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Enhanced and suppressed effects of ionic liquid on the photocatalytic activity of TiO_2

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Abstract The effects of a room temperature ionic liquid, 1-butyl-3-methylimidazolium terafluoroborate ([Bmim]BF_4), on the photocatalytic performance of Degussa P25 TiO_2 were investigated. Also, the photocatalysis mechanism was systematically analyzed by conducting different reactive radical trapping experiments. The results showed that photogenerated electrons were the main reactive species involved in the photocatalytic degradation of methyl orange (MO), while •OH radicals and photogenerated holes played an important role in the photocatalytic decomposition of rhodamine B (RhB). The addition of ionic liquid (IL) could slightly enhance the photocatalytic degradation rate of MO because adsorption of $[Bmim]^+$ ions on the TiO_2 surface not only enhanced traping and transfer of photogenerated electrons, but also facilitated adsorption of negatively charged MO. On the contrary, IL suppressed the degradation rate of RhB because $[Bmim]^+$ on the TiO_2 surface not only hindered the access of positively charged RhB to TiO_2, but also restricted the diffusion of positively charged holes to the TiO_2/solution interface.

Keywords Titania (TiO_2) · Photocatalytic activity · Ionic liquid · Adsorption

1 Introduction

Heterogeneous semiconductor photocatalysis is considered as one of the most promising technologies for the elimination of organic contaminants in environment and for the production of H_2 by water splitting (Fujishima and Honda 1972; Hoffmann et al. 1995; Park et al. 2006; Xiang et al. 2012a, b; Li et al. 2011; Zhang et al. 2011a, b). In particular, TiO_2-based photocatalytic purification of air and water has attracted a widespread attention (Choi et al. 1994; Cheng et al. 2007; Tan et al. 2012; Fan et al. 2011; Liu et al. 2010; Xiang et al. 2011a, b; Liu et al. 2011; Zhang et al. 2008; Li et al. 2003; Wang et al. 2009). However, the photocatalytic performance of TiO_2 must be further enhanced from the viewpoint of practical applications and commercial benefits (Ksibi et al. 2008; Frank and Bard 1977; Yu et al. 2010; Qi et al. 2011). Since heterogeneous photocatalytic reactions mostly take place at the liquid/solid and/or gas/solid interfaces, the properties of TiO_2 such as the phase structure, chemical composition, surface defects, surface area, and the concentration and type of surface functional groups are critical for the photocatalytic reaction efficiencies. Up to now, TiO_2 surfaces have been widely modified via manipulating the above parameters to improve the photocatalytic performance (Park and Choi 2004; Yu et al. 2009; Vohra et al. 2003; Liu et al. 2012; Lv et al. 2012).

Ionic liquids (IL), typically composed of organic cations and large anions, have received considerable attention due to their unique properties, such as extremely low volatility, good dissolving ability, wide electrochemical window, and high ionic conductivity (Dupont et al. 2002). Recently, IL have been widely used as solvents, templates, or reactants for the fabrication and functionalization of inorganic nanomaterials with enhanced catalytic performance (Guo

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et al. 2010; Lee et al. 2011). For instance, Ding et al. (2007) have proposed a facile method for the fabrication of high quality TiO_2 nanocrystals in IL. Zhang et al. (2009) have reported an efficient microwave-assisted ionothermal recipe for the preparation of anatase TiO_2 single crystal photocatalyst with tunable percentage of reactive facets. Guo et al. (2010) have found that IL may play an important role in accelerating electron transfer when it is adsorbed at the electrochemical interface, which is beneficial for tuning the electrocatalytic properties of carbon nanotubes (CNTs)/IL/Pt hybrids. However, to the best of our knowledge, there are no articles yet reporting on the effects of IL on the photocatalytic performance of TiO_2.

Herein, for the first time, we investigate the effects of IL on the mechanism of photocatalysis on TiO_2 for the photocatalytic degradation of MO and RhB. It is shown that the addition of a room temperature ionic liquid can facilitate the photocatalytic degradation rate of MO and reduce that rate in the case of RhB, which is attributed to the different photocatalytic degradation mechanisms due to the difference in the molecular structures of MO and RhB.

2 Experimental

2.1 Photocatalytic performance

All the reagents were of analytical grade and were used without further purification. Deionized water was used in all experiments. The effects of IL on the photocatalytic performance of TiO_2 were evaluated via the photocatalytic decomposition of RhB and MO in the absence and presence of 1-butyl-3-methylimidazolium terafluoroborate ($[Bmim]BF_4$) or 1-butyl-3-methylimidazolium hexafluorophosphate ($[Bmim]PF_6$) under xenon lamp irradiation at ambient temperature. The molecular structures of $[Bmim]BF_4$, $[Bmim]PF_6$, MO and RhB are shown in Fig. 1. Experimental procedures were as follows: The catalyst samples were firstly prepared by coating an aqueous suspension of P25 powders (0.05 g) onto one 7.0 cm culture dish and then dried in an oven at 100 °C for about 4 h to evaporate water. 25 mL of mixed aqueous solution of dye and $[Bmim]BF_4$ with different concentrations (0 and $3.2 * 10^{-3}$ M) were added into the culture dish coated with catalyst in each experiment. The dyes used in these experiments were MO ($5.0 * 10^{-5}$ M) and RhB ($1.0 * 10^{-5}$ M) aqueous solutions, respectively. Before xenon lamp irradiation, the culture dish containing catalyst and the mixed aqueous solution of the aforementioned dyes was kept in the dark for 40 min to ensure the establishment of an adsorption–desorption equilibrium. A 300 W xenon lamp positioned 7.0 cm above the dish was used as a light source to trigger the photocatalytic reaction. The average light intensity striking on the surface of the reaction solution was about 20 mW/cm^2, measured using a UV meter (the photoelectric instrument factory of Beijing Normal University, China) with the peak intensity of 365 nm. The concentration of RhB and MO was monitored by a UV-2550 UV–visible spectrophotometer (Shimadzu, Japan). After UV light irradiation for 90 min, the reaction solution was taken out to measure the change in the concentration of RhB and MO.

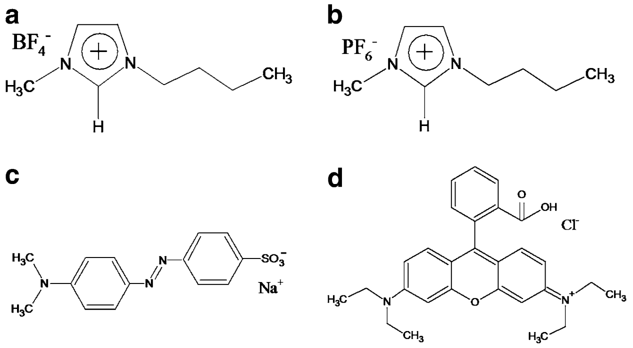

Fig. 1 Molecular structures of $[Bmim]BF_4$ (**a**), $[Bmim]PF_6$ (**b**), MO (**c**) and RhB (**d**)

2.2 Analysis of photocatalysis mechanism

Different radical and hole trapping experiments for photocatalytic reactions on TiO_2 were designed and carried out to investigate the specific reactive species involved in the photocatalytic degradation of MO and RhB dyes. Experimental procedure was similar to the measurement of photocatalytic activity except 25 mL of dye aqueous solution was replaced by 25 mL of mixed aqueous solution of dye and triethanolamine (TEOA, $1.0 * 10^{-2}$ M), potassium dichromate ($K_2Cr_2O_7$, $5.0 * 10^{-4}$ M), or isopropanol (IPA, $1.0 * 10^{-2}$ M).

3 Results and discussion

3.1 Photocatalytic activity

The effects of IL on the photocatalytic performance of TiO_2 were evaluated through the photocatalytic decomposition of MO or RhB in the absence and presence of $[Bmim]BF_4$ under xenon lamp irradiation at ambient temperature. As shown in Fig. 2, the addition of $[Bmim]BF_4$ affected the photocatalytic activity of TiO_2. For MO, the addition of $[Bmim]BF_4$ slightly improved the photocatalytic activity of TiO_2. This is probably due to the fact that adsorption of $[Bmim]BF_4$ on the TiO_2 surface can accelerate the effective separation of photogenerated electrons and holes. On the contrary, for RhB, the photocatalytic activity of TiO_2 decreased after the addition of $[Bmim]BF_4$. This is not surprising because of competitive

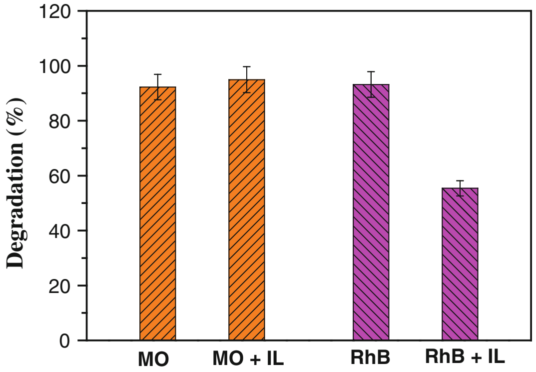

Fig. 2 Comparison of photocatalytic degradation rates of MO and RhB over P25 powders in the absence and presence of IL ($[Bmim]BF_4$) under UV irradiation for 90 min

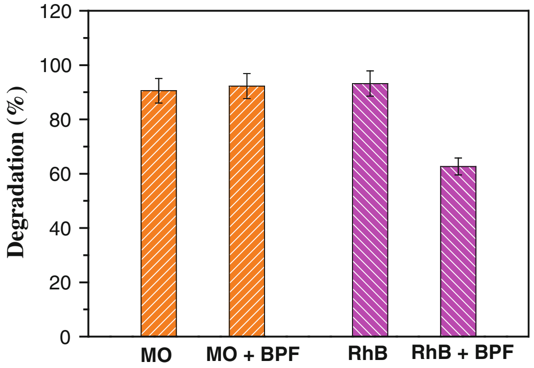

Fig. 3 Comparison of photocatalytic degradation rates of MO and RhB over P25 powders in the absence and presence of $[Bmim]PF_6$ (BPF) under UV irradiation for 90 min

adsorption of positively charged RhB and positively charged cationic imidazolium moiety of $[Bmim]BF_4$ on the surface of negatively charged TiO_2. In addition, $[Bmim]PF_6$ was also used to investigate the influence of IL on the performance of TiO_2, and the similar results were observed. Fig. 3 indicates that the photocatalytic degradation rate of MO was also slightly enhanced in the presence of $[Bmim]PF_6$; contrarily, the photocatalytic degradation rate of RhB was greatly reduced in the presence of $[Bmim]PF_6$ (Fig. 3).

3.2 Photocatalysis mechanism

In order to further clarify the mechanism of the photocatalytic degradation of MO and RhB on TiO_2 in the absence and presence of IL, it is necessary to investigate the specific reactive species involved in the MO and RhB photocatalytic reactions. TEOA is a strong electron donor and has been widely used as a scavenger for photogenerated holes, while IPA is a generally accepted scavenger for hydroxyl radicals (•OH) (Huang et al. 2008; Hu et al. 2011). In addition, $K_2Cr_2O_7$ has been chosen as a scavenger for electrons (Chen et al. 2005; Gazi et al. 2010; Zhuang et al. 2010). Therefore, the aforementioned scavengers (TEOA for holes, IPA for •OH radicals, and $K_2Cr_2O_7$ for electrons) were used in the photocatalytic experiments (Fig. 4). As can be seen from Fig. 4a, the addition of $K_2Cr_2O_7$ significantly suppressed the degradation rate of MO, while the addition of TEOA and IPA had no obvious effect on the photocatalytic efficiency. This result suggests that photogenerated electrons are mainly responsible for the photodegradation of MO on TiO_2 because they can produce superoxide radicals ($\bullet O_2^-$), while the valence-band (VB) holes and •OH radicals are the minor reactive species involved in the photodegradation of MO. Contrarily, for the degradation of RhB on TiO_2, as shown in Fig. 4b, the degradation efficiency of RhB on TiO_2 decreased significantly after the addition of TEOA, confirming that photogenerated holes are involved in the degradation of RhB. Meanwhile, a similar suppression effect was also observed for the degradation of RhB in the presence of IPA, implying that •OH radicals also play an important role in the degradation of RhB. However, in the presence of electrons scavenger $K_2Cr_2O_7$, there was no obvious change in the photodegradation efficiency of RhB,

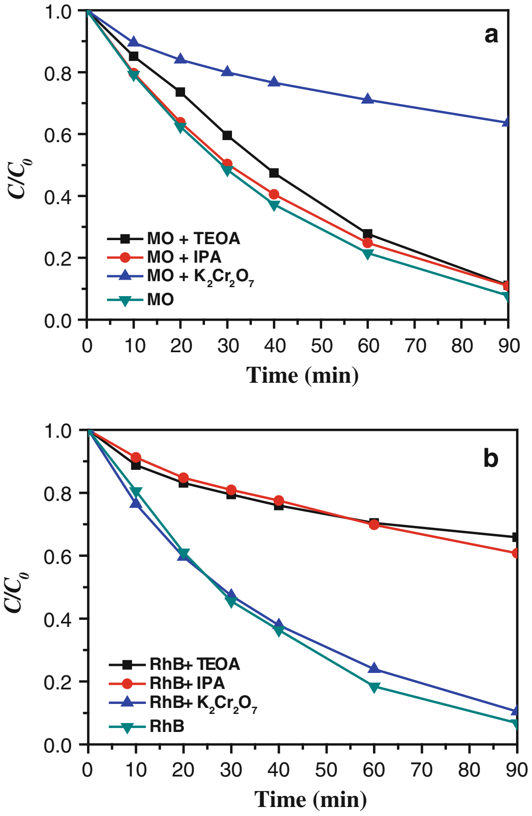

Fig. 4 Temporal concentration changes of MO (**a**) and RhB (**b**) during the photocatalytic degradation reactions over P25 powders in the absence and presence of TEOA, IPA and $K_2Cr_2O_7$

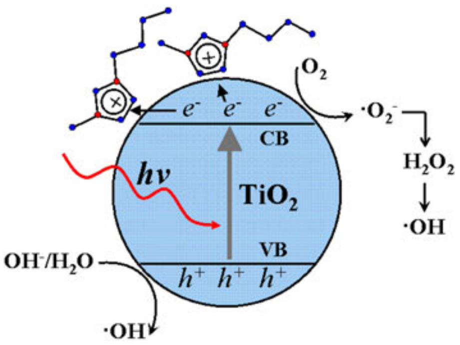

Fig. 5 Enhanced separation of photogenerated electrons and holes on the surface of TiO_2 in the presence of $[Bmim]BF_4$

indicating that photogenerated electrons are not the main reactive species in the degradation of RhB.

Based on the above results, we propose the possible degradation mechanism to explain the effects of IL on the photocatalytic degradation rates of different dyes over TiO_2 (Fig. 5). Under UV irradiation, TiO_2 undergoes photoexcitation to produce electrons and holes in the corresponding conduction and valence bands, respectively. In the absence of IL ($[Bmim]BF_4$), the photogenerated holes react with –OH/H_2O to produce •OH radicals and the electrons transfer to the adsorbed O_2 (from air) on the surface of TiO_2 to form the superoxide radicals ($\bullet O_2^-$) or •OH radicals generated via multi-step reduction of O_2 ($e^- \rightarrow \bullet O_2^- \rightarrow H_2O_2 \rightarrow \bullet OH$) (Liu et al. 2000). The produced holes, •OH and $\bullet O_2^-$ radicals all show high oxidizing ability and make different contributions to the oxidative decomposition of organic pollutants such as MO and RhB. In the presence of $[Bmim]BF_4$, the surface of TiO_2 can be partly occupied by the cationic imidazolium moiety of $[Bmim]BF_4$ ($[Bmim]^+$) through the electrostatic attraction between the negatively charged surface of TiO_2 and the positively charged $[Bmim]^+$ ions. It is necessary to note that the adsorption of $[Bmim]^+$ ions on the surface of TiO_2 could not only enhance trap and transfer of the photogenerated electrons, but also facilitate the adsorption of MO due to the electrostatic attraction between the positively charged $[Bmim]^+$ ions on the surface of TiO_2 and the negatively charged MO in the solution. Therefore, it is not surprising that the photocatalytic degradation rate of MO slightly increased after the addition of $[Bmim]BF_4$. However, the photocatalytic degradation rate of RhB decreased remarkably. This is not difficult to understand this decrease in the light of the results obtained by the aforementioned reactive radical trapping experiments. Since the photogenerated holes and •OH radicals are the main reactive species involved in the degradation of RhB, adsorption of $[Bmim]^+$ on the surface of TiO_2 not only hinders the access of positively charged RhB to the surface of TiO_2, but also restricts the diffusion of positively charged holes to the TiO_2/solution interface due to the electrostatic repulsion between $[Bmim]^+$, RhB and holes because they are all positively charged. Therefore, it is not surprising that the degradation rate of RhB on TiO_2 was decreased in the presence of the IL studied.

4 Conclusions

In conclusion, the effects of the IL studied on the photocatalytic degradation of organic dyes on TiO_2 are dependent on the photocatalysis mechanism and the type of dyes. For the photocatalytic reactions dominantly initiated by photogenerated electrons (the case of MO), the addition of IL can enhance the photocatalytic degradation of MO because adsorption of $[Bmim]^+$ ions on the surface of TiO_2 can not only enhance trapping and transfer of the photogenerated electrons, but also can facilitate adsorption of MO due to the electrostatic attraction between positively charged $[Bmim]^+$ ions and negatively charged MO in the solution. On the contrary, for the photocatalytic reactions dominantly initiated by photogenerated holes and •OH radicals (the case of RhB), the addition of IL can suppress the photocatalytic degradation of RhB because $[Bmim]^+$ on the surface of TiO_2 not only hinders the access of positively charged RhB to the surface of TiO_2, but also restricts the diffusion of positively charged holes to the TiO_2/solution interface due to the electrostatic repulsion between $[Bmim]^+$ and holes. This study may provide a new insight into the photocatalysis mechanism occurring on TiO_2 and the design of novel photocatalytic materials with enhanced photocatalytic performance.

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