Synthesis of Expanded Graphite-Titanium Oxide Composite and its Photocatalytic Performance

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ABSTRACT

In this study, an expanded graphite-titanium oxide composite is developed from expanded graphite (EG) and titanium n-butoxide (TNB). EG is synthesized by chemical intercalation of natural graphite (NG) and rapid expansion at high temperature. TNB is used as the titanium source. The performances of the prepared EG-TiO\(_2\) composite are characterized by BET surface area measurements, scan electron microscope (SEM), X-ray diffraction patterns (XRD) and energy dispersive X-ray analysis (EDX). The catalytic activities of the EG-TiO\(_2\) composite are investigated by analysis of the degradation of methylene blue (MB) in aqueous solution under irradiation of UV light. Compared with the pristine TiO\(_2\) and activity carbon-TiO\(_2\) (AC-TiO\(_2\)) composite, the EG-TiO\(_2\) composite shows very high efficiency against MB solution, and the EG could improve the photocatalytic effect of TiO\(_2\) in the MB degradation reaction under the irradiation of UV light.

Key words: Expanded graphite, Titanium n-butoxide, Photocatalysis, Methylene blue

1. Introduction

Graphite consisting of single atomic carbon layers has the thinnest layer thickness of all layered materials.\(^1\)\(^2\) The use of graphite as a precursor to obtain carbon-related nanoporous materials having very thin pore walls is highly attractive because these materials can have very high specific surface areas.\(^3\) Natural graphite (NG), which is abundant and highly conductive (electrical conductivity at an ambient temperature of 104 S/cm) and has a unique layered nano-structure, is considered an ideal candidate for manufacturing conductive polymer composites. The layered structure has a c-axis lattice constant of 0.66 nm, and there are no reactive surface groups on the graphite layers. It is rather difficult to intercalate organic molecules or polymers directly into the interlayer of graphite through an ion-exchange reaction in preparing polymer-graphite nanocomposites. Exfoliated or expanded graphite (EG) is a kind of modified and low-density graphite with a good surface area, electrical conductivity and high temperature resistance.\(^4\) When graphite intercalation compounds (GICs) are given a thermal shock, the intercalates vaporize and tear the layers apart, which leads to an expansion in the c direction and in a puffed-up material. EG contains abundant multi-pores ranging from 20 to 50 nm. The interlayer spacing of EG increases from 0.335 nm to approximately 0.8 nm and the expansion is several hundred times along the c-axis.\(^5\)\(^6\) EG is used to absorb the polluted oil and various kinds of polluted gas. It has been also applied widely as a kind of functional carbon material used in sealing, catalyzing, space flight, military affairs, environmental protection, etc.\(^7\)\(^8\) The expanded graphite keeps a layered structure similar to natural graphite flakes but with larger interlayer spacing.\(^9\)

Titanium dioxide (TiO\(_2\)) is an important semiconductor material, which has been applied as white pigment, cosmetics, catalyst and carrier owing to its excellent physical and chemical properties.\(^9\)\(^10\) One of its most important applications is to act as a photocatalyst for some chemical reactions, especially for the decontamination of water polluted with organic pollutants.\(^9\)\(^10\)\(^11\)\(^12\)\(^13\)

In this paper, we report on the synthesis and performance of a composite of expanded graphite (EG) and sol-gel derived titanium oxide (titanium n-butoxide, TNB). This composite is expected to have the attributes of EG as well as titanium oxide. BET surface area measurements, scan electron microscope (SEM), X-ray diffraction patterns (XRD) and energy dispersive X-ray analysis (EDX) are used to characterize the performance of the EG-TiO\(_2\) composite. To determine the photocatalytic decomposition of the EG-TiO\(_2\) composites, methylene blue (MB) is chosen as the model pollutant under irradiation of UV light. The EG-TiO\(_2\) composite is found capable of both adsorption concentration and photocatalytic activity toward organic molecules.

2. Experimental

2.1. Materials

Natural graphite with an 80-100 mesh size was obtained...
from Sangjin Co., Ltd, Korea. TNB (TiOC(CH₃)₃, 99.9%) was purchased from Acros Organics Co., Ltd, USA, as the titanium source. Sulphuric acid (H₂SO₄, 95%) and ammonia sulfate ((NH₄)₂SO₄, 95%) were intercalant and were obtained from SAMCHUN PURE CHEMICAL Co., Ltd, Korea and DUKSAN PHARMACEUTICAL Co., Ltd, Korea, respectively. To oxidize the EG, m-chloroperbenzoic acid (MCPBA) was used as an oxidizer, which was purchased from Acros Organics Co., Ltd, USA. Benzene (99.5%) was used to dissolve the MCPBA and was purchased from SAMCHUN PURE CHEMICAL Chemical Co., Ltd, Korea.

2.2. Preparation of expanded graphite

EG was prepared from natural graphite (NG). Graphite intercalation compounds (GICs) yielding EG upon a thermal shock were obtained using chemical oxidation intercalation. The schematic illustrating the preparation of EG is shown in Fig. 1. At first, 3 g (NH₄)₂SO₄ was melted in 100 mL H₂SO₄. Then 1 g NG was put into the (NH₄)₂SO₄-H₂SO₄ solution and stirred at 323 K for 30 min. The mixture was carefully washed and filtrated with distilled water until the pH level of the solution reached 7. After being dried at 373 K for 24 h, the GICs were rapidly expanded at 873 K for 1 h to form EG.

2.3. Synthesis of EG-TiO₂ composites

The preparation of the composite of EG and titanium oxide was based on a sol-gel method. The schematic illustrating the preparation of the EG-TiO₂ composite is shown in Fig. 2. For oxidization of the EG, 1 g MCPBA was melted in 60 mL benzene to prepare the MCPBA-benzene solution beforehand. The prepared EG was suspended in the MCPBA-benzene solution, refluxed at 353 K for 6 h until solid precipitates were formed and dried at 363 K. The oxidized EG was put into a constant volume of TNB solution. The mixture solution was stirred at 343 K for 5 h using a magnetic stirrer in a vial until the solution were transformed into EG-TiO₂ gels. After being dried at 373 K for 24 h, the resulting product was heat treated at 973 K for 1 h to obtain the EG-TiO₂ composite. A simple mechanism during the preparation of the EG and EG-TiO₂ composite is also shown in Fig. 3.

2.4. Characterizations

The synthesized EG-TiO₂ composite was characterized by various techniques. The BET surface area was measured using a Quantachrome Surface Area analyzer (MONOSORB, USA). SEM (JOEL, JSM-5200, Japan) was used to observe the surface state and structure of the EG-TiO₂ composites. XRD was used for crystal phase identification of the composite and estimation of the anastase-to-rutile ratio. XRD

Fig. 1. A schematic illustration of the formation of EG.

Fig. 2. A schematic illustration of the synthesis of the EG-TiO₂ composite.

Fig. 3. A simple mechanism during the preparation of the EG and EG-TiO₂ composite.
patterns were obtained at room temperature with a Shimata XD-D1 (Japan) using CuKα radiation. EDX was used to measure the elemental analysis of the EG-TiO₂ composites. UV-vis spectra for the MB and RhB solution degraded by EG-TiO₂ composites under the irradiation of UV light were recorded using a Genapoe III (Hitachi, Japan) spectrometer.

2.5 Photocatalytic decomposition

The photocatalytic effect of the EG-TiO₂ composite was determined using MB decomposition in an aqueous solution under an UV lamp (356 nm, 1.2 mW/cm²). Because the characteristic dyes concentrations in wastewater from textile industry were in the range of 3.0 × 10⁻⁵ to 1.5 × 10⁻⁴ mol/L, the initial MB concentration was chosen to be 1.0 × 10⁻⁵ mol/L, which was considered as initial concentration (c₀). The amount of suspended composites was kept at 1 g/L in a 50 mL MB solution. The solution was irradiated with UV light. The samples were taken out at 10 min, 20 min, 30 min and 40 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed with a UV-vis spectrophotometer. The spectra for MB (550~750 nm) were recorded and the absorbance was determined at a characteristic wavelength of 660 nm for each degraded MB solution. In this paper, for comparing the degradation effect of MB solution of EG-TiO₂ composite, a pristine TiO₂ and AC-TiO₂ composite (prepared in my previous work) was used as contrast samples under the same experimental conditions.

3. Results and Discussion

3.1 Characteristics of EG-TiO₂ composite

The BET surface area of the pristine TiO₂, AC-TiO₂ composite and EG-TiO₂ composite are shown in Table 1. It could be clearly seen that the AC-TiO₂ composite had the largest BET surface area of 976 m²/g, which indicated the AC-TiO₂ composite would show a very high adsorption effect. The pristine TiO₂ also had a high BET surface area of 132 m²/g, but the BET surface area of the EG-TiO₂ composite was only 27 m²/g. As shown in Fig. 3, the wide pore size distribution revealed that the EG was a mesoporous material with a macroporous network structure. The EG maintained a layered structure similar to NG but with larger interlayer spacing. The special “sandwich” structure and long distance between the carbon layers made it easy to insert atoms or molecules into the carbon layers. When the EG was used to react with TNB in the liquid phase, it was very easy to insert the TiO₂ particles from the reactant and product. As a result of the large number of TiO₂ particles inserted into the carbon layers, the BET surface area of the EG-TiO₂ composite decreased.

The intercalants, which were H₂SO₄ and (NH₄)₂SO₄, were dispersed into the graphite layers to form GICs. After rapid expansion of the GICs at a high temperature, EG was formed. Fig. 4 shows the SEM photomicrographs of NG (a) and EG (b). Comparing (a) and (b), the differences in microstructures could be clearly observed. The as-received NG was composed of thin graphite flakes. The structure of the layers of graphite flakes was regular and the distance between the layers distance was small (Fig. 2 (a)). After chemical intercalation treatment and heat treatment at 873 K, it was clearly seen that the spacing of the interlayers of graphite flakes increased and the structure became porous (Fig. 2 (b)). In EG, the expansion process caused destruction of the graphite crystal structure and a consequent expansion in the c-direction of about a hundred times and resulted in an enormous increase in volume as a consequence of sudden evaporation of intercalate. After expan-
sion, EG emerges as a loose structure and porous material consisting of numerous graphite sheets with thicknesses in nanometers and diameters in micrometers. This structure endows EG with a high surface area. Fig. 2 (c-d) shows the SEM micrograph of the AC-TiO\textsubscript{2} composite. It was observed that the TiO\textsubscript{2} particles were regularly dispersed on the activity carbon surface with a homogeneous distribution of activity carbon. The AC-TiO\textsubscript{2} composite could provide a large surface area and promote the degradation effect of MB in aqueous solution. Fig. 2 also presents the SEM photographs of the EG-TiO\textsubscript{2} composite (e-f, ×200, ×1000). As shown in Fig. 2 (e-f), the preparation process of the composite had an obvious effect on the morphology of EG support. The EG was exfoliated and broken up into shorter fragments under stirring, resulting in many tiny EG fragments in the planar direction. These EG fragments still maintained the layered structure of the NG and the porous structure of the EG. From Fig. 2 (e-f), it was also seen that TiO\textsubscript{2} particles were formed and well spread on the surface of the graphite layers as single or multi-layer, and the size distribution was homogeneous.

Fig. 5 shows the XRD patterns of the AC-TiO\textsubscript{2} composite and EG-TiO\textsubscript{2} composite after heat treatment at 973 K for 1 h. According to former studies,\textsuperscript{23-25} the anatase phase formed below 773 K began to transform to a rutile-type structure above 873 K and changed into single phase of rutile at 973-1173 K. The peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase, indicating the developed composites existed in an anatase state. There are no peaks found at 27.4, 36.1, 41.2 and 54.3 that belong to the diffraction peaks of (110), (101), (111) and (211) of rutile. Therefore, we concluded that both the AC-TiO\textsubscript{2} composite and the developed EG-TiO\textsubscript{2} composite have a single crystal structure, just is the anatase structure. As demonstrated in previous works, the TiO\textsubscript{2} particles with an anatase structure have better photocatalytic activity.\textsuperscript{26,27} Thus, these two composites show a very high photocatalytic effect for the MB solution. On the other hand, there no carbon peaks can be observed from the XRD pattern of the AC-TiO\textsubscript{2} composite. However, the sharp diffraction peak at 2θ= 25-26° appeared in the composite, suggesting that the expanding and reaction with TNB did not alter the scale structure of the NG. As shown in the XRD pattern of the EG-TiO\textsubscript{2} composite, the most distinct peak appearing at 2θ= 26.5° (d= 0.336 nm) corresponded to the “002” diffraction of graphite.

Fig. 6 shows the EDX spectra of the AC-TiO\textsubscript{2} composite (a) and the EG-TiO\textsubscript{2} composite (b). Table 2 shows the EDX elemental microanalysis (wt%) of the AC-TiO\textsubscript{2} composite and EG-TiO\textsubscript{2} composite. Both of the EDX data clearly showed that the two kinds of composites contained three kinds of main elements, C, O and Ti.

### Table 2. EDX Elemental Microanalysis (wt%) of the AC-TiO\textsubscript{2} Composite and EG-TiO\textsubscript{2} Composite

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elements</th>
<th>C</th>
<th>O</th>
<th>Ti</th>
<th>Others</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-TiO\textsubscript{2} composite</td>
<td></td>
<td>57.8</td>
<td>21.1</td>
<td>18.5</td>
<td>2.60</td>
<td>100</td>
</tr>
<tr>
<td>EG-TiO\textsubscript{2} composite</td>
<td></td>
<td>41.12</td>
<td>22.73</td>
<td>35.60</td>
<td>0.55</td>
<td>100</td>
</tr>
</tbody>
</table>

3.2. Photocatalytic activity of EG-TiO\textsubscript{2} composite

Fig. 7 shows the absorption spectra of the MB solution under the irradiation of UV light as a function of various time conditions for the EG-TiO\textsubscript{2} composite. In the present case, the absorbance maxima of the MB solution were appeared at 660 nm. There was a linear relationship between the absorbance and irradiation time, so 660 nm
was used to monitor the photocatalytic efficiency on the degradation of MB. We observed that the absorbance maxima for the EG-TiO$_2$ composite decreased with an increasing of UV irradiation time from the spectra of Fig. 7. This result suggested that the color of the MB solution is removed increasingly with an increasing of UV irradiation time, so the concentration of the MB solution was also decreased increasingly with an increasing of UV irradiation time (shown in further results).

Fig. 8 shows the changes in concentration ($c$) of MB in the aqueous solution at the time of UV irradiation for the pristine TiO$_2$, AC-TiO$_2$ composite and EG-TiO$_2$ composite. The concentration of the MB solution for the AC-TiO$_2$ composite decreased 36% after the first 10 min and gradually decreased with UV irradiation. However, the concentration of the MB solution for the EG-TiO$_2$ composite decreased 96% after the first 10 min and gradually decreased by UV irradiation. From the BET surface area data, the EG-TiO$_2$ composite had an $S_{BET}$ of only 27 m$^2$/g. Thus, we see that electron transfer might play an important role in the MB degradation reaction. Moreover, the characteristics and structure of graphite could be very important. EG is a multifunctional inorganic material with many functional groups and loose carbon sheets, which may facilitate the anchoring and dispersion of TiO$_2$ atoms. Moreover, the graphite sheets have extraordinary electronic transporting properties and high electronic conductivity, and may absorb a large number of electrons under UV irradiation. Furthermore, these electrons will transfer into the TiO$_2$/UV system and thus improve the photocatalytic effect of TiO$_2$.

4. Conclusion

In this investigation expanded graphite was prepared by chemical oxidation and reacted with titanium n-butoxide by the sol-gel method to obtain the EG-TiO$_2$ composite. SEM results showed that EG was exfoliated and broken up in shorter fragments, and TiO$_2$ particles were formed and well spread on the surface of graphite layers in single or multi-layer, and the size distribution was homogeneous. XRD pattern showed that the most distinct peak appearing at $2\theta \approx 26.5^\circ$ corresponded to the "002" diffraction of graphite, and the developed EG-TiO$_2$ composite had a single crystal structure, just as did the anatase structure. EDX spectra and elemental microanalysis (wt%) showed that the composite contained three kinds of main elements, C, O and Ti. Finally, the degradation of the MB solution for the EG-TiO$_2$ composite was studied. Compared with other samples, the MB solution was almost completely decomposed by the EG-

![Fig. 7. UV-vis spectra of the MB solution under the irradiation of UV light as a function of various time conditions: (a) the AC-TiO$_2$ composite and (b) the EG-TiO$_2$ composite.](image)

![Fig. 8. Dependence of concentration ($c$) of MB in the aqueous solution on the time of reaction for the pristine TiO$_2$, AC-TiO$_2$ composite and EG-TiO$_2$ composite.](image)
TiO$_2$ composite, and the EG could improve the photocatalytic effect of TiO$_2$ in the MB degradation reaction under the irradiation of UV light.

REFERENCES