probably lead to an increasing demand. The combination of ionic liquids with nanotechnology has led to some major advances in materials science. Nanorods, nanospheres, nanotubes, mesostructures of TiO_2 phases have been synthesized using ionic liquid as the solvent, electrolyte and template[14-17]. However, little effort has been devoted to the study of the photocatalytic performances of the ionic liquid-modified TiO_2 materials under visible light. Here, different kind of ionic liquids modified TiO_2 nanocomposites were synthesized *via* a hydrothermal procedure. The influence of [Bmim]OH amount, pH value, reactant concentration and ionic liquid types on the photocatalytic performane under visible light were investigated.

EXPERIMENTAL

Titanium(IV) chloride (0.8 mL) was added dropwise into 10 mL ethanol to form solution A. A desired amount of ionic liquid ([Bmim]OH, [Bmim]Br, [Bmim]BF_4) was added into another 10 mL ethanol to form solution B. These two solutions were mixed under stirring to form a clear solution. Ammonia was then added dropwise into the solution and TiO_2 precipitates were formed. More ammonia was added dropwise until the pH of the mixture reached[8]. The formed suspension was stirred for 0.5 h and then transferred into a 30 mL stainless steel autoclave, which was then heated to 160 °C and kept for 24 h. The solid product was separated by filtration, followed by washing and drying at 80 °C for 8 h. The obtained orange sample was denoted as OH-TiO_2(x), Br-TiO_2(x) and BF_4-TiO_2(x), where x stands for the molar ratio of ionic liquid to $TiCl_4$. For comparison, neat TiO_2 was prepared by the same procedure described above but in the absence of ionic liquid.

XRD patterns of the prepared TiO_2 nanocomposites were recorded on a Rigaku D/max-2400 instrument using Cu-K_α radiation (l = 1.54 Å). The zeta-potential of the catalyst was measured at room temperature on Zetasizer Nano S90 (Malvern Instruments). The pH was adjusted by dropwise addition of dilute HCl or NaOH solution. UV-visible spectroscopy measurement was carried out on a Jasco V-550 spectrophotometer, using $BaSO_4$ as the reference.

Photocatalytic reaction: Methylene blue (MB) was selected as model compound to evaluate the photocatalytic performance of the prepared TiO_2 particles in an aqueous solution under visible light irradiation. 0.1 g TiO_2 powders were dispersed in 100 mL aqueous solution of methylene blue (50 ppm) in an ultrasound generator for 10 min. The suspension was transferred into a self-designed glass reactor and stirred for 0.5 h in darkness to achieve the adsorption equilibrium. In the photoreaction under visible light irradiation, the suspension was exposed to a 110-W high-pressure sodium lamp with main emission in the range of 400-800 nm and air was bubbled at 130 mL/min through the solution. The UV light portion of sodium lamp was filtered by 0.5 M $NaNO_2$ solution. All runs were conducted at ambient pressure at 30 °C. At given time intervals, 4 mL suspension was taken and immediately centrifuged to separate the liquid samples from the solid catalyst. The concentrations of methylene blue before and after reaction were measured by means of a UV-visible spectrophotometer at a wavelength of 665 nm. It is the linear relationship between absorbance and concentration of liquid sample in the experimental concentration range. Therefore, the percentage of degradation D % was determined by the absorbances of the liquid sample before and after degradation.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the synthesized TiO_2 nanocomposites. There are three phases, rutile, brookite and anatase, in TiO_2. Pure anatase TiO_2 with characteristic diffractions at 25.2° (1 0 1), 37.8° (0 0 4), 48.1° (2 0 0), 54.7° (1 0 5) and 62.7° (2 1 1) was shown in all TiO_2 samples. The modification of TiO_2 by ionic liquids did not cause any change in peak positions in XRD pattern. However, the peak intensity was slightly decreased whereas the full width at half-maximum (FWHM) increased on increasing the concentration of ionic liquids. It is therefore suggested that ionic liquids modification did not change the crystalline structure of TiO_2 particles but reduced the particle size. The calculation by Debye-Scherrer equation revealed that the average particle sizes of neat TiO_2, OH-TiO_2(3), Br-TiO_2(3) and BF_4-TiO_2(3) were 10.3, 8.5, 8.9 and 9.1 nm, respectively. When different amount of [Bmim]OH was used to modify TiO_2 sample, the XRD result (not shown here) indicated that the crystalline structure of TiO_2 particles also did not changed and the particle size reduced with increasing the [Bmim]OH amount.

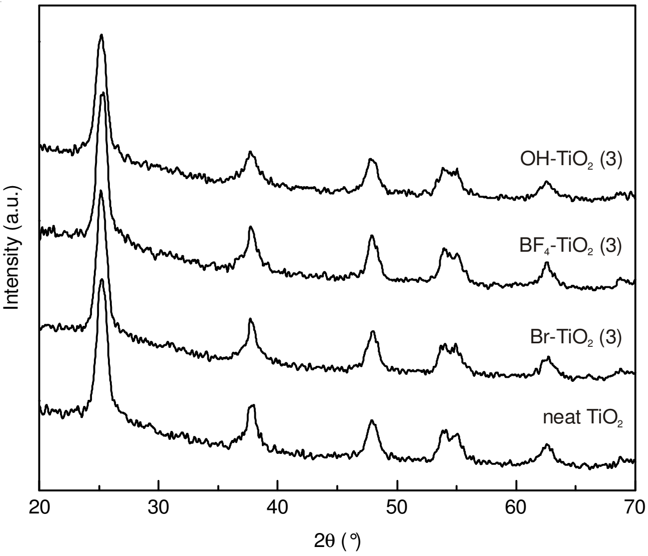

Fig. 1. XRD patterns of prepared TiO_2 samples

In Fig. 2, UV-visible spectra of prepared catalysts, no absorption in visible light region for neat TiO_2 was observed. After [Bmim]Br and [Bmim]BF_4 modification, a slight increased absorption in visible light region were observed for Br-TiO_2(3) and BF_4-TiO_2(3). However, after [Bmim]OH modification, the obvious increased absorption was shown in visible light region, indicating [Bmim]OH modification could extend the absorption ability to visible light region. This increased absorption coud be due to the electrons transfer between TiO_2 and [Bmim]OH. Such absorption is significant for its application under visible light.

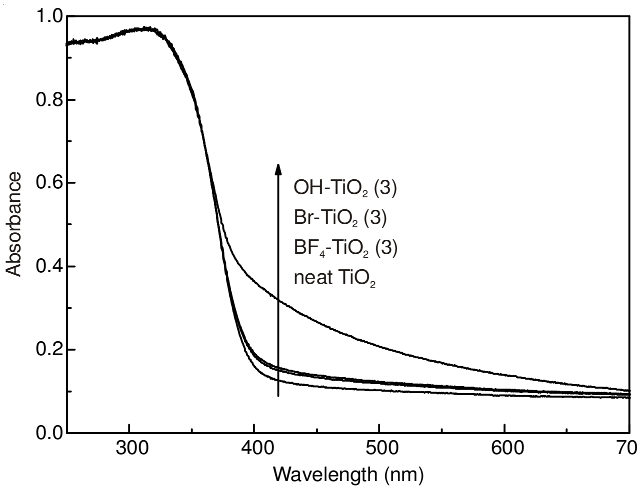

Fig. 2. UV-visible diffuse reflectance spectra of prepared TiO_2 samples

Fig. 3 shows the photocatalytic activities of ionic liquids modified TiO_2 catalysts under visible light. Neat TiO_2 shows almost no activity under visible light. After [Bmim]Br and [Bmim]BF_4 modification, slight increase in activities were observed. However, for [Bmim]OH modified TiO_2, obviously increase in activity was shown, over 80 % methylene blue was degraded. This result is consistent with the UV-visible result that [Bmim]Br and [Bmim]BF_4 modification only slight increase the visible light absorption whereas [Bmim]OH modified TiO_2 exhibit obvious increase absorption. It has been reported that the Ti-OH can react with phenolic hydroxyl of organic compounds, such as catechol[18], salicylic acid[19] and binaphthol[20], to form Ti-O-C bond on TiO_2 surface. Therefore, this is probably due to that the surface of TiO_2 particles is supposed to be positively charged, so Ti-OH may react with [Bmim]OH to form a Ti-O-C bond by elimination of a molecular H_2O. For other two ionic liquids, such reaction can not occurred.

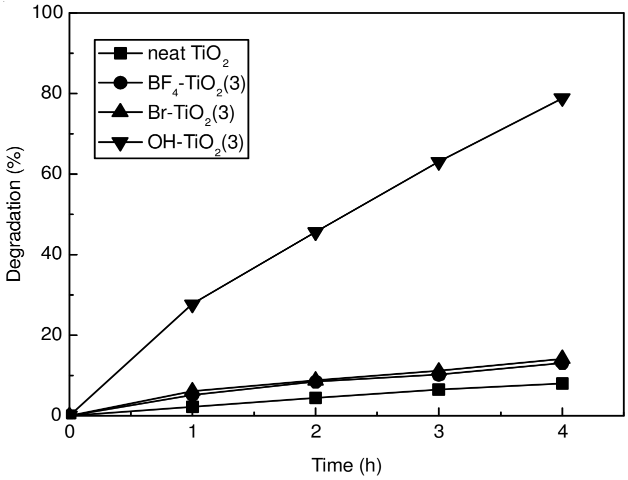

Fig. 3. Photocatalytic performance of ionic liquids modified TiO_2 catalysts

Fig. 4 shows the effect of modification amount of [BMIM]OH on photocatalytic performances of OH-TiO_2(3) under visible light irradiation. Obviously, the activity increased with incrasing the [BMIM]OH modification amount firstly from molar ratio 1:1 to 1:3. Further increase the [BMIM]OH modification amount to molar ratio 1:4, the activity decreased. This may be attributed to the coverage of the TiO_2 surface by excess [Bmim]OH, leading to a decreased adsorption of methylene blue. Therefore, the optimal molar ratio is 1:3.

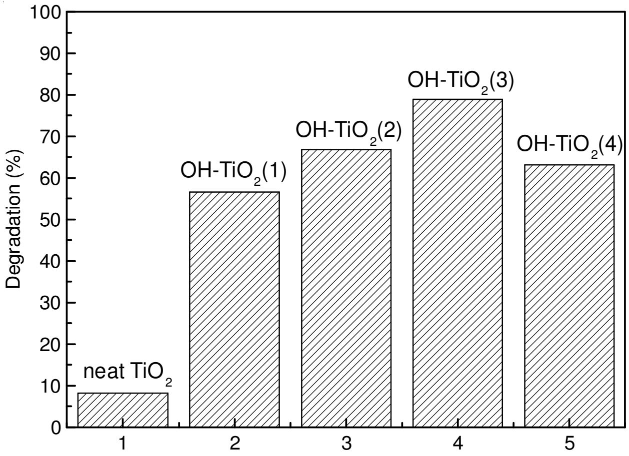

Fig. 4. Effect of modification amount of [BMIM]OH on photocatalytic performances of prepared TiO_2 catalysts under visible light irradiation

Fig. 5 shows the effect of reactant concentration on photocatalytic performances of OH-TiO_2(3) under visible light irradiation. For reactant concentration of 25 ppm, the degradation rate was over 60 %. Increasing the reactant concentration to 50 ppm, the degradation rate increase to 80 %. Further increase the reactant concentration to 75 and 100 ppm lead to the obviously decreased activities. This is probably due to the excess methylene blue molecule can not be adsorbed on TiO_2 simultaneously. Besides, the excess methylene blue concentration cause the light can not penetrate the solution and irradiate the TiO_2 surface effectively. Thus, the optimal reactant concentration was 50 ppm.

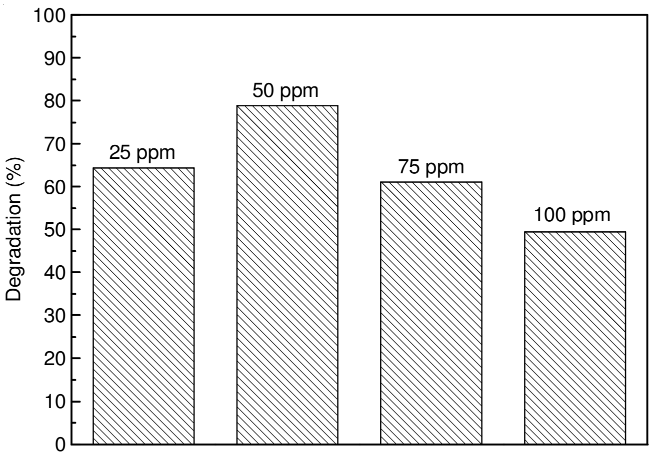

Fig. 5. Effect of reactant concentration on photocatalytic performances of OH-TiO_2(3) under visible light irradiation

Fig. 6 shows the effect of pH value on photocatalytic performances of OH-TiO_2(3) under visible light irradiation. It is shown that the solution with pH = 7 exhibit the highest photocatalytic activity. No matter acidic and basic system lead to the poor activity. It is concluded that the Ti-OH may react with [Bmim]OH to form a Ti-O-C bond. Thus [Bmim]OH could effective modify TiO_2 whereas other two ionic liquid can not. Therefore, under acidic and basic system, this reaction will be restrained, thus leading to the decreased activity.

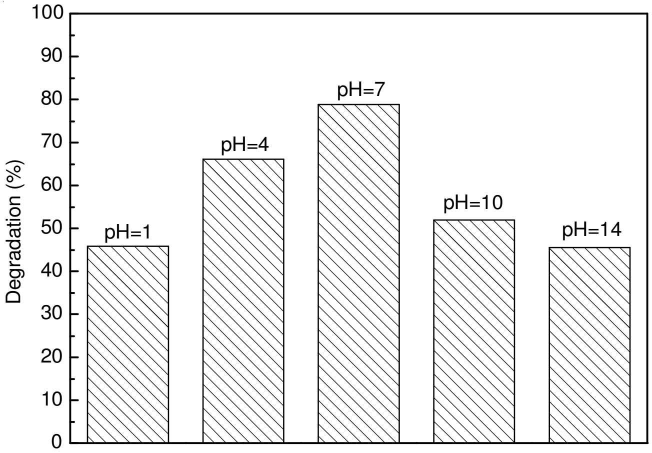

Fig. 6. Effect of pH value on photocatalytic performances of OH-TiO_2(3) under visible light irradiation

Conclusion

Ionic liquid ([Bmim]OH, [Bmim]Br, [Bmim]BF_4) modified TiO_2 catalysts were prepared by hydrothrmal method. Ionic liquid modification did not change the crystalline structure of TiO_2 particles but reduced the particle size. [Bmim]OH modified TiO_2 shows the obviously enhanced visible light absorption whereas other two ionic liquid can not. This is probably due to Ti-OH react with [Bmim]OH to form a Ti-O-C bond. Thus [Bmim]OH could modify TiO_2 effectively. The optimal reaction condition was molar ratio of ionic liquid to $TiCl_4$ of 3:1, methylene blue concentration of 50 ppm, pH value = 7.

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