Photocatalytic Activity of EG-TiO\(_2\) Composite for Various Dye Solutions Under UV Light and Visible Light

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Abstract Expanded graphite (EG) is synthesized by chemical intercalation of natural graphite (NG) and rapid expansion at high temperature, with titanium n-butoxide (TNB) used as titanium source by a sol-gel method to prepare EG-TiO\(_2\) composite. The performances of the prepared EG-TiO\(_2\) composite are characterized by BET surface area measurement, scanning electron microscopy (SEM), X-ray diffraction patterns (XRD) and energy dispersive X-ray analysis (EDX). To compare the photocatalytic activities of the EG-TiO\(_2\) composite, three kinds of dye solutions, methylene blue (MB), methylene orange (MO) and rhodamine B (RhB), and two kinds of light source, UV light and visible light (VL), are used. Comparing the results, it can be clearly seen that the degradation of all of the dye solutions under irradiation by UV light is much better than that under irradiation by visible light, and the decomposition of MB solution was better than that of both of MO and RhB solution.

Key words expanded graphite, Titanium n-butoxide, photocatalysis, methylene blue.

1. Introduction

A number of carbon materials have been used to prepare carbon-supported catalysts (activated carbon, activated carbon fiber, graphite, carbon black, graphite intercalation compounds and carbon nanotubes).\(^1\)\(^-\)\(^5\) Among them, graphite has many unique properties and is attracting increasing attention as a novel candidate of supporting material in heterogeneous catalysis. Graphite is the most stable allotrope of carbon in STP conditions, and there is a vast amount of natural graphite mined worldwide. Graphite provides good electrical conductivity (\(10^6\) S/m at ambient temperature) and layered structure with a c-axis lattice constant. However, very little graphite is currently used as a catalyst support due to its low surface area and low surface activity. Expanded graphite (EG), however, is a kind of wormlike material came from the vaporization of the graphite intercalation compounds (GICs) and hence, a significant expansion of the material along the crystallographic c-axis occurs. As a result, the volume of EG increased tens and hundred times compared to GICs,\(^6\) and meso-porous structure, big surface area and high surface activity were created in the structure of EG. The special “sandwich” structure and long distance between the carbon layers made it easy to insert atoms or molecules into the carbon sub-layers. Furthermore, the multi-pores, functional acids and the OH groups will facilitate physical and chemical adsorption between the graphite and the transition metal solution.\(^7\) These functional groups on the graphite surfaces that anchor the metal cations and benefit the dispersion provided crucial necessities to prepare the supported catalysts using EG as substrates. The morphology and pore structure of EG can be modified by altering preparation conditions, and there are several reports on the preparation procedures, pore structures and applications of EG.\(^8\)\(^,\)\(^9\)

EG has been widely used in gasketing, adsorption, electromagnetic interference shielding, vibration damping, electrochemical applications, stress sensing, thermal insulator and supporting material. However, the information about the use of EG as a catalyst support in photocatalyst synthesis is sparse. As we known, titania is well-known as an environmentally benign photocatalyst and widely used for mineralization of harmful organic substances.\(^10\)\(^,\)\(^11\) Furthermore, according to our previews works, it has been indicated that carbon-TiO\(_2\) composites which using pitch, activity carbon and activity carbon fiber as carbon sources showed much more photocatalytic activity than pristine TiO\(_2\).\(^12\)\(^,\)\(^13\) So in this paper, we study on the
synthesis and performance of a composite of expanded graphite (EG) used as carbon source and titanium oxide derived from titanium n-butoxide (TNB) by using a sol-gel method. The performances of prepared EG-TiO₂ composite are characterized by BET surface area measurement, scan electron microscope (SEM), X-ray diffraction patterns (XRD) and energy dispersive X-ray analysis (EDX). To compare the photocatalytic activity of the EG-TiO₂ composite, methylene blue (MB, C₁₆H₁₈N₃SCl), methyl orange (MO, C₁₄H₁₄N₃NaO₃S) and rhodamine B (RhB, C₂₉H₃₁ClN₂O₃) are chosen as the model pollutant under irradiation of two kinds of light source which are UV light and visible light.

2. Experimental Procedure

2.1 Materials

Natural graphite with an 80~100 mesh size was obtained from SangJin Co., Ltd, Korea. TNB (Ti(OC(CH₃)₃)₄, 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 intercalates which obtained from SamChun Pure Chemical Co., Ltd, Korea and Duksan Pharmaceutical Co., Ltd, Korea, respectively. To oxidize the EG, m-chlorperbenzoic 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 which purchased from SamChun Pure Chemical Co., Ltd, Korea. The MB, MO and RhB were selected as analytical grade which was purchased from Dukan Pure Chemical Co., Ltd. Because it can be readily under anaerobic conditions to produce potentially more hazardous aromatic amines. The structures of MB, MO and RhB were shown in Fig. 1.

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 was shown in Fig. 2. At first, 3 g (NH₄)₂SO₄ was melted in 100 mL H₂SO₄. Then 1 g NG was put into (NH₄)₂SO₄-H₂SO₄ solution and stirring at 323 K for 30 min. The mixture was carefully washed and filtrated with distilled water until the pH level of 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. The physical properties of EG were shown in Table 1.

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 preparation of EG-TiO₂ composite was shown in Fig. 3. For oxidation of 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 then 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 resulted product was heat treated at 973 K for 1 h to obtain the EG-TiO₂ composite. A simple mechanism during the preparation of EG and EG-TiO₂ composite was also shown in Fig. 4.

2.4 Characterizations

Synthesized EG-TiO₂ composite was characterized by various techniques. BET surface area was measured using a Quantachrome Surface Area analyzer (MONOSORB,
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USA). SEM (JOEL, JSM-5200, Japan) was used to observe the surface state and structure of the EG-TiO\textsubscript{2} composites. XRD was used for crystal phase identification of the composite and estimation of the anastase-to-rutile ratio. XRD patterns were obtained at room temperature with a Shimata XD-D1 (Japan) using CuK\textsubscript{α} radiation. EDX was used to measure the elemental analysis of the EG-TiO\textsubscript{2} composites. UV-vis spectra for the MB, MO and RhB solution degraded by EG-TiO\textsubscript{2} composites under the irradiation of UV light and visible light were recorded using a Genspec III (Hitachi, Japan) spectrometer.

2.5 Photocatalytic decomposition

The photocatalytic effect of EG-TiO\textsubscript{2} composite was determined using MB, MO and RhB decomposition in aqueous solution under an UV lamp (356 nm, 1.2 mW/cm\textsuperscript{2}) and visible light (30 W/cm\textsuperscript{2}). The initial dye solution concentration was chosen 1.0 \times 10^{-5} mol/L, which was considered as initial concentration (c\textsubscript{0}). The amount of suspended composites was kept at 1 g/L in 50 mL MB solution. The solution was irradiated with UV light and visible light, respectively. The samples were taken out by an order of 30 min, 60 min, 90 min and 120 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-vis spectrophotometer.\textsuperscript{12-14} The absorbance of MB, MO and RhB was determined at characteristic wavelength 660 nm,\textsuperscript{12} 467 nm\textsuperscript{15} and 554 nm,\textsuperscript{16} respectively.

3. Results and discussion

3.1 Characteristics of EG-TiO\textsubscript{2} composite

Table 2 showed the BET surface area of EG-TiO\textsubscript{2} composite. It could be clearly seen that the BET surface area of EG-TiO\textsubscript{2} composite is only 27 m\textsuperscript{2}/g. Comparing with the surface area of EG (54 m\textsuperscript{2}/g) which showed in Table 1, the BET surface area of EG-TiO\textsubscript{2} composite was decreased almost 2 times. The reason might be explained as in Fig. 4. The wide pore size distribution revealed that EG was a mesoporous material with a macroporous network structure. 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, and thus, it was very easy to insert the TiO\textsubscript{2} particles from the reactant and product. As a result, due to a lot amount of TiO\textsubscript{2} particles get into the

![Fig. 2. A schematic illustration of the formation of EG.](image-url)
carbon layers, the BET surface area of the EG-TiO$_2$ composite was decreased.

In the presence of the intercalants, which were H$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$, were dispersed into the graphite layers to form GICs. After rapid expansion of GICs at a high temperature, EG was formed. Fig. 5 showed the SEM photomicrographs of NG (a), EG (b) and EG-TiO$_2$ composite (c and d). Comparing (a) to (b), the differences in microstructures could be clearly observed. The as-received NG was composed of thin graphite flake. The layers structure of graphite flake was regular and the layers distance was small (Fig. 2(a)). After chemical intercalation treatment and heat treatment at 873 K, it is clearly seen that in graphite flakes interlayer spacing is separated by increased distance and leads into porous structure (Fig. 2(b)). In EG, expansion process causes destruction of graphite crystal structure, as a consequence expansion in the c-direction is about hundred times and resulted in an enormous increase in volume as a consequence of sudden evaporation of intercalate. After expansion, EG emerges as a loose structure and porous material consisting of numerous graphite sheets of thickness in nanometers and micrometer in diameter. This structure endows EG with high surface area. After reacted with TNB, the SEM images of EG-TiO$_2$ composite were also shown in Fig. 5 (c and d). It could be seen that the preparation process of composite had an obvious effect on the morphology of EG support. And the

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>C</th>
<th>O</th>
<th>Ti</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG-TiO$_2$ composite</td>
<td>27.0</td>
<td>41.12</td>
<td>22.73</td>
<td>35.60</td>
<td>0.55</td>
</tr>
</tbody>
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Fig. 3. A schematic illustration of the synthesis of EG-TiO$_2$ composite.

Fig. 4. A simple mechanism during the preparation of EG and EG-TiO$_2$ composite.

Table 2. The BET surface area ($S_{BET}$) and EDX elemental microanalysis (wt. %) of EG-TiO$_2$ composite.
EG was exfoliated and broken up in shorter fragments under stirring, resulting in many tiny EG fragments in planar direction. These EG fragments still maintained the layered structure as that of NG and porous structure as that of EG. It could be also observed that 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.

Fig. 6 showed the XRD pattern of EG-TiO$_2$ composite after heat treatment at 973 K for 1 h. The sharp diffraction peak at $2\theta = 25-26^\circ$ appeared in composite, suggesting that the expanding and reaction with TNB did not alter the scale structure of the NG. As shown in XRD pattern of EG-TiO$_2$ composite, the most distinct peak appearing at $2\theta = 26.5^\circ$ ($d = 0.336$ nm) was corresponded to the “002” diffraction of graphite. And the peaks also appeared 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, with no peaks at 27.4, 36.1, 41.2 and 54.3 that belong to the diffraction peaks of (110), (101), (111) and (211) of rutile, indicating the developed composites existed in anatase state. The results were agreed with the results of former study$^{[17-18]}$ the anatase phase formed below 773 K begin to transform to rutile-type structure above 873 K and changed into single phase of rutile at 973 ~1173 K. However, the phase transformation from anatase to rutile could be inhibited when the carbon was existed in the composite.
The EDX spectra and EDX microanalysis (wt. %) of EG-TiO$_2$ composite were shown in Fig. 7 and Table 2, respectively. From both of the EDX data, it could be clearly seen that the composite contained three kinds of main elements C, O and Ti. It could be considered that after heat treatment at 973 K, the composite was successful prepared.

3.2 Photocatalytic activity of EG-TiO$_2$ composite

In our previous work, we had been studied that the expanded graphite from Li-intercalated graphite had excellent sorption capacity of crude oil. So in this study, we prepared the EG-TiO$_2$ composite by using expanded graphite with titanium $n$-butoxide, and determined their photocatalytic activity for three kinds of dye solutions MB, MO and RhB under irradiation of two kinds of light source UV light and visible light. Fig. 8 and Fig. 9 showed the relative concentration ($c/c_0$) of MB, MO and RhB in the aqueous solution on time under irradiation of UV light and visible light, respectively. As showed in Fig. 8, the concentration of MB, MO and RhB solution was decreased 100%, 75% and 45%, respectively, when under irradiation of UV light after 120 min. However, the concentration of MB, MO and RhB solution was decreased 80%, 38% and 27%, respectively, when irradiation under visible light after 120 min as showed in Fig. 9. Comparing of irradiation of UV light and visible light, it could be clearly seen that the concentration of all of dye solutions under irradiation of UV light is much lower than that under irradiation of visible light. It could be considered that the TiO$_2$ under irradiation of UV light have more efficiency than that under irradiation of visible light. Comparing of decomposition of three kinds of dye solutions, it could be also observed that the decomposition of MB solution was better than both of MO and RhB solution. It might be explained as followed. A simple illustration of degradation of MB, MO and RhB solution was showed in Fig. 10. In the case of MB solution, the MB molecule size is smaller than the distance of lays of expanded graphite, thus it could be get into the lays and contact with the TiO$_2$ particles which mostly stayed between the lays. When irradiation under UV light or visible light, the electron transfer would be occurred. Due to the graphite had extraordinary electronic transporting properties and high electronic conductivity, and might absorb a lot amount of electrons under UV irradiation. Furthermore, these electrons would transfer into the TiO$_2$/UV system, and thus improved the photocatalytic effect of TiO$_2$ for MB solution. However, in the case of MO and RhB solution, the molecule size of MO and RhB was bigger than the distance of lays of expanded graphite. So they could not get into the lays and a few of
them could contact with the TiO$_2$ particles, thus the photocatalytic effect was lower.

4. Conclusion

In this investigation EG-TiO$_2$ composite was obtained by expanded graphite which prepared by chemical oxidation and titanium $n$-butoxide which used as titanium precursor. The BET surface area of EG-TiO$_2$ composite was only 27 m$^2$/g. 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. XRD pattern showed that the most distinct peak appearing at 2$\theta = 26.5^\circ$ was corresponded to the “002” diffraction of graphite, and the developed EG-TiO$_2$ composite have a single crystal structure, just is anatase structure. EDX spectra and elemental microanalysis (wt. %) showed that the composite contained three kinds of main elements C, O and Ti. At last, the photocatalytic activity of EG-TiO$_2$ composite for various dye solutions under irradiation UV light and visible light was determined. In comparison of the results, it could be clearly seen that the degradation of all of dye solutions under irradiation of UV light is much better than that under irradiation of visible light, and the decomposition of MB solution was better than that of both of MO and RhB solution.

References