Preparation of Carbon-TiO₂ Composites by Using Different Carbon Sources with Titanium n-Butoxide and Their Photocatalytic Activity

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ABSTRACT: We used activated carbon (AC), activated carbon fiber (ACF) and multi-walled carbon nanotube (MWCNT) as carbon sources and titanium n-butoxide as titanium source to prepare carbon-TiO₂ composites. For characterization their properties, scanning electron microscopy (SEM), transmission electron microscopy (TEM), BET surface area, X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX) were used. And the photoactivity of the carbon-TiO₂ composites, under UV irradiation, was tested using the fixed concentration of methylene blue (MB, C₁₆H₁₈N₃S·Cl·3H₂O) in aqueous solution. After UV irradiation for a certain time, the concentration of MB solution was determined by UV-vis absorption spectroscopy.

Keywords: Carbon source; Titanium n-butoxide; TEM; Photocatalytic decomposition

Ⅰ. Introduction

Titanium (IV) dioxide or titania (TiO₂) has been recognized as one of the most important oxide used in industrial applications because of its physical and chemical properties, such as catalytic activity, photocatalytic activity for pollutant removal, good stability toward adverse environment, sensitivity to humidity and gas, dielectric characteristic, photo-electro-chemical conversion, nonlinear optics, photoluminescence. Its applications include the use as catalysts, catalyst supports, cosmetics, pigments and filler coating. Nevertheless, photocatalysis is one of the most important uses of titania. Titania is known to have three natural polymorphs: rutile, anatase, and brookite. Rutile is thermodynamically stable polymorph, but anatase is more suitable form for catalytic applications. Several attempts have been adopted to enhance the photocatalytic performance of TiO₂, such as immobilization of TiO₂ powder onto supports like activated carbon (AC), activated carbon fiber (ACF) and so on. AC is highly adsorptive owing to its developed pore structure and high specific area; moreover the particle size of commercial AC is usually in the micro-scale range. Comparing with AC, ACF are produced in the form of felt or cloth, with high BET surface area and micropore volume. Moreover, since the discovery of carbon nanotubes (CNT) efforts have been made to explore their applications using various approaches, as they are in fact one of the most remarkable emergent materials. Especially, Multi-walled carbon nanotube (MWCNT) offers enormous potential for their high electron-carrying capability, high thermal conductivity and high mechanical strength. MWCNTs are the best candidates for the preparation of photocatalytic composites.
pared from activated carbon, activated carbon fiber and carbon nanotube. So in this paper, we did a comparison of three kinds of carbon-TiO$_2$ composites prepared from activated carbon (AC), activated carbon fiber (ACF) and multi-walled carbon nanotube (MWCNT) with titanium $n$-butoxide (TNB), respectively, and determined the influence of carbon sources on the photocatalytic activity. To compare the properties of these carbon-TiO$_2$ composites, the corresponding composites were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), BET surface area, X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX).

To compare the photocatalytic decomposition, the carbon-TiO$_2$ composites were also determined by the methylene blue (MB, C$_{16}$H$_{18}$N$_3$S·Cl·3H$_2$O) in an aqueous solution under UV irradiation.

Ⅱ. Experimental

1. Materials

Activated carbon (AC, ca. 80 μm), activated Carbon Fiber (ACF) and multi-walled carbon nanotube (MWCNT, diameter: ~ 20 nm, length: ~ 5 μm) as carbon sources, were purchased from Dong Yang Carbon Co., Ltd (Korea), EAST ASIS Carbon Fibers Co., Ltd (China) and Nanokanbon Co., Ltd (Korea), respectively. Titanium $n$-butoxide (TNB, Ti(OC(CH$_3$)$_3$)$_4$, 97%) as a titanium source for the preparation of carbon-TiO$_2$ composites was purchased from Acros Organics (New jersey, USA). For the oxidization the surface of MWCNTs, $m$-chlorperbenzoic acid (MCPBA) was used as an oxidized reagent which was purchased from Acros Organics, New Jersey, USA. Benzene (99.5%) was used as organic solvents which were purchased from Samchun Pure Chemical Co., Ltd (Korea). The methylene blue (MB) was used as analytical grade which was purchased from Dukan Pure Chemical Co., Ltd. It was selected because it shows less absorption at the absorption edge (~ 380 nm) of anatase TiO$_2$ and is relatively stable against UV irradiation.

2. Synthesis of carbon-TiO$_2$ composites

AC is powder type, so it could be used directly. However, ACF is the form of fiber, so it is needed to mill to powders. And the MWCNT had a stability structure, so it is needed to pre-treat to introduce active function groups on their surface. According to our previous works,$^{25-28}$ we used $m$-chlorperbenzoic acid (MCPBA) to oxidize the MWCNT. 0.96 g MCPBA was melted in 60 mL Benzene at first. Then MWCNT was put into the oxidizing agent. The mixture was stirred with a magnet for 6 h at 343 K. Then the MWCNT was dried at 373 K. For preparing the carbon-TiO$_2$ composites, the AC, ACF powder and oxidized MWCNT were put into the TNB solution, respectively. At the same time, the mixtures were stirred with a magnet in a container for 5 h at 343 K. The mixtures were kept at room temperature until it formed uniform suspension. After thermally treating at 873 K for 1 h with a heating rate of 279 K/min, the TNB in the mixture would change to TiO$_2$, and consequence the carbon-TiO$_2$ composites were obtained. The preparation condition and code of samples were listed in Table 1.

3. Characterization

Synthesized carbon-TiO$_2$ composites were characterized by various techniques. SEM and TEM were used to observe the surface state and structure of the carbon-TiO$_2$ composites were carried out by using a JSM-5200 JOEL electron microscope (Japan). The Brunauer-Emett-Teller (BET) surface area of the carbon-TiO$_2$ composites was measured using a Quantachrome Surface Area analyzer (MONOSORB, USA). XRD was used for crystal phase identification and estimation of the anatase-to-rutile ratio. XRD patterns were obtained at room temperature with a meter Shimata XD-D1 (Japan) using CuK α radiation. EDX was used to measure the elemental analysis of the carbon-TiO$_2$ composites. UV-vis spectra for the MB solution obtained from degradation by carbon-TiO$_2$ composites dispersion under UV ray irradiation were recorded using a Genspec IⅢ (Hitachi, Japan) spectrometer.

4. Photocatalytic decomposition

The photocatalytic effect of carbon-TiO$_2$ composites was determined using MB decomposition in aqueous solution under an ultraviolet (UV) lamp (356 nm, 1.2 mW/cm$^2$). The initial MB concentration was 1.0×10$^{-5}$ mol/L (c$_0$). The amount of suspended composites was kept at 1 g/L in 50 mL MB solution. Before turning on UV lamp, the solution mixed with composites was kept in the dark for at least 2 h, allowing the adsorption-desorption equilibrium to be reached. Then, the solution was irradiated with UV. The first sample was taken out at the end of the dark adsorption period (just before the

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>Nomenclatures</th>
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<tbody>
<tr>
<td>Activated carbon + Titanium n-butoxide (99.99%)</td>
<td>ACT</td>
</tr>
<tr>
<td>Activated carbon fiber + Titanium n-butoxide (99.99%)</td>
<td>ACFT</td>
</tr>
<tr>
<td>Mutil-walled carbon nanotube + Titanium n-butoxide (99.99%)</td>
<td>CNTT</td>
</tr>
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</table>
light was turned on), in order to determine the MB concentration in solution, which was hereafter considered as the initial concentration \(c_{ads}\) after dark adsorption. Samples were then withdrawn regularly from the reactor by an order of 30 min, 90 min, 120 min and 300 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-vis spectrophotometer (250–600 nm). The spectra (550-750 nm) for each sample were recorded and the absorbance was determined at characteristic wavelength 660 nm for the each MB solution degraded.

### III. Results and Discussion

#### 1. Characteristics of carbon-TiO₂ composites

Morphology of carbon-TiO₂ composites prepared from different carbon sources with TNB is characterized by SEM and TEM. The SEM images of the carbon-TiO₂ composites are shown in Figure 1. In the case of sample ACT (Figure 1 a), the TiO₂ particles are mixed with AC very well and distributed regularly on the surface of AC with small aggregation. The morphology of sample ACFT is observed in Figure 1 (b). It is clear that the particles of TiO₂ aggregated into clusters and are fixed on the surface of ACF. As shown in Figure 1 (c), the sample CNTT is an irregular aggregate of particles with large amount of TiO₂ particles and small amount of CNT particles. And the MWCNTs are embedded into TiO₂ particle aggregates. Furthermore, the TEM image in Figure 1 (d) confirms the more detailed morphology of sample CNTT. It is cleanly seen that TiO₂ particles are coated on the surface of MWCNT irregularly with some agglomeration.

The results of BET surface area of pristine AC, ACF, MWCNT and carbon-TiO₂ composites prepared from different carbon sources with TNB are shown in Table 2. The BET

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**Figure 1.** SEM images of the carbon-TiO₂ composites; (a) ACT, (b) ACFT, (c) CNTT and (d) TEM image of the sample CNTT.
Table 2. The BET surface area of carbon-TiO$_2$ composites prepared by different carbon sources and titanium n-butoxide

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$ (m$^2$/g)</th>
</tr>
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<tbody>
<tr>
<td>As-received AC</td>
<td>1083</td>
</tr>
<tr>
<td>As-received ACF</td>
<td>1842</td>
</tr>
<tr>
<td>As-received MWCNT</td>
<td>232</td>
</tr>
<tr>
<td>ACT</td>
<td>728</td>
</tr>
<tr>
<td>ACFT</td>
<td>978</td>
</tr>
<tr>
<td>CNTT</td>
<td>84</td>
</tr>
</tbody>
</table>

The surface area of pristine AC, ACF and pristine MWCNT is 1083 m$^2$/g, 1842 m$^2$/g and 232 m$^2$/g, respectively. Comparing with these pristine materials, it can be clearly seen that there is a markedly decrease of BET surface area after pristine AC, ACF and pristine MWCNT reacting with TNB, which is 728 m$^2$/g, 978 m$^2$/g and 84 m$^2$/g, respectively. As the TNB is solution, so it can be reacted with carbon sources very well and introduced the pore of carbon sources easily. Moreover, the TiO$_2$ particles which coated on the surface of carbon sources are agglomerated together thus decreased the BET surface area.

Figure 2 shows typical XRD patterns of carbon-TiO$_2$ composites prepared from different carbon sources with TNB. As we know,\textsuperscript{18-20} the anatase phase formed below 773 K starts to transform to rutile-type structure above 873 K and changed into single phase of rutile at 973 K-1173 K, the crystal structure of the titanium dioxide is mainly determined by the heat treatment temperature, and the peaks at 25.3, 37.8, 48.0 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase without any other peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks of (110), (101), (111) and (211) of rutile, indicating all of the composites only existed in an anatase state. On the other hand, the charac-
teristic peaks of MWCNTs could hardly be identified from the XRD patterns of carbon-TiO\textsubscript{2} composites. These high angle diffractions are complicated and not easily detected in the figure because of the overlapping of diffraction peaks attributed to TiO\textsubscript{2} and those of the MWCNTs support.

The carbon-TiO\textsubscript{2} composites prepared from different carbon sources with TNB are characterized by EDX. The EDX spectra and EDX elemental microanalysis (wt. %) are shown in Figure 3 and Table 3. From these data, we can see that the main elements such as C, O and Ti are existed in each sample. And the samples ACT and ACFT are richer in C element than sample CNTT, indicated that they have better adsorption effect than sample CNTT. However, the sample CNTT are richer in Ti and O elements than samples ACT and ACFT, indicated sample CNTT have better photocatalytic effect than both of samples ACT and ACFT.

2. Photocatalytic degradation of the MB solution

The changes in relative concentration (c/c\textsubscript{0}) of MB in the aqueous solution on time of UV irradiation for the carbon-TiO\textsubscript{2} composites were determined and the results are shown in Figure 4. As mentioned above, before turning on UV lamp, the MB solution mixed with composites was kept in the dark for at least 2 h, allowing the adsorption-desorption equilibrium to be reached. From the Figure 4, we can see that the concentration of MB solution is reduced 65% and 53% after adsorption by samples ACT and ACFT, respectively. However, the sample CNTT shows lowest adsorption ability for MB solution, only remove 13%. It can be explained from the data of BET surface showed above. After turning the UV lamp, the photocatalytic effect is started. The concentration of MB solution for all samples is decreased by an increasing order of UV irradiation time. As we forecasting, the sample CNTT have most excellent photocatalytic effect, which removed 30% of MB solution. The sample ACFT also has excellent photocatalytic effect, which removed 27% of MB solution. And the sample ACT has lowest photodegradation ability, which only removed 9% of MB solution. The apparent kinetic constant (k\textsubscript{app}) of photocatalytic effect by the synthesized catalysts was also showed in Table 4.

The samples ACFT and CNTT gave the apparent constant of 1.98×10\textsuperscript{-3} min\textsuperscript{-1} and 2.0×10\textsuperscript{-3} min\textsuperscript{-1}, respectively. However, comparing the samples ACFT and CNTT, the sample ACT gave much lower apparent kinetic constant, which is only 9.6×10\textsuperscript{-4} min\textsuperscript{-1}. It can be indicated that the samples ACFT and CNTT have much more photocatalytic activity than sample ACT.

According to our previous works,\textsuperscript{20,21,29} the degradation of MB solution for carbon-TiO\textsubscript{2} composites may have several effects. Firstly, adsorption effect, because the AC, ACF and MWCNT have large surface areas and different aperture structure, can adsorb oxygen and MB particles in solution on the inside or outside of the surface. Secondly, photocatalytic effect, the TiO\textsubscript{2} has excellent photocatalytic effect under the UV irradiation. Furthermore, the carbon sources can also absorb the photo-induced electron (e\textsuperscript{-}) by UV irradiation. Oxygen will get electron from MWCNTs to form very reactive superoxide radical ion O\textsubscript{2}\textsuperscript{•-}, which not only enhances oxidation ability but also absorbs electron on the surface of carbon sources. Thus the photocatalytic activities can be strongly improved. In this

<table>
<thead>
<tr>
<th>Samples</th>
<th>C</th>
<th>O</th>
<th>Ti</th>
</tr>
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<tbody>
<tr>
<td>ACT</td>
<td>51.91</td>
<td>20.72</td>
<td>27.37</td>
</tr>
<tr>
<td>ACFT</td>
<td>40.70</td>
<td>27.42</td>
<td>31.56</td>
</tr>
<tr>
<td>CNTT</td>
<td>22.51</td>
<td>37.17</td>
<td>40.32</td>
</tr>
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Table 3. EDX elemental microanalysis (wt. %) of carbon-TiO\textsubscript{2} composites prepared by different carbon sources and titanium n-butoxide

<table>
<thead>
<tr>
<th>Samples</th>
<th>k\textsubscript{app} (min\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACT</td>
<td>9.6×10\textsuperscript{-4}</td>
</tr>
<tr>
<td>ACFT</td>
<td>1.98×10\textsuperscript{-3}</td>
</tr>
<tr>
<td>CNTT</td>
<td>2×10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Pure TiO\textsubscript{2}</td>
<td>3.14×10\textsuperscript{-4}</td>
</tr>
</tbody>
</table>

Table 4. Apparent kinetic constant (k\textsubscript{app}) of pure TiO\textsubscript{2} and carbon-TiO\textsubscript{2} composites prepared by different carbon sources and titanium n-butoxide

![Figure 4. Dependence of relative concentration of MB in the aqueous solution c/c\textsubscript{0} on time of UV irradiation for the pure TiO2 and carbon-TiO2 composites prepared by different carbon sources and titanium n-butoxide; the concentration of MB solution: 1.0×10\textsuperscript{-5} mol/L.](image-url)
study, we used AC, ACF and MWCNT as carbon sources which have different structures. From the SEM images, we can observe that AC is formed by powder structure, ACF is formed by column structure, and MWCNT is formed by tube structure. It can be considered that the column structure and tube structure could adsorb the photo-induced electron (e\(^{-}\)) by UV irradiation more strongly, due to they have much bigger surface area to adsorb the UV light than powder structure. In conclusion, the sample ACFT has best degradation of MB solution.

IV. Conclusions

The carbon-TiO\(_2\) composites were prepared from AC, ACF and MWCNT with titanium n-butoxide. By the SEM and TEM observations, the TiO\(_2\) particles were coated on the surface of carbon sources and with some aggregations. There is a markedly decrease of BET surface area after carbon sources reacting with TNB, and the samples ACT and ACFT have large BET surface area. XRD results were indicating all of the composites only existed in an anatase state. From the EDX data, the main elements such as C, O and Ti were existed. Finally, according to the results of MB degradation experiment, we could see that sample ACFT had most excellent degradation of MB solution. And the degradation of MB solution for carbon-TiO\(_2\) composites could be considered by adsorption effect of carbon sources and photocatalytic effect of TiO\(_2\). Furthermore, carbon sources could also adsorb the photo-induced electron (e\(^{-}\)) by UV irradiation, which could be strongly improved the photocatalytic activities.

References