Characterization of a Novel MnS-ACF/TiO₂ Composite and Photocatalytic Mechanism Derived from Organic Dye Decomposition

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ABSTRACT

Activated carbon fiber (ACF) was modified with MnS nanoparticles to prepare MnS-ACF, and it was employed for preparation of MnS-ACF/TiO₂ composites with titanium (IV) n-butoxide (TNB). The properties of MnS-ACF/TiO₂ composites were characterized by XRD, SEM, and EDX. EDX results showed the presence of C, O, and Ti as major elements and traces of the metal elements Mn and S. The photocatalytic activity was evaluated by degradation of methyl blue (MB) and methyl orange (MO) dye. The results demonstrated that as-prepared samples could effectively photodegrade MB and MO under UV irradiation. Subsequently, the decomposition of MB solution showed the combined effects of absorptions by ACF and enhanced photocatalytic effect by TiO₂. Finally, the photocatalytic effect increased due to photo-induced-electron absorption effect by ACF and electron trap effect by co-modified MnS nanoparticles.

Key words : MnS, Methyl blue, Methyl orange, Activated carbon fiber, UV light

1. Introduction

Wastewater effluents from textile and other dyestuff industries contain a large number of toxic dyes and industrial dyestuffs, which constitute the largest groups of organic compounds. They are represent an increasing environmental danger. If these effluents are improperly treated, they will pose severe threats to all species on the earth because the hydrolysis of the pollutants in the wastewater can produce a great deal of toxic products. So the disposal of dyestuff wastewaters is necessary to settle the problem of environmental pollution. Recently, many methods, including physical, chemical, and biological methods, have been used in wastewater treatment and recycling. Among them, heterogeneous photocatalysis appears to be an emerging destructive technology leading to the total mineralization of most organic pollutants. TiO₂ is the most widely used photocatalyst because of its good activity, chemical stability, commercial availability, and inexpensiveness. Anatase has higher photocatalytic activity and has been studied more than the other two forms of TiO₂. However, the TiO₂ powders have two obvious drawbacks that restrict the practical application of this technology: (1) the rapid recombination of photogenerated electron (e⁻)/hole (h⁺) VB) pairs significantly diminish the efficiency of photocatalytic reactions, and (2) the TiO₂ powders are easy to lose and not suitable for recycling. For the first problem, great efforts have been made to prevent the recombination of charge carriers in the semiconductor and to improve the photocatalytic efficiency of TiO₂ including the following: (a) doping metal ions, in particular transition metal ions (iron, chromium, copper, vanadium and cobalt) into the TiO₂ lattice, (b) dye photosensitization on the TiO₂ surface, and (c) deposition of noble metals and so on.

Meanwhile, several attempts have been made to enhance the photocatalytic performance of TiO₂, such as immobilization of TiO₂-powder onto supports like activated carbon fiber (ACF) and MₓSᵧ or MₓOᵧ nanoparticles including CdS, Bi₂S₃, WO₃, or ZnS for heterogeneous photocatalysis. Provided that ACFs are used as support material and all those advantages of both ACFs and TiO₂ are utilized, a powerful photocatalyst could be produced. Activated carbon fiber (ACF) has an excellent adsorption capacity and shows very fast adsorption/desorption rates compared with conventional activated powder or activated granular carbons. ACFs are produced in the form of felt or cloth, with high BET surface area and micropore volume. As a p-type semiconductor with wide band energy (3.7 eV) and varied crystal structures (rock-salt structure α-MnS, zinc blende structure β-MnS, and wurtzite structure γ-MnS), MnS shows promising optoelectronic properties and has numerous potential applications in optoelectronic devices.

In this study, activated carbon fiber (ACF) was treated by Mn²⁺, S²⁻ to prepare MnS-ACF, and it was employed for preparation of MnS-ACF/TiO₂ composites. X-ray diffraction was used to determine crystallinity. Scanning electron microscopy (SEM) was used to elucidate the mixing phenomenon and the size of MnS-ACF/TiO₂ composites. Energy dispersive X-ray (EDX) analysis was used to analyze the elements and their content in MnS-ACF/TiO₂ composites.
and a spectrophotometry was used to determine the decolorization of methylene blue (MB) and methylene orange (MO) solution which irradiation under UV light by different time.

2. Experimental Procedure

2.1. Materials

TNB (99.9%) as the titanium source was purchased from Acros organics Co., Ltd, USA. Manganese(II) chloride anhydrous (MnCl₂) and sodium thiosulfate anhydrous (Na₂S₂O₃) were supplied by Daejung Chemical Co., Ltd, Korea. ACF were purchased from EAST ASIS Carbon Fibers Co., Ltd, An Shan, and China. The acids, HNO₃ and H₂SO₄, used to modify the ACF, were obtained from Duksan Pure Chemical Co., Ltd, Korea. The methyl orange was used as analytical grade that was also obtained from Duksan Pure Chemical Co., Ltd, Korea. The methylene blue (MB) and methylene orange (MO), selected as analytical grade, were purchased from Duksan Pure Chemical Co., Ltd, Korea. Table 1 shows the structure and properties of MB and MO pollutant.

2.2. Preparation of MnS-ACF composites

These ACFs were washed with deionized water and dried for 24 h at ambient temperature. The ACFs were pulverized by a pulverizer. 20 g of carbon fiber material was milled at room temperature in a laboratory tumbling ball milling for 48 h, and then the methanol-chemically carbon materials were milled for another 1 h with a laboratory single-Pulverisette 6 planet high energy grinding machine (TMC Fritsch, Germany). H₂SO₄ and HNO₃ mixed solution (volume ratio of 30 : 70, solution A) was used to oxidize the ACF particles. 8 g of pulverized ACF were mixed with 800 ml of solution A, stirred 7-8 h, and flushed with distilled water three times and dried at 323 K. Oxidized ACFs were formed.

The dried ACF powders were mixed in a mixing solution containing 0.1M MnCl₂, followed by ultrasonication for 0.5 h. Afterwards, sodium thiosulfate anhydrous (Na₂S₂O₃) and 10mL ammonium hydroxide (NH₃H₂O) were added to the mixture under various stirring for another 6 h at 343K. The final product was rinsed with distilled water and ethanol several times and dried for 12 h.

2.3. Preparation of MnS-ACF/TiO₂ composite photocatalyst

The MnS-ACF-supported TiO₂ composites were fabricated via a sol-gel method and thermal annealing. 10 mL of TNB was dissolved into 80 mL benzene to form solution A. 0.5g of as-prepared MnS-ACF powder was added to solution A at 333K under stirring for 5 h. The samples were filtrated and dried at 373K for 8 h and then calcinated at 773K for 1 h and the MnS-ACF/TiO₂ composite photocatalysts was obtained. Fig. 1 gives the procedure for preparing the MnS-ACF/TiO₂ composites. For comparison, other photocatalysts named TiO₂ were prepared using similar procedures.

2.4. Characteristics and photocatalytic decomposition for MB and MO solution

The crystalline phase, particle size, and morphology of the MnS-ACF/TiO₂ composites was examined via an SEM (JSM-5200, Japan). The crystalline phases were determined using XRD (Shimadz XD-D1, Japan) with Cu Kα radiation. For the elemental analysis of the as-prepared composites, EDX was also employed. For MB and MO, an initial concentration was set to about 1.0×10⁻⁵ mol/L. Then, each of the 0.01 g composite photocatalysts was used to decompose 100ml MB, MO solution. The mixture was laid up for at least 2 h in the dark until saturation of adsorption. After adsorption, the photodecomposition of MB and MO solution was performed under UV irradiation. For UV irradiation, a UV lamp (20W, 365 nm) was used at the distance of 100 mm from the solution in darkness box. After irradiation at 30 min, 60 min, 90 min, and 120 min, the samples were examined to test the change of the concentration to compare the different photocatalytic effects between the TiO₂ and MnS-ACF/TiO₂ composites. Specifically, by sampling 3 mL

Table 1. The Molecular Structure and Absorbance Maximum (λ_max) of Organic Dyes

<table>
<thead>
<tr>
<th>Organic dyes</th>
<th>Molecular structure</th>
<th>λ_max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene blue (MB)</td>
<td><img src="image" alt="Methylene blue" /></td>
<td>665 nm</td>
</tr>
<tr>
<td>Methylene orange (MO)</td>
<td><img src="image" alt="Methylene orange" /></td>
<td>465 nm</td>
</tr>
</tbody>
</table>

![Fig. 1. Preparation procedure of the MnS-ACF and MnS-ACF/TiO₂ composites.](image)
of solution after removal of the dispersed powders using a centrifuge, the concentration of MB and MO in the solution was determined as a function of irradiation time from the absorbance change.

3. Results and Discussion

3.1. Structural analysis

XRD patterns of the TiO$_2$ and MnS-ACF/TiO$_2$ composites are demonstrated in Fig. 2. After heat treatment at 873 K, major peaks were observed at 25.3, 37.9, 48.0, 53.8, 54.9, and 62.5° (2θ), which were assigned to the (101), (004), (200), (105), and (211) planes of anatase, indicating that the prepared TiO$_2$ is anatase$^{19}$, matching with JCPDS No. 21-1272 (Anatase, syn). No other peaks corresponding to rutile or brookite were observed. These results suggest that MnS-ACF/TiO$_2$ also has a pure anatase phase structure with the current preparation conditions, which would be an efficient catalyst, as it is believed that anatase phase is more catalytically active$^{20,21}$. And the peaks at around 2θ of 29.5, 34.2, 49.3, 58.8, and 82.7, assigned to the (111), (200), (220), (311), and (420) planes, match well with the JCPDS data for MnS$^{22}$.

3.2. Surface characteristics of the samples

It was clear that the prepared nanoscale TiO$_2$ observed in Fig. 3(a) show us a favorable morphology but a slight tendency to agglomerate. Fig. 3 shows an SEM photograph of the as-prepared compound. The TiO$_2$ and MnS particles are uniformly coated on the surface of the ACF, which leads to an increase in size of the antiparticles. It has been reported that small particles can provide better dispensability than the reactive sites of the aggregated particles of reactant. Due to a number of grain aggregates, it causes higher surface roughness. As shown in Fig. 3(b), we can see that the large number of pores on ACF surface reduces with pore blocking by the particles of titanium dioxide or MnS. This is one reason why the pores on an ACF particle are filled with titanium oxide particles with an increase of the pore size and pore volume.

3.3. Elemental analysis of the preparation

The results of EDX patterns and quantitative results analysed by EDX spectra of TiO$_2$ and MnS-ACF/TiO$_2$ composites was shown in Fig. 4(a) and c. Fig. 4(a) shows strong Kα and Kβ peaks from Ti at 4.51 and 4.92 KeV, whereas a moderate Kα peak for O appears at 0.52 KeV. Fig. 4(b) shows the quantitative results of TiO$_2$. In addition to the above peaks, Mn, S was also observed in Fig. 4(c). In most of the samples, carbon and titanium were present as major elements with small quantities of oxygen in the composite. And Fig. 4(d) shows the quantitative results of C, O, Ti and Mn, S as the major elements for the composites. It can be indicated that the MnS-ACF/TiO$_2$ composite with high purity has been successfully synthesized in this study. According to former study, the small concentration of dop- ant in TiO$_2$ matrix can be prevented in formation of hole/ electron recombination centers and an increase of negative charge capabilities.

![Fig. 2. XRD patterns of TiO$_2$ and MnS-ACF/TiO$_2$ composites.](image)

![Fig. 3. SEM images obtained from powdered TiO$_2$ (a) and MnS-ACF/TiO$_2$ (b) composites.](image)
3.4. Photocatalytic activity of samples

Photodegradation of MB and MO organic dye solution under UV light irradiation is employed to evaluate the photocatalytic activity of the prepared catalysts. Initially, control tests on degradation of dye solution (ca. $1 \times 10^{-5}$ mol/L) were carried out in specified conditions described below: the data are obtained following two step experiments. The first step is placed in dark to adsorb dye, and the second step is exposed to UV light to degrade dye solution. Fig. 5 shows the relative absorbance of MB and MO in the aqueous solution on time under irradiation of UV light for TiO$_2$ and MnS-ACF/TiO$_2$ composites, and the concentrations of MB and MO solution decreased regularly with an increase of irradiation time for all of samples. As mentioned at experiment, when the samples irradiated under UV lamp by an order of 30 min, 60 min, 90 min, and 120 min. Comparing with our previous studies of photodegradation of MB and MO for pure TiO$_2$, the MnS-ACF/TiO$_2$ sample produced a significantly higher efficiency of MB and MO, it can be considered that using appropriate amount of MnS as dopant. On the other hand, as shown in Table 1, for MB molecules, which have obverse end tropism (1.43 nm × 0.4 nm), its width and height were lower than that of MO, it can be found MB were decomposed at a higher degree than that of MO, as shown with the curves of degradation. During the photo degradation process, suitable adsorption capacity is crucial for high photocatalytic activity. An important step in the photocatalytic process is the adsorption of reacting substances onto the surface of the catalyst. ACF has a well-developed pore structure, very large surface area about 967.4 m$^2$/g and strong adsorption capacity and is widely used as an adsorbent and catalyst support.

It is considered that the ACF component absorbed the dye solution and then the TiO$_2$ component degrades due to a photocatalytic reaction. Reactivity of TiO$_2$ depends on many factors: the adsorption of dye on catalyst surface, band-gap energy, surface area, crystal size, crystallinity, and electron–hole recombination rate, therefore an explanation of reactivity order is complicated. The addition of MnS on the nanocrystalline TiO$_2$ photocatalyst surface can enhance the photocatalytic degradation activity due to the lower crystal size, higher surface area, higher efficiency for the electron hole regeneration, and the charge trapping. The charge trapping can be demonstrated by the following equations:

\[
\begin{align*}
\text{MnS/TiO}_2 + \text{hv} & \rightarrow \text{MnS (h$^+$,e$^-$)/TiO}_2 \quad (1) \\
\text{MnS(h$^+$,e$^-$)/TiO}_2 & \rightarrow \text{MnS(h$^+$)/TiO}_2 \quad (2) \\
\text{e}^- + \text{O}_2 & \rightarrow \cdot\text{O}_2^- \quad (3) \\
\text{h}^+ + \text{OH}^- & \rightarrow \cdot\text{OH} \quad (4) \\
\text{h}^+ + \text{H}_2\text{O} & \rightarrow \cdot\text{OH} + \text{h}^+ \quad (5) \\
\text{O}_2^- \text{ or } \cdot\text{OH}^- & + \text{dye} \rightarrow \text{degradation products} \quad (6)
\end{align*}
\]

The photocatalytic reaction is initiated by the absorption of UV-light photons. Local excitation of the MnS by UV light affords charge transfer. The MnS intermediate will rapidly

Fig. 4. Typical EDX microanalyses and element weight % of TiO$_2$ (a,b) and MnS-ACF/TiO$_2$ (c,d) composites.

Fig. 5. Comparing to the decomposition of MB (a) and MO (b) in the aqueous solution in the presence of MnS-ACF/TiO$_2$ composites.
transfer an electron to the CB of C-TiO₂, while the chlorine atom abstracts an electron from the oxygen lattice. At the same time, UV light irradiation of C-TiO₂ results in the creation of photogenerated holes in its VB and electrons in its CB. In this way, the photogenerated electrons and holes are efficiently separated. The VB-holes in C-TiO₂ and electrons trapped in MnS react with OH⁻ and molecule O₂, respectively. The photogenerated hole-based oxidation is thought to play an important role in photocatalytic reactions. Hydroxyl radicals (OH•) have been deemed to play an important role in photocatalytic oxidation. Hydroxyl radicals (OH•) have been deemed to be the most oxidizing species for the degradation of organic compounds. A simple schematic mechanism of the photocatalytic activity of MnS-ACF/TiO₂ composites is shown in Fig. 6.

4. Conclusion

Uniform and fine well-dispersed MnS and ACF co-modified TiO₂ composite photocatalyst has been successfully prepared via a sol-gel method. The experimental results clearly demonstrate that MnS-ACF/TiO₂ photocatalysts have strong combination properties and effective electron transfer between MnS and TiO₂. The surface properties seen by SEM present a favorable morphology of the as-prepared composites. The photocatalytic results showed that the improved degradation rate of MB solution should be accounted to both the excellent organic pollutant adsorption effects and the interparticle electron transfer effect. In addition, ACF may act as support, absorbent, and photogenerated electron transfer station.

REFERENCES


