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ABSTRACT

ACF and WO$_3$, modified TiO$_2$ composites (ACF/WO$_3$/TiO$_2$) were prepared using a sol-gel method. The composites were characterized by Brunauer–Emmett–Teller (BET) surface area measurements, X-ray diffraction (XRD), energy dispersive X-ray (EDX) analysis and scanning electron microscope (SEM) analysis. A methyl orange (MO) solution under visible light irradiation was used to determine the photocatalytic activity. The degradation of the MO was determined using UV/Vis spectrophotometry. An increase in photocatalytic activity was observed and attributed to an increase of the photo-absorption effect by the WO$_3$ and the cooperative effect of the ACF.

Key words : WO$_3$, ACF, MO, Visible light, Photocatalytic

1. Introduction

Semiconductor oxides have been widely used in optical coating and microelectronic devices, and using them for purifying contaminants in air and water has been recognized recently. Photocatalytic reactions of semiconductors, such as splitting water and decomposing waste materials have received special attention because of the possible application to the conversion of solar energy into chemical energy and pollution control using solar energy. In these investigations, various semiconductor materials, such as TiO$_2$, CdS, ZnS, ZnO and WO$_3$, have been used to study photocatalytic reduction of pollution in water, among which TiO$_2$ was proved to be the most efficient photocatalyst due to its exceptional optical and electronic properties, chemical stability, non-toxicity, and low cost. TiO$_2$ shows the highest quantum yield among the popular semiconductors. However, in many cases, the photocatalytic activity of TiO$_2$ is not enough to be useful for industrial purposes.

The general photocatalytic process of a semiconductor involves forming photoinduced electrons at the conduction band and holes at the valence band, and the subsequent chemical reactions with the surrounding media after photo-stimulated charges move to the powder surface. In this way, water can be split into hydrogen and oxygen, and organic pollutants in water or gas can be effectively decomposed or purified. Thus, an efficient photocatalytic process over a semiconductor demands the high mobility for photoinduced electron-hole separation and for their transportation in a crystal lattice, which would lower the probability for electron-hole recombination.

WO$_3$ has attracted much attention because it shows an appropriate band gap energy level (2.8 eV) and also has a lower conduction band ($E_{cb} = +0.4$ V$_{gp}$) than that of TiO$_2$. Many studies on the combined semiconductors for an efficient electron-hole separation have been reported using WO$_3$ with coupled materials, such as WO$_3$/SrNb$_2$O$_6$ and WO$_3$/TiO$_2$. Moreover, activated carbon fiber (ACF) is highly microporous and has a high surface area, a larger pore volume and a uniform microspore size distribution. TiO$_2$ particles have been easily fixed on ACF surfaces and thus have improved defects at low interface areas. Thus ACF/TiO$_2$ composites are typically used to obtain the combined effects of photo activity.

In the present work, the ACF/WO$_3$/TiO$_2$ photocatalyst was prepared with the sol-gel method and the photocatalytic activity for the MO solution was investigated under visible light irradiation. The effect of the composition was tested to clarify the mechanism of the charge separation process. X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy were used to characterize the new complexes.

2. Experimental Procedure

2.1. Materials

ACFs were obtained from the EAST ASIS Carbon Fibers Co., Ltd, An Shan, China), and used as the carbon matrix. Titanium (IV) oxysulfate hydrate (TiOSO$_4$·H$_2$O (TOS), Sigma-Aldrich, Germany) was used as the titanium source. The ammonium metatungstate hydrate (H$_4$N$_2$O$_{12}$W$_2$xH$_2$O) purchased from Sigma-Aldrich Chemie GmbH (Germany) was used as a raw material to generate WO$_3$ at high temperatures. The methyl orange (MO, C$_{14}$H$_{14}$N$_2$O$_5$S, 99.9%, Duksan Pure Chemical Co., Ltd) was of analytical grade.

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2.2. Preparation of ACF/WO₃ composites

The 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 materials were ball milled for 48 h at room temperature in a laboratory tumbling ball mill, and then the mechano-chemically carbon materials were obtained using a laboratory Pulverisette 6 mono-planetary high energy mill (Ikar-Oberstein, Frisch, Germany) for 1 h with ZrO₂ ball (1 mm × 300 g). 20 g of carbon fiber materials were ball-milled for 48 h at room temperature in a laboratory tumbling ball mill, and then the mechano-chemically carbon materials were obtained using a laboratory Pulverisette 6 mono-planetary high energy mill (Ikar-Oberstein, Frisch, Germany) for 1 h with ZrO₂ ball (1 mm × 300 g). H₂SO₄ and H₃PO₄ mixed solution (volume ratio of 70: 30, solution A) was used to oxidize the ACF particles. 10 g of pulverized ACF was mixed with 100 ml of solution A, stirred 7-8 hours and flushed with distilled water three times and dried at 323 K. Oxidized ACFs were formed.

For WO₃ coating, 3.8 × 10⁻⁵ mol H₂N₆O₆WₓH₂O was added to 50 ml of distilled water (shown in Table 1). The resulting mixture was heated under reflux in air and stirred at 343 K for 6 h using a magnetic stirrer in a vial. After heat treatment (N₂ atmosphere) at 623 K for 3 h, the ACF/WO₃ composites were formed.

2.3. Preparation of ACF/WO₃/TiO₂ composites

ACFWO₃ was prepared using pristine concentrations for the preparation of ACF/WO₃/TiO₂ composites. ACF/WO₃ powder was mixed with 100 ml of 0.1 M TiOS solution. The mixture was homogenized under reflux at 343 K for 3 h, while being stirred in a vial. After stirring, the solution transformed to ACF/WO₃ gels and heat treated (N₂ atmosphere) at 773 K to produce the ACF/WO₃/TiO₂ composites.

2.4. Characterization of ACF/WO₃/TiO₂ compounds

XRD (Shimata XD-D1, Japan) was used for crystal phase identification and to estimate the anatase ratio of TiO₂ and estimate the crystal phase of WO₃. The XRD patterns were obtained at room temperature using Cu Ka radiation. SEM (JSM-5200, JOEL, Japan) was used to observe the surface state and porous structure of the ACF/WO₃/TiO₂ composites. The elemental composition of the ACF/WO₃/TiO₂ composites was examined by EDX. SEM was used to observe the surface state and structure of the ACF/WO₃/TiO₂ composites using a scanning electron microscope (JSM-5200, JOEL, Japan).

Table 1. Nomenclature of the Samples Prepared with the Photocatalysts

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>Nomenclatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 g ACF + 3.8 × 10⁻⁵ mol H₂N₆O₆WₓH₂O + 100 ml (0.1 M) TiOS</td>
<td>ACF/WO₃</td>
</tr>
<tr>
<td>3.8 × 10⁻⁵ mol H₂N₆O₆WₓH₂O + 100 ml (0.1 M) TiOS</td>
<td>WO₃/TiO₂</td>
</tr>
<tr>
<td>10 g ACF + 3.8 × 10⁻⁵ mol H₂N₆O₆WₓH₂O + 100 ml (0.1 M) TiOS</td>
<td>ACF/WO₃/TiO₂</td>
</tr>
</tbody>
</table>

Table 2. Results and Discussion

3.1. Elemental analysis of the preparation

Fig. 1 shows the EDX patterns of the ACF/WO₃/TiO₂ (a) and ACF/WO₃/TiO₂ (b). The elemental composition of the sample ACF/WO₃/TiO₂ was analyzed and the characteristic elements were identified. Fig. 1 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. In addition to the above peaks, Ni was also observed. Fig. 1 presents the quantitative microanalysis of C, O, Ti and Ni as the major elements for the composites by EDX. Table 1 lists the composition ratios of the samples. There were some small impurities, which are believed to have been introduced from the unpurified ACF or H₂N₆O₆WₓH₂O. In most of the samples, tungsten, carbon and titanium were present as major elements with small quantities of oxygen in the composite (shown in Table 2).

3.2. Surface characteristics of the samples

Fig. 2 shows the SEM images of the micro-surface structures and the morphology of the compounds. The TiO₂ and ACF particles were coated uniformly over the tungsten oxide surface, which led to an increase in nanoparticle size. Zhang et al. reported that a good dispersion of small particles could provide more reactive sites for the reactants than aggregated particles. The surface roughness appears to be high due to some grain aggregation. We did not find ACF particles from the SEM image because the content of ACF was so small (Table 2). Figs. 2(a), (b) and (c) show the SEM images of

Brunauer-Emmett-Teller (BET) surface area was determined by N₂ adsorption measurements at 77 K (Monosorb, USA).

2.5. Photocatalytic tests

A specified quantity of the photocatalyst composite was added to 100 ml of MO solution. The reactor was placed in the dark for 2 h to allow the maximum adsorption of MO molecules to the photocatalyst composite particles. In all the experiments, the initial concentration of the MO was 1 × 10⁻⁵ mol/L, and the amount of the photocatalyst component was 0.01 g(100 ml solution). After adsorption, photodecomposition of the MO solution was performed under visible light in a dark-box to ensure that the reactor was irradiated by a single light source. The visible light source was an 18 W lamp with the main emission wavelength was 460 nm. Visible light irradiation of the photo-reactor was performed for 10 min, 30 min, 60 min, 90 min, 120 min, and 150 min. The experiments were performed at room temperature. In the process of MO degradation, a glass reactor was used and the reactor was placed on a magnetic churn dasher. Samples were withdrawn regularly from the reactor and the dispersed powders were removed by a centrifuge. The MO concentration in the solution was then determined as a function of the irradiation time from the change in absorbance at a wavelength of 660 nm. After treatment with the centrifuge the centrifugalizations were analyzed using a UV-vis spectrophotometer.
ACF/WO₃, WO₃/TiO₂ and ACF/WO₃/TiO₂, respectively. The level of aggregation increased with an increasing amount of addition. Comparing Figs. 2(a), (b) and (c), we see that when TiO₂ was added, the aggregation became stronger. TiO₂ can enhance aggregation.

Table 2 lists the BET surface areas of the samples. The BET surface areas of pristine TiO₂, as well as the prepared ACF/WO₃, WO₃/TiO₂ and ACF/WO₃/TiO₂, were 18.95 m²/g, 73.25 m²/g, 32.20 m²/g and 50.11 m²/g, respectively. The TiO₂ and WO₃ particles were introduced to the pores of the ACF, which decreased the BET surface area. The ACF/WO₃ sample had the largest area, which can affect the adsorption reaction. The BET surface area of the photocatalyst ACF/WO₃/TiO₂ decreased by 31.59% when ACF/WO₃ particles were doped by TiO₂. This is because TiO₂ particles filled the pores of the ACF/WO₃ particles, thereby reducing the pore size and pore volume of the ACF/WO₃ particles (Table 2).

3.3. Structural analysis

Fig. 3 shows XRD patterns of the ACF/WO₃, WO₃/TiO₂ and ACF/WO₃/TiO₂ composites. After heat treatment at 873 K, major peaks were observed at 25.3°, 37.9°, 48.9°, 53.8°, 54.9°, and 62.5°(2θ), which were assigned to the (101), (004), (200), (105), (211), and (204) planes of anatase, indicating that the prepared TiO₂ is anatase. These results suggest that ACF/WO₃/TiO₂ also has a pure anatase phase structure with the current preparation conditions. The XRD pattern shows the
characteristic peaks of WO$_3$. Additional WO$_3$ diffraction peaks for the (002), (020), (120), (112), −(202), (222), (320), (123), (312), (004), (040), (140), −(114) and (114) planes were observed at 23.14°, 23.47°, 24.29°, 26.53°, 28.67°, 33.3°, 34.5°, 35.45°, 41.48°, 44.27°, 45.70°, 47.24°, 48.25°, 49.93°, 50.34° and 50.74° (2θ), respectively. The peaks of TiO$_2$ were also observed in the XRD pattern of the ACF/WO$_3$ compound at 37.9° (2θ). In the XRD pattern of the WO$_3$/TiO$_2$ and ACF/WO$_3$/TiO$_2$ composites, the intensity of the peaks about TiO$_2$ was decreased. This is because the content of TiO$_2$ was decreased, and the peaks of WO$_3$ affected the TiO$_2$ peak. There were a few other peaks which were probably introduced from the unpurified ammonium metatungstate hydrate and TiOSO$_4$.xH$_2$O.$^{[30]}

### 3.4. Photocatalytic activity of samples

Fig. 4 shows the times of the MO degradation using pure TiO$_2$, ACF/WO$_3$, WO$_3$/TiO$_2$ and ACF/WO$_3$/TiO$_2$ under visible light irradiation. The spectra for the MO solution after visible light irradiation showed relative degradation yields at different irradiation times. The decrease in dye concentration continued with an oppositely gentle slope, which was due to visible light irradiation. The concentration of MO was 1.0 × 10$^{-3}$ mol/l, the absorbance for MO decreased with an increasing visible light irradiation time. Moreover, the MO solution increasingly lost its color, and the MO concentration continued to decrease. Two steps are involved in the photocatalytic decomposition of dyes: the adsorption of dye molecules and degradation. After adsorption in the dark for 2 h, the samples reached adsorption-desorption equilibrium. In the adsorptive step, the ACF/WO$_3$, WO$_3$/TiO$_2$ and ACF/WO$_3$/TiO$_2$ composites showed adsorptive effects different from ACF/WO$_3$ and had the best adsorptive effect. The adsorptive effect of pure TiO$_2$ was the lowest. ACF/WO$_3$ has the largest BET surface area, which can enhance the adsorptive effect. In the degradation step, the ACF/WO$_3$, WO$_3$/TiO$_2$ and ACF/WO$_3$/TiO$_2$ composites showed a good degradation effect. A comparison of the decoloration effect of the catalysts showed that ACF/WO$_3$/TiO$_2$ composites have best degradation effect, which is due to the synergistic reaction of WO$_3$, ACF and TiO$_2$.

Fig. 5 presents the corresponding −ln(C/C$_0$) vs. t plots at 0-120 min irradiation times. The photodegradation followed first-order kinetics. The kinetics can be expressed as follows: −ln(C/C$_0$) = k$_{app}$t where k$_{app}$ is the apparent reaction rate constant, C and C$_0$ are the initial concentration and the reaction concentration of MO, respectively. Table 2 shows the rate constant values (k$_{app}$) of pure TiO$_2$, ACF/WO$_3$, WO$_3$/TiO$_2$ and ACF/WO$_3$/TiO$_2$ composites for the degradation of the MO solution. The k$_{app}$ value of the ACF/WO$_3$/TiO$_2$ sample is the largest, which is in accord with the photocatalytic activity.

WO$_3$/TiO$_2$ has a better degradation effect than pure TiO$_2$ because WO$_3$ is an energy sensitizer that improves the quantum efficiency and increases charge transfer. The TiO$_2$ deposited on the WO$_3$ surface can retain its photodegradation activity. When WO$_3$ (E$_g$ = 2.8 eV) and TiO$_2$ (E$_g$ = 3.2 eV) form a coupled photocatalyst, WO$_3$ can be excited by photons under visible illumination, and TiO$_2$ remains unexcited. Hole and electron pairs were generated and separated on the interface of WO$_3$ by visible light irradiation. The level of the conduction band in TiO$_2$ was lower than the reduction potential of WO$_3$. Therefore, the photogenerated electron with an interaction between WO$_3$ and TiO$_2$. The synergistic effect WO$_3$ and TiO$_2$ both promoted the separation efficiency of the photogenerated electron-hole pairs, resulting in the higher photocatalytic activity of WO$_3$/hybridized TiO$_2$ samples. In this case, the WO$_3$ coupled TiO$_2$ system improved the reaction state.$^{[30-40]}$ Therefore, the WO$_3$ coupled TiO$_2$ had photocatalytic activity under visible light.

With a ACF/WO$_3$/TiO$_2$ system, the photocatalytic activities were enhanced mainly because of the high efficiency of the charge separation induced by the synergistic effect of ACF, WO$_3$ and TiO$_2$. Because WO$_3$ has the least band gap (0.5-3.2 eV), hole and electron pairs were generated and separated on the interface of WO$_3$ easily by visible light irradiation. Because both the conduction band (CB) and the valence band (VB) of WO$_3$ were higher than the CB and VB of TiO$_2$ when the hole...
and electron pairs also generated and separated on the interface of WO$_3$, the electrons at the CB of WO$_3$ migrated to the CB of TiO$_2$, and the holes at the VB of WO$_3$ migrated to the VB of TiO$_2$. This allowed the transfer of photogenerated electrons, which facilitated effective charge separation and decreased the rate of recombination about the electron-hole pairs. ACF acts as an adsorb effect and increases the surface area of the compounds, which can increase the adsorption effect for the samples, adsorb more O$_2$ and dye molecules, and make sure this systems takes full advantage of yield oxidizing species.

Fig. 6 is the schematic diagram of the separation of photogenerated electrons and holes on the WO$_3$/TiO$_2$ interface.

4. Conclusions

This study examined the preparation and characterization of ACF/WO$_3$, WO$_3$/TiO$_2$ and ACFWO$_3$/TiO$_2$. The BET surface area of ACFWO$_3$ was higher than that of the ACF/WO$_3$/TiO$_2$ composite. XRD revealed a WO$_3$ structure and anatase. ACF/WO$_3$ exhibited a good photo-degradation effect under visible light irradiation, due to the photosensitive and enhancing BET surface area effect of ACF. The ACFWO$_3$/TiO$_2$ composite showed the best photocatalytic degradation activity of the MO solution under visible light irradiation. This was attributed to three different effects, the photocatalytic reaction of the supported TiO$_2$, the energy transfer effects of ACF and WO$_3$, such as electrons and light, and the separation effect in this system.

REFERENCES


