Ionic Liquid-Assisted Fabrication of Nanoscale Microporous TiO$_2$ with Enhanced Photocatalytic Performance

Junbo Zhong$^{1,2}$*, Jianzhang Li$^1$, Famei Feng$^1$, Shengtang Huang$^1$, Weidong Jiang$^1$ and Clemens Burda$^{2,*}$

$^1$Key Laboratory of Green Catalysis of Higher Education Institutes of Sichuan, College of Chemistry and Pharmaceutical Engineering, Sichuan University of Science and Engineering, China
$^2$Department of Chemistry, Case Western Reserve University, USA

Abstract

In this work, microporous TiO$_2$ photocatalyst (IL-TiO$_2$) with high photocatalytic performance was prepared via a sol-gel method using the ionic solvent 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF$_6$). The specific surface area, structure, morphology, the surface hydroxyl content, the photoinduced charge separation efficiency and the transport of the photogenerated charges of the photocatalysts prepared were characterized by Brunauer-Emmett-Teller (BET) measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and surface photovoltage spectroscopy (SPS) studies, respectively. The results show that adding [BMIm]PF$_6$ into the synthesis alters the specific surface parameters, the morphology and the transport of the photogenerated charges. It increases the hydroxyl content on the surface of TiO$_2$. The photocatalytic activity toward decolorization of methyl orange (MO) aqueous solution was investigated. The results demonstrate that the photocatalytic activity of IL-TiO$_2$ is more than 22 times that of the reference TiO$_2$, and the underlying mechanisms are discussed.

INTRODUCTION

As an advanced oxidation process, photocatalysis has received a great deal of attention for wastewater treatment and air purification in recent years [1-4]. Among the various photocatalysts, TiO$_2$ based photocatalysts have been intensely investigated [5-9]. However, its wide band gap, high recombination rate of electron and hole pair, and the slow transfer rate of electrons to oxygen limit the practical application of TiO$_2$ photocatalyst [10,11]. Therefore, the photocatalytic performance of TiO$_2$ has to be further improved. Thus, enormous efforts have been developed to enhance the photocatalytic activity of TiO$_2$ to meet the practical demands. Many synthesis methods have been pursued to promote the photocatalytic activity of TiO$_2$ [12-15]. Among these synthesis approaches, the sol-gel method has been widely employed due to the low cost of the equipment required and the resulting high purity of the products [16].

More recently, room-temperature ionic liquids (RTILs) have attracted significant attention as a new kind of reaction media [7,17]. RTILs have following attractive advantages: good ion conductivity, good thermal stability, good dissolving ability, wide electrochemical window, nonflammability and negligible vapor pressure [18-21]. More importantly, the self-structuring of RTILs originating from the extended H-bond systems makes RTILs suitable as template for the synthesis of inorganic materials with ultrafine structure [20,22-23]. Compared to traditional surfactants, the outstanding physicochemical properties, such as tunable solvent features, adjustable polarities, and low vapor pressures, make RTILs more diverse in shape control and for a wide range of operating conditions [24-26]. As a result, new catalysts with new properties are now synthetically accessible.

Here, we present a study on the synthesis of an RTIL-prepared TiO$_2$ photocatalyst and its light-induced surface photovoltage (SPV) response. Surface photovoltage spectroscopy (SPS) method is a well-established non-destructive technique for semiconductor characterization that detects and analyzes illumination-induced changes in the surface photovoltage [27]. It is an effective and useful approach for investigating the photoexcited states of photocatalysts.
The primary goals of this work is to study the effect of [BMIm]PF$_6$ on the morphology, surface texture, the hydroxyl content, bandgap, the photoinduced charge separation and their relation to the photocatalytic activity of the prepared photocatalyst. The photocatalytic activity has been evaluated via the decolorization of methyl orange (MO) solution.

**EXPERIMENTAL SECTION**

**Preparation of photocatalysts**

[BMIm]PF$_6$ was purchased from Shanghai Chengjie Chemical Co. LTD. All other chemicals (analytical grade reagents) were supplied from the Chengdu Ke long Chemical Reagent Factory and used as received. TiO$_2$ was fabricated by the sol-gel process according to the procedure in reference [28]. 1g [BMIm]PF$_6$ and Tetrahydrofuran (397.7 mL) were dissolved in ethanol (673.3 mL). After stirring vigorously for 2 h at room temperature, a mixed solution of water (0.9 mL) and ethanol (10 mL) was added dropwise to the above solution until stirring. The resulting alkoxide solution was kept standing at room temperature for hydrolysis during 2 h, resulting in the TiO$_2$ sol. Then the TiO$_2$ sol was aged for one week at room temperature and air. Finally, the sample obtained was evaporated, dried, and baked in air at 723 K for 2 h in a muffle furnace. Finally, the sample obtained was evaporated, dried, and then the [BMIm]PF$_6$ was washed with ethanol and used as received.

**Characterization of photocatalysts**

The specific surface area and pore size measurements were performed with a SSA-4200 automatic surface analyzer (Builder Inc., Beijing, China). The samples were evacuated at 623K for 2 h in a muffle furnace. The sample was and air. Finally, the sample obtained was evaporated, dried, and baked in air at 723 K for 2 h in a muffle furnace. The sample was labeled as IL-TiO$_2$. IL-TiO$_2$ was also prepared as the same procedure mentioned above without the presence of [BMIm]PF$_6$.

**Evaluation of the photocatalytic activity**

Photocatalytic decolorization experiments were performed in a SGY-II photochemical reactor (Kaifeng HXSCI Science Instrument Factory, China). The radiation source was a 500 W high-pressure mercury lamp with a maximum emitting radiation at 365 nm, the lamp was encapsulated in a cooling quartz jacket and positioned in the middle of the reactor, two quartz test tubes were located around the lamp, the distance from the lamp to the quartz test tubes was 10 cm. The initial concentration of MO solution was 10 mg/L. 50 mg of prepared photocatalyst was added into 50 mL MO solution (10 mg/L) and the reaction mixture was continuously aerated with a pump to provide oxygen and also for the complete mixing of the reaction solution. The decolorization reaction was performed at room temperature. The pH value of the reaction solution was 7.0. At regular intervals, samples were withdrawn and centrifuged (6000 rpm) to separate photocatalyst from photoproducts for analysis. The concentration of MO was measured with a 756 PC spectrophotometer (Shun Yu Heng Ping Inc., Shanghai) at 460 nm using the Lambert-Beer law. Measurements have all been repeated at least three times.

**RESULTS AND DISCUSSION**

The specific surface parameters of the photocatalysts are shown in (Table 1). As shown in (Table 1), [BMIm]PF$_6$ greatly the specific surface parameters of TiO$_2$. The specific surface area increases from 72 m$^2$/g for TiO$_2$ to 121 m$^2$/g for IL-TiO$_2$, the pore volume also increases from 0.26 cc/g to 0.35 cc/g. The mean pore size decreases from 7.3 nm to 5.9 nm.

It is found that [BMIm]PF$_6$ greatly alters the distribution of the pores, as shown in (Figure 1). Appropriate distribution of the pores is beneficial to the diffusion of the reactants and products, which can help promote the photocatalytic performance. It is generally recognized that the photocatalytic process is related to the effective adsorption and desorption of molecules on the surface of the photocatalyst [31]. A high specific surface area can provide more reactive adsorption/desorption sites for photocatalytic reactions [32]. The photocatalytic performance benefits from a high surface area and an appropriate distribution of pores of the photocatalyst, this result can be further confirmed by the results of photocatalytic activity measurements presented below.

The XRD patterns of the photocatalysts prepared are shown in (Figure 2). As shown, all strong patterns can be indexed as pure anatase-type TiO$_2$ (JCPDS No. 89-4921). No other patterns can be observed, indicating high crystallinity of the as-prepared TiO$_2$ samples. Based on the XRD results, the crystallite size D of the photocatalysts was calculated using the Scherrer equation as follows: $D = K \lambda / \beta \cos \theta$, where $\lambda$ is the wavelength of the X-ray radiation ($\lambda = 0.154$ nm), K is the Scherrer constant, a dimensionless shape factor K=0.89, and $\theta$ is the Bragg angle $\beta$.

<table>
<thead>
<tr>
<th>photocatalyst</th>
<th>$S_{ss}$ (m$^2$/g)</th>
<th>Pore volumes(cc/g)</th>
<th>Pore size(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>72 ± 3</td>
<td>0.26 ± 0.02</td>
<td>72.7 ± 3</td>
</tr>
<tr>
<td>IL-TiO$_2$</td>
<td>121 ± 5</td>
<td>0.35 ± 0.03</td>
<td>59.3 ± 2</td>
</tr>
</tbody>
</table>

Table 1: Surface parameter of the prepared photocatalysts.

is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. From the equation, the crystal sizes of the IL-TiO₂ and TiO₂ were found to be 9 and 15 nm, respectively. This result illustrates that the increased crystal size leads to a decrease in BET surface area, which is consistent with the results of the BET surface area measurements.

The morphology of photocatalysts plays an important role in affecting the photocatalytic activity. The SEM images of photocatalysts prepared are shown in (Figure 3). As shown in (Figure 3), IL-TiO₂ looks rather irregular and porous, while TiO₂ appears less porous. In addition, the particle size of IL-TiO₂ is smaller than that of TiO₂. The microporous structure is attributed to the strong hydrogen bonds formed between the anions of the RTIL and the hydroxyl groups of the TiO₂ gel during the sol-gel process [34]. This may have caused the anions to be oriented along the pore walls and the cations to be aligned along with the anions because of the Coulomb interaction, molecular stacking via Van der Waals forces, or other noncovalent interactions between neighboring imidazolium rings [25,35-37]. Furthermore, the strong hydrogen bond formation is beneficial to produce uniformly adsorbed nuclei at the initial stage of the photocatalytic reaction. In general, the shape will greatly influence the chemistry and properties of nanomaterials [38]. This result can further be confirmed by the results of photocatalytic activity measurements.

It is commonly accepted that the UV-Vis diffuse absorption and reflection properties may have a strong effect on the photocatalytic activity. As shown in (Figure 4), the two photocatalysts have similar UV-Vis diffuse reflectance spectra, which demonstrates that [BMIm]PF₆ is not effectively changing the band-gap of TiO₂.

The X-ray photoelectron spectroscopy (XPS) was carried out to determine the surface chemical composition of TiO₂ and IL-TiO₂ as well as the valence states of various species. As shown in (Figure 5), the two XPS spectra reveal characteristic peaks for titanium, oxygen, and carbon. In the IL-TiO₂, XPS spectrum P and F were detected at ≤1% levels as remnants of the IL solvent on the IL-TiO₂ surface.

Figure 6 shows the high resolution XPS spectra of the Ti2p₃/2 region taken from TiO₂ and IL-TiO₂. Considering the measurement error of 0.2 eV, Ti2p₃/2 of the two photocatalysts shows no obvious difference, which suggests that no anionic doping into IL-TiO₂ and no substitution for the lattice O²⁻.

Figure 7 shows high resolution XPS spectra of the O1s region taken on the surface of the TiO₂ and IL-TiO₂. The O1s can be fit with their curves appearing at 529.8 and 531.9 eV, which can be attributed to Ti-O (529.8 eV) and O-H (531.9 eV) components [39]. The hydroxyl groups existing on TiO₂ and IL-TiO₂ are attributable to the chemically adsorbed H₂O [39]. The adsorbed H₂O can react with TiO₂ to form Ti–OH, such as, H₂O + Ti=O–Ti → 2Ti–OH [40]. (Table 2) lists the curve-fitting results of the O1s XPS spectra for the two photocatalysts in (Figure 7) where % represents the percentage of the two kinds of oxygen contributions.

As indicated in (Table 2), the hydroxyl content on photocatalyst obtained with the addition of [BMIm]PF₆ is doubled compared to that without [BMIm]PF₆. Usually, the increase of hydroxyl content on the surface of TiO₂ is beneficial to the enhancement of photocatalytic performance in aqueous environments [40,41]. This result is then further confirmed by the results of photocatalytic activities.

The surface photovoltage (SPV) of the TiO₂ and IL-TiO₂ samples are shown in (Figure 8). As shown, the TiO₂ and IL-TiO₂ samples display obvious SPV response peaks at about 320-380 nm.
nm, which is attributed to the electronic transitions from the valence band to the conduction band (O2p → Ti3d) according to TiO2 energy band structure and the diffuse reflectance spectroscopy.

In general, strong SPS response corresponds to high separation efficiency of photoinduced charge carriers on the basis of the SPS principle [42,43]. The strong and complex SPV signal of TiO2 nanocrystals (NCs) indicates that TiO2 has many trapping states. Or, in other words, photoexcited TiO2 NCs have many surface net charges. Surface net charge potentially promotes the flow of electrons and holes. In a potential gradient this can be detected as surface current. Compared with the TiO2 NCs, the diameter of the individual nanoparticles of IL-TiO2 is small. The surface net charges are absent or small, and therefore, the SPV signal of IL-TiO2 is weak. Often, higher charge separation efficiency can promote the photocatalytic performance. However, combined with the results of photocatalytic performance, it becomes obvious that the charge separation efficiency is not the decisive factor influencing the photocatalytic activity in this current case. It becomes evident that the measured surface photovoltage in TiO2 NCs is mainly due to localized photoinduced carriers. Thus, it is interesting to study which carriers are mobile and which ones are localized. Therefore, phase spectra of TiO2 NCs and IL-TiO2 NCs were measured. Phase spectra of the as-prepared photocatalysts are shown in (Figure 9).

The phase values of TiO2 are positive, which means that the photogenerated electrons transfer to the electrode from which light is incident, [44] while the phase values of IL-TiO2 are in the negative range. This means that the photogenerated holes transport to the irradiated electrode [44]. It is clear that adding [BMIm]PF6 into the synthesis of TiO2 has a strong effect on the transport properties of the photogenerated charges. However, it is still unclear which element (F, P or together) or structural change caused this difference. More detailed studies will be needed in the future.

**Photocatalytic activity**

Photocatalytic control experiments were carried out under two conditions: one with illumination but no photocatalysts and the other with photocatalysts (TiO2 and IL-TiO2) but no illumination. The results demonstrate that the decay curves of MO under the two conditions show barely any decay. The photocatalytic activities of TiO2 and IL-TiO2 are compared to the
control experiments and presented in (Figure 10).

As shown in (Figure 10), the logarithmic expressions for these MO concentration curves show that the decolorization rates fit a first-order decay model well. The integral equation of \( \ln(C/C_0) = K_{obs}t \) describes the tendency, where \( C \) and \( C_0 \) are the observed pseudo-first-order rate constant. The decolorization rate constant of MO solution over TiO\(_2\) and IL-TiO\(_2\) are 0.004 min\(^{-1}\) and 0.088 min\(^{-1}\), respectively. The decolorization rate constant of MO solution over IL-TiO\(_2\) is 22 times faster than over TiO\(_2\). Adding [BMIm][PF\(_6\)] into the synthesis dramatically promotes the photocatalytic activity of the prepared TiO\(_2\) photocatalyst. Despite only a small increase in BET surface area (factor 1.68), the IL-based catalyst is much more photoactive (factor 22) than the one without IL addition. This is ascribed to the channel within the microporous structure of IL-TiO\(_2\), which can facilitate access to new active sites on the catalyst walls [39]. Furthermore, the improved photocatalytic activity may be attributed to higher specific surface area, appropriate distribution of the pore size, high hydroxyl content and small nanocrystal size, as summarized above in (Table 1).

**CONCLUSIONS**

In conclusion, microporous TiO\(_2\) with high photocatalytic efficiency has been synthesized successively by the sol-gel method with the aid of the ionic liquid ([BMIm][PF\(_6\)]). The results show that [BMIm][PF\(_6\)] not only alters the surface parameters, the morphology and the transport of the photogenerated charges, but also increases the hydroxyl content on the surface of the catalyst. The photocatalytic decolorization rate constant of MO solution over the IL-TiO\(_2\) is 22 times of that over the reference TiO\(_2\) photocatalyst. The unique morphology and high hydroxyl content may assist in more efficient adsorption and catalytic sites. Fabrication of TiO\(_2\) with the assistance of ionic liquids is an effective way to promote the photocatalytic performance of nanoscale TiO\(_2\).

**ACKNOWLEDGMENTS**

This project was supported financially by the program of Science and Technology Department of Sichuan province (No.2013JY0080), the Project of Zigong city (10X03), Research Fund Projects of Sichuan University of Science and Engineering (2012PY05), Construct Program of the Discipline in Sichuan University of Science and Engineering, and the Opening Project of Key Laboratory of Green Catalysis of Sichuan Institutes of High Education (No. LZJ1202, LYJ1203).

**REFERENCES**


Cite this article