Preparation and Characterization of Nano-TiO$_2$ Loaded Bamboo-based Activated Carbon Fibers by H$_2$O Activation

Dongna Li, Xiaojun Ma,* Xinyan Liu, and Lili Yu

As the support for loading TiO$_2$, bamboo-based activated carbon fibers (BACFs) were obtained from *Phyllostachys pubescens* Mazel after liquefaction using phenol, melt-spinning, curing carbonization, and H$_2$O activation. TiO$_2$/BACFs were prepared by the sol–gel method and characterized by SEM, XRD, FTIR, and XPS. Anatase TiO$_2$ film with high photocatalytic activity was formed on the surface of BACFs, and the average crystallite size of the TiO$_2$ film was 17 to 30 nm. The characteristic absorbance peaks of anatase TiO$_2$ were observed at 1402 and 541 to 605 cm$^{-1}$ on the infrared spectrum of TiO$_2$/BACFs. The surface of TiO$_2$/BACFs was mainly comprised of C–C, C–O, C=O, and Ti–O bonds. With increased calcination temperature, the contents of element Ti and Ti–O bonds of lattice oxygen on the surface of TiO$_2$/BACFs increased and then decreased. The degradation rate of TiO$_2$/BACFs for methylene blue (MB) solution reached more than 98% after 7 h of UV illumination.

Keywords: Bamboo-based activated carbon fibers; Nano-TiO$_2$ Loaded; Photocatalyst; Characterization

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INTRODUCTION

Nano-TiO$_2$ has numerous excellent characteristics, including high oxidative property, good stability, low cost, and non-toxicity. However, suspension system powder-type TiO$_2$ photocatalyst degrades more slowly when the target pollutant content is lower (Vinodgopal et al. 1994). Activated carbon fibers (ACFs), with good adsorption and uniform pore structure, have been used as a catalyst support for TiO$_2$ loading (Uraki et al. 2001; Fu et al. 2004; Liu et al. 2006; Mo and Ye 2009; Yao et al. 2010). But ACFs as the support are mainly prepared from fossil resources and are adverse to sustainable use of support materials.

Over the last few decades, some researchers have paid attention to biomass-based activated carbon fibers (Asakura et al. 2004; Okabe et al. 2005; Senthilkumaar et al. 2005; Phan et al. 2006; Tan et al. 2007; Zhao et al. 2010). However, biomass constituents such as cellulose and lignin have been used only to a relatively minor extent. The utilization ratio of raw materials is quite low, which limits the development and application of biomass resources. In recent years, due to the development of biomass liquefaction technique, the liquefaction of biomass materials has been developed for preparing carbon fibers (Ma and Zhao 2010, 2011). This will provide a new method for
the preparation of biomass based activated carbon fibers and biomass photocatalytic composite material.

The objective of this study was to prepare TiO$_2$-loaded activated carbon fibers from liquefied bamboo powder (TiO$_2$/BACFs) by the sol–gel method. In order to determine the catalytic performance of TiO$_2$/BACFs, the surface structure and characterization of TiO$_2$/BACFs were addressed in detail. At the same time, the photocatalytic degradation of TiO$_2$/BACFs for methylene blue (MB) is also discussed.

**EXPERIMENTAL**

**Materials**

The raw material was moso bamboo. The powder of 20 to 80 mesh size was dried in an oven at 100 °C for 24 h prior to being used. All other chemicals in the study were reagent grade, and they were used without further purification.

**Preparation of Photocatalytic Composite Material**

A mixture composed of dried bamboo (*Phyllostachys pubescens* Mazel) powder (20 to 80 mesh) and phenol at a mass ratio of 1:6 was liquefied for 2.5 h at 160 °C with 8% phosphoric acid (based on the mass ratio of phenol). The as-prepared liquefaction mixture was placed into a reaction tube with 5% hexamethylenetetramine (based on the mass ratio of liquefaction) as the synthetic material. The mixture was heated to prepare the spinning solution, and the initial fibers were prepared by melt-spinning in a spinning machine.

After melt-spinning, the spun filaments were cured by soaking in a solution HCHO and HCl as main components at 95 °C for 4 h, washed with deionized water and finally dried. The precursors were activated for 40 min at different activation temperature in a 100 mL/min stream of N$_2$ and a certain amount of water vapor. BACFs from liquefaction were prepared.

Adding 10 mL of (TiOC$_4$H$_9$)$_4$ dropwise into 2/3 ethyl alcohol, solution A was obtained after stirring for 1 h with a magnetic stirring apparatus. Glacial acetic acid was added dropwise into the remaining 1/3 ethyl alcohol, which was mixed with deionized water to obtain solution B. Then, solution B was slowly added to solution A and stirred for 1 h until it became transparent. The mixture was placed in a thermostatic water bath at 35 °C for 2 h aging to obtain a milky white colloidal solution. The measured BACFs were put into the solution and vibrated for 30 min. After a certain time of still dipping, the fibers were weighed after drying at 105 °C for 2 h, and calcined for several hours in a 100 mL/min stream of N$_2$, and then naturally cooled. TiO$_2$/BACFs photocatalytic material was prepared.

**Characterization of TiO$_2$/BACFs**

The surface morphologies of TiO$_2$/BACFs were examined using an SEM (SS-550, SHIMAPZU) device with an acceleration voltage of 15 Kv.

The crystal structures of TiO$_2$/BACFs were measured with a Power X-ray Diffractometer (D/max-2500, Japan Rigaku) using Cu Kα radiation (wavelength was 0.154 nm, powdery samples), diffraction angle range of 2θ= 5 to 60° with a count time of...
20 s at each point. The accelerating voltage and applied current were 40 kV and 100 mA, respectively. The average crystallite size \( D \) was calculated according to the Scherrer’s equation,

\[
D = \frac{0.89 \lambda}{\beta \cos \theta}
\]  

(1)

where \( D \) is the crystallite size (nm), \( \lambda \) is X-ray wavelength (0.154 nm), \( \theta \) is the Bragg angle of diffraction peaks (º), and \( \beta \) is full width at half maximum (FWHM). The FWHM of each diffraction line was determined from the profile measured with a scanning rate of \( 1/2^\circ (2\theta) \) min\(^{-1} \), which was calibrated by standard silicon powder for instrumental broadening.

The chemical characterization of functional groups was detected using pressed potassium bromide (KBr) pellets containing 5% of sample by Fourier transform infrared spectrometry (Nicolet-6700, Thermo electron) in the scanning range of 4000 to 400 cm\(^{-1} \). XPS measurements of the samples at various calcination temperatures were carried out on a Kratos Axis UltraDLD multi-technique X-ray photoelectron spectroscopy with a monochromated Al K\( \alpha \) X-ray source \( (h\nu = 1486.6 \text{ eV}) \). XPS survey spectra were recorded with pass energy of 80 eV and high resolution spectra with a pass energy of 40 eV.

The photocatalytic property of TiO\(_2\)/BACFs was determined using a self-made photocatalytic reaction device (darkroom with ultraviolet lamp and magnetic stirring apparatus). A 100 mL sample of methylene blue (MB) solution with a certain content (the maximal absorption wavelength was 665 nm) was used as the target degradation product. Up to 0.1 g of shredded TiO\(_2\)/BACFs were poured into the solution to be degraded and stirred for 15 min in a darkroom to reach adsorption equilibrium. Then, the ultraviolet lamp (254 nm) was turned on. After a period of illumination, the absorbance of the sample was measured at 665 nm by ultraviolet-visible spectrophotometry. The degradation rate of MB was calculated using the following equation,

\[
\alpha = \frac{A_0 - A}{A_0} \times 100\%
\]  

(2)

where \( A_0 \) is the solution content before illumination and \( A \) is the solution content after illumination at a moment.

RESULTS AND DISCUSSION

Morphological Characteristics of TiO\(_2\)/BACFs

The SEM images of TiO\(_2\)/BACFs are shown in Fig. 1. Parts 1 (a), (b), and (c) show that TiO\(_2\) was deposited on almost every BACF with a near-uniform coating thickness. However, cracking and spalling of the formed film were observed on the surface of TiO\(_2\)/BACFs. This is due to loose loading of the TiO\(_2\) film before calcination and the shrinkage of TiO\(_2\) film during calcination. Figure 1 (d) shows that some TiO\(_2\) particles were present. It was found that the granular TiO\(_2\) was deposited onto the surface of TiO\(_2\)/BACFs during the reaction. Figure 1 (e) shows TiO\(_2\)-filled BACFs’ pore and not
TiO$_2$-filled BACFs’ pore structure, respectively. This indicates that the pore structure of BACFs is not blocked completely after loading with TiO$_2$. Such loading evidently did not reduce the absorption performance of the BACFs.

![SEM images showing the structure of TiO$_2$-loaded BACFs](image)

**Fig. 1.** SEM of TiO$_2$ loaded on activated carbon fibers (a,b,c,d,e-- Surface)

### Effects of Preparation Condition on the Degradation Rate of MB

Figure 2 shows the effect of lighting time on the degradation rate of MB. After 7 h of UV light exposure, the degradation rate of TiO$_2$/BACFs for MB was 98.12%, 99.06%, 98.76%, and 98.55%, respectively. The product exhibited much higher photocatalytic activity than commercial TiO$_2$ (Degussa P-25), about 90% of degradation rate after 7 h of UV illumination (Wang et al. 2010, Zhang et al. 2013). As the lighting time was extended, the photocatalytic degree of TiO$_2$/BACFs on MB became enhanced significantly. The best photocatalytic activity was observed at 450 °C, and when the temperature was too high or too low, the activity was reduced. This is mainly because
when the calcination temperature was 400 °C, the anatase crystal TiO$_2$ with high photocatalytic activity was not formed. When the temperature was above 500 °C, particles of nano-TiO$_2$ would grow and shrink, leading to the enlargement of particle size. As a result, the atoms on the surface decrease quickly and the light adsorption efficiency also decreases, so a saturation state is easily reached, reducing photocatalytic activity (Teruhisa et al. 1997).

**Fig. 2.** The effect of lighting time on the degradation rate of MB for samples at different calcination temperatures

**XRD analysis of TiO$_2$/BACFs**

Figure 3 shows XRD spectra of TiO$_2$/BACFs at various calcination temperatures. The diffraction peaks at 25.36°, 37.92°, 48.18°, 53.88°, and 54.94° are attributed to the (101), (004), (200), (105), and (201) planes of anatase TiO$_2$, respectively. All the TiO$_2$ films on the surface of BACFs were composed of anatase, indicating that TiO$_2$ was transformed from an amorphous structure to anatase crystal with high photocatalytic property.
Fig. 3. XRD of TiO$_2$/BACFs at various temperatures

From Fig. 3, it could be seen that with increased calcination temperature, the diffraction peaks of anatase TiO$_2$ were narrowed and became more prominent. This means that the crystallization degree of TiO$_2$ was enhanced. It also has been found that the rutile TiO$_2$ diffraction peak does not appear (Inagaki et al. 2003; Zhang et al. 2005; Rong et al. 2010), indicating that the high calcination temperature does not lead to the transformation of TiO$_2$ from anatase to rutile.

Table 1. Relationship between Temperature and Particle Size of TiO$_2$/BACFs

<table>
<thead>
<tr>
<th>Calcination temperature/ °C</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average crystallite size/ nm</td>
<td>17.09</td>
<td>17.50</td>
<td>25.16</td>
<td>29.11</td>
</tr>
</tbody>
</table>

Table 1 shows the particle size of TiO$_2$/BACFs as calculated by the Scherrer formula. It could be seen that with increased calcination temperature, the average crystallite size of TiO$_2$ increased. However, the average crystallite size D was rather small, in the range of 17 to 30 nm and D<< 100 nm, which corresponds to nano-size.

FTIR Analysis of TiO$_2$/BACFs

Figure 4 shows FTIR spectra of BACFs and TiO$_2$/BACFs at various temperatures. It could be seen that BACFs and TiO$_2$/BACFs both presented widely distributed adsorption bands in the range 3200 to 3600 cm$^{-1}$ (-OH). The intensity of the TiO$_2$/BACFs’ stretching vibration (-OH) was slightly larger than that of the BACFs, because the TiO$_2$/BACFs’ vibration was the result of the combined action of phenolic hydroxide (BACFs) and water molecules on the surface of loaded nano-TiO$_2$. With increased calcination temperature, the adsorption intensity of TiO$_2$/BACFs gradually decreased. The broad-band adsorption peak began to shift towards higher wave number, with a narrowed peak shape. This indicates that the thermal treatment had removed most of the water from the samples. However, there was still some residual water in the TiO$_2$. Both BACFs and TiO$_2$/BACFs showed weak adsorption peaks at 2921 and 2854 cm$^{-1}$, which were related to C-H. With increased calcination temperature, the strength of two
adsorption peaks increased and then decreased, and the adsorption peaks at 1633 to 1635 cm\(^{-1}\) (C=C) also decreased. This suggests that the C=C bond of the samples was not completely damaged during calcination.

BACFs and TiO\(_2\)/BACFs present adsorbance peaks near 1402 cm\(^{-1}\). The adsorbance peaks was due to the stretching vibration of aromatic ring C-H. A weak adsorbance peak was also observed in the range 541 to 605 cm\(^{-1}\) (Ti-O), which is the characteristic adsorbance range for anatase TiO\(_2\). It indicates that the precursor of Ti was transformed to anatase TiO\(_2\) with high photocatalytic property. As the loading rate of nano-TiO\(_2\) was lowered, its adsorption peak became relatively weak.

In addition, a strong adsorption peak appeared near 1114 cm\(^{-1}\), which corresponds to the P-O-C bond (Rincon et al. 2006). The adsorption peak was the result of adding phosphoric acid catalyst during liquefaction.

**Fig. 4.** FTIR of TiO\(_2\)/BACFs at various temperatures

### XPS Analysis of TiO\(_2\)/BACFs

Figure 5 shows XPS spectra of TiO\(_2\)/BACFs at various temperatures. These results indicate the presence of primarily C, O, and Ti on the surfaces and relatively smaller amounts of P (Fig. 5(a)). The presence of P could also be explained from the addition of phosphoric acid catalyst for liquefaction. The main elemental composition on the surface of TiO\(_2\)/BACFs is shown in Table 2. As seen from Table 2, carbon was found to be the most abundant constituent of all of the samples. With increased calcination temperature, titanium first increased and then decreased. The crystals of nano-TiO\(_2\) became more complete and TiO\(_2\) content increased upon exposure to the proper calcination temperature. However, if the calcination temperature was excessively high, TiO\(_2\) particles would be sintered, and TiO\(_2\) films will contract, crack, and even fall off, which result in fewer elements Ti. By contrast the elements C, O, and P did not exhibit any significant changes in any of the samples.

In order to obtain information about the chemical composition and the binding characteristics of the elements on the surface of TiO\(_2\)/BACFs, measurements of the XPS spectra of the C1s, O1s, and Ti 2p region were analyzed. The spectra of four samples
were almost the same; thus only the sample prepared at 450 °C is taken as an example, with its XPS spectra shown in Fig. 5 (b-d). Figure 5(b) indicates that the C1s curve fitting was optimized into three independent peaks: the graphitic carbon (C-C, BE=284.5 eV), ether or hydroxy group (C-O, BE=285.5-285.7 eV), and carbonyl or quinine groups (C=O, BE=286.4-286.6 eV) (Bourgeois et al. 1995; Zhang et al. 2006; Zhu et al. 2011), respectively. It is clear that the loaded nano-TiO$_2$ did not affect the formation of graphite structure of BACFs.

The XPS spectrum of O1s shown in Fig. 5(c) presents three obvious peaks after peak fitting: the lattice oxygen (O$_L$), hydroxyl oxygen (O$_{OH}$), and adsorbed oxygen (O$_{ad}$), respectively. The former mainly corresponds to Ti-O in the TiO$_2$ crystal (BE=530.5-530.6 eV). In Fig. 5(d), the binding energy of Ti 2p1/2 and Ti 2p3/2 is 465.0 and 459.3 ev, respectively, with an energy level interval of 5.7 ev. This is consistent with previous studies and indicates that Ti of the TiO$_2$/BACFs is in the binding state of Ti$^{4+}$(TiO$_2$).

![XPS spectra of TiO$_2$/BACFs at various temperatures](image)

**Fig. 5.** XPS spectrum of TiO$_2$/BACFs at various temperatures

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>C1s BE (eV)</th>
<th>M (%)</th>
<th>O1s BE (eV)</th>
<th>M (%)</th>
<th>Ti 2p BE (eV)</th>
<th>M (%)</th>
<th>P 2p BE (eV)</th>
<th>M (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>284.6</td>
<td>80.69</td>
<td>532.3</td>
<td>16.98</td>
<td>459.2</td>
<td>1.80</td>
<td>133.6</td>
<td>0.54</td>
</tr>
<tr>
<td>450</td>
<td>284.5</td>
<td>84.62</td>
<td>532.0</td>
<td>9.42</td>
<td>459.1</td>
<td>5.54</td>
<td>133.9</td>
<td>0.42</td>
</tr>
<tr>
<td>500</td>
<td>284.5</td>
<td>82.15</td>
<td>532.5</td>
<td>12.39</td>
<td>459.3</td>
<td>5.09</td>
<td>133.7</td>
<td>0.38</td>
</tr>
</tbody>
</table>

**Table 2.** Elemental Composition of the Surface of TiO$_2$/BACFs

The results of the fits of the C1s and O1s regions are listed in Table 3. It could be seen that the main peak of C1s corresponded to graphitic carbon. With increased calcination temperature, the contents of C-C bond and -OH decreased, while that of C-O and C=O bonds increased overall. Mainly because with the rising of temperature, the graphite carbon involved in the reaction was increased, which broke C-C bonds and formed new C-O or C=O bonds. High-temperature calcination would remove the water molecules contained in the TiO2/BACFs, resulting in a decrease of -OH. The content of Ti-O bonds first increased and then decreased. This was mainly because the loading degree of TiO2 on the surface of BACFs was enhanced, with a higher loading rate of TiO2 and more Ti-O bond. But under higher temperature, the TiO2 films loaded on the surface of BACFs cracked and finally fell off, so Ti-O bonds showed a lower content.

<table>
<thead>
<tr>
<th>T /°C</th>
<th>C-C BE /eV</th>
<th>M /%</th>
<th>C-O BE /eV</th>
<th>M /%</th>
<th>C=O BE /eV</th>
<th>M /%</th>
<th>O_L (Ti-O) BE /eV</th>
<th>M /%</th>
<th>O_OH BE /eV</th>
<th>M /%</th>
<th>O_ad BE /eV</th>
<th>M /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>284.5</td>
<td>54.93</td>
<td>285.5</td>
<td>11.37</td>
<td>286.4</td>
<td>33.71</td>
<td>530.5</td>
<td>16.68</td>
<td>531.9</td>
<td>24.48</td>
<td>533.0</td>
<td>58.84</td>
</tr>
<tr>
<td>450</td>
<td>284.5</td>
<td>54.15</td>
<td>285.5</td>
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<td>286.5</td>
<td>33.46</td>
<td>530.6</td>
<td>33.06</td>
<td>531.9</td>
<td>17.23</td>
<td>533.2</td>
<td>49.71</td>
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<tr>
<td>500</td>
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<td>53.33</td>
<td>285.7</td>
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<td>33.34</td>
<td>530.6</td>
<td>25.82</td>
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<td>533.2</td>
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<tr>
<td>550</td>
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<td>34.29</td>
<td>530.6</td>
<td>20.93</td>
<td>531.9</td>
<td>10.56</td>
<td>533.1</td>
<td>68.51</td>
</tr>
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</table>

CONCLUSIONS

TiO2/BACFs were prepared by the sol-gel method and with BACFs as the support, which were obtained after phenol liquefaction, melt spinning, and curing treatment from the phenolated bamboo by H2O activation. The degradation rate of TiO2/BACFs on MB improved with longer exposure to UV illumination. All TiO2 films on the surface of BACFs were composed of anatase with high photocatalytic activity, and the average crystallite size of TiO2 was 17 to 30 nm. The characteristic adsorption peaks of TiO2 emerged at 1402 and 541 to 605 cm⁻¹ on the infrared spectrum of TiO2/BACFs. With increased calcination temperature, content of titanium and the amount of Ti-O bonds of lattice oxygen on the surface of TiO2/BACFs increased and then decreased, with no major changes to C, O, and P contents. Ti was in the binding state of Ti⁴⁺ (TiO₂) on the TiO₂/BACFs.

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REFERENCES CITED


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