Preparation and Characterization of ZnO-ACF/TiO$_2$ Composite Catalysts for the Photocatalytic Degradation of MO under Visible Light

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ABSTRACT

ACF and ZnO modified TiO$_2$, composite materials (ZnO-ACF/TiO$_2$) were prepared by a sol-gel method. The composites were characterized by 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 spectrophotometers. An increase in the photocatalytic activity was observed and attributed to an increase of the photo-absorption effect by the ZnO and the cooperative effect of the ACF.

Key words : ACF, ZnO, TiO$_2$, MO, Visible light, Photocatalytic

1. Introduction

Semiconductor photocatalysts, widely using in optical coating applications and microelectronic devices and in purifying air and water by removing contaminants, have attracted considerable attention in recent years. Photocatalytic reactions of semiconductors, such as splitting water and the decomposition of waste materials, have been the subject of many papers due to the possible use of such reactions in the areas of solar energy conversion into chemical energy and pollution control using solar energy.

Currently, TiO$_2$ is typically used as the photocatalyst due to its feasible activity, chemical stability, commercial availability and low price. TiO$_2$ has three main crystal structures. The first of these is anatase, which tends to be more stable at low temperatures. The second is brookite, which is usually found in minerals and has an orthorhombic crystal structure, and the third is rutile, which is a stable form at higher temperatures. Anatase has higher photocatalytic activity and has been studied more than the other two forms of TiO$_2$. However, TiO$_2$ powder has a number of disadvantages, such as agglomeration and low light utilization. In addition, it is difficult to separate TiO$_2$ powder from bulk solutions, catalysts, and other materials.

Much effort has been devoted to improving photocatalytic efficiency on TiO$_2$ surfaces. The activity of TiO$_2$ as a photocatalyst is well recognized to depend strongly on the preparation method. The sol-gel route is widely considered to be an excellent method with which to prepare TiO$_2$-based materials. This approach includes modifications in which foreign ions are incorporated, the creation of TiO$_2$ films by dip-coating processes and the creation of titanium/carbon composites.

Provided that ACFs are used as support material and all of the advantages of both the ACFs and TiO$_2$ are utilized, a powerful photocatalyst can be produced. Activated carbon fiber (ACF) has an excellent adsorption capacity and shows very fast adsorption/desorption rates in comparison with conventional activated powders or activated granular carbons. ACFs are produced in the form of felt or cloth with high BET surface areas and micropore volumes. However, ordinary ACFs for toxic gases (especially for basic gases) do not have sufficient adsorption capacities because they typically have a non-polar surface manufactured under high-temperature conditions. It is known that including a carboxyl group and a phenol hydroxyl group of the surface oxygen complex lead to acidic properties and that an acidic adsorbent interacts strongly due mainly to adsorption by Lewis acid-base interactions.

In particular, zinc oxide, a wide-bandgap II-VI semiconductor (bandgap = 3.37 eV, 298 K), shows a significant quantum confinement effect when its size reaches the Bohr radius, i.e., 1.8 nm. Moreover, ZnO is an interesting material due to its many applications such as in varistor devices, gas sensors, electrical and optical devices.

Therefore, in this work, we focused on the characterization of ZnO-ACF/TiO$_2$ composites during the formation of TiO$_2$ derived from titanium n-butoxide (TNB). An acid treatment was applied to the ACF surface in order to introduce surface oxygen complexes, and ACF was also used as an adsorptive supporting material for TiO$_2$ loading. The ZnO-ACF/TiO$_2$ composites were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive X-ray (EDX) analysis. To determine the photocatalytic decomposition of the composites, methylene
blue (MB) was chosen as the model pollutant. It was used under UV irradiation.

2. Experimental Procedure

2.1. Materials

TNB (99.9%) as a titanium source was purchased from Acros Organics Co., Ltd., USA. Zinc nitrate (Zn [NO₃]₂) as a zinc source was purchased from Duksan Pure Chemical Co., Ltd., Korea. ACF was purchased from East Asia Carbon Fibers Co., Ltd., An Shan, China. The acids HNO₃ and H₂SO₄, used to modify the ACF, were obtained from Duksan Pure Chemical Co., Ltd., Korea. Methyl orange (analytical grade) was also obtained from Duksan Pure Chemical Co., Ltd., Korea.

2.2. Preparation of ACF/TiO₂ Composites

The ACF samples were washed with demonized water and dried for 24 h at an ambient temperature. They were then pulverized by a pulverizer. 20 g of carbon fiber material at room temperature was milled in a laboratory tumbling ball milling for 48 h, after which the methanol chemical carbon materials were milled for another hour with a Pulverisette 6 planetary high-energy grinding machine (TMC Frisch, TaemYong Scientific Co., Ltd.). A mixed solution of H₂SO₄ and HNO₃ (volume ratio of 30 : 70, solution A) was used to oxidize the ACF particles. 8 g of pul- verized ACF was mixed with 800 ml of solution A, stirred 7-8 h, 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 of TNB and benzene with a regular ratio of 2:50 and stirred at 343 K for 5 h in an airtight container. After stirring, the solution was transformed into ACF and TiO₂ mixed gels, and these gels were heat treated at 973 K for 1 h.

2.3. Preparation of the ZnO-ACF/TiO₂ Composites

ACF/TiO₂ was prepared using pristine concentrations for the preparation of the ZnO-ACF/TiO₂ composites. The typical procedure is as follows: 0.25 g of ACF/TiO₂ powder was mixed with 0.67, 1.73, and 2.06 g of Zn (NO₃)₂ · 6H₂O, with each then added to 50 ml of distilled water. The mixtures were then stirred for 5 h. ZnO and the support particles were initially dried at 323 K for 6 h, after heat-treated at 773 K for each 2 h. ZnO-ACF/Ti₁, ZnO-ACF/Ti₂ and ZnO-ACF/Ti₃ photocatalyst composites were obtained. The designations for the different prepared materials are summarized in Table 1.

2.4. Characterization of the Prepared Photocatalysts

A specified quantity of the photocatalyst composite was added to 100 ml of a methyl orange (MO) solution. The reactor was placed in the dark for 30 minutes to allow the adsorption of MO molecules into the photocatalyst composite particles. The crystalline phase, particle size, and morphology of the photocatalysts nanocrystals were investigated by specific surface area (BET) analysis, X-ray diffraction analysis (XRD), energy dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM). The specific surface area (BET) was determined by N₂ adsorption measurements at 77 K. An XRD analysis using radiation was conducted to assess the crystalline phases. The EDX spectra were used for an elemental analysis of the samples. SEM measurements were taken using a JEOL apparatus operating at 10 KV of specimens upon which a thin layer of gold or carbon had been evaporated. A specified quantity of the photocatalyst composite was added to 100 ml of a methyl orange (MO) solution at a concentration of 1.0 × 10⁻⁴ M, in the dark, until saturation adsorption of the mixture, allowing at least 2 h for the adsorption of the MO molecules into the photocatalyst composite particles. After adsorption, we degraded the MO solution under visible light. Visible light (35 watts LED lamp) was irradiated onto the reactor for 30, 60, 90 and 120 minutes to completely degrade the MO solution samples. The experiments were performed at room temperature.

3. Results and Discussion

3.1. Elemental Analysis of the Preparation

Figure 1 shows the EDX patterns of the ZnO-ACF/Ti₁, ZnO-ACF/Ti₂, and ZnO-ACF/Ti₃ samples. The elemental compositions of these samples were 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, Zn was observed. Fig. 1 shows the quantitative microanalyses results of C, O, Ti and Zn as the major elements of the composites by EDX. There were some small impurities, thought to be introduced from the unpurified ACF or Zn (NO₃)₂ · 6H₂O. In most of the samples, carbon and titanium were present as major elements with small quantities of oxygen in the composite. In addition, fig. 2 shows the quantitative results of C, O, Ti and Zn as the major elements of the composites. In a comparison of the three types of composites, the ZnO-ACF/Ti₁ and ZnO-ACF/Ti₂ composites have C, O, and Ti as the main elements, with a small amount of Zn; the ZnO-ACF/Ti₃ composite has

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>Nomenclatures</th>
<th>BET (m²/g)</th>
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<tr>
<td>0.25 g ACF/TiO₂ + 0.67g Zn(NO₃)₂ · 6H₂O + 50 ml H₂O</td>
<td>ZnO-ACF/Ti₁</td>
<td>32.20</td>
</tr>
<tr>
<td>0.25 g ACF/TiO₂ + 1.73g Zn(NO₃)₂ · 6H₂O + 50 ml H₂O</td>
<td>ZnO-ACF/Ti₂</td>
<td>51.24</td>
</tr>
<tr>
<td>0.25 g ACF/TiO₂ + 2.06g Zn(NO₃)₂ · 6H₂O + 50 ml H₂O</td>
<td>ZnO-ACF/Ti₃</td>
<td>47.26</td>
</tr>
</tbody>
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Table 1. Nomenclature and BET Surface Area of Prepared Samples
C, O, Ti and Zn as the main elements. Thus, we can conclude that the ZnO-ACF/Ti1, ZnO-ACF/Ti2 and ZnO-ACF/Ti3 composites were formed using different amounts of Zn(NO$_3$)$_2$·6H$_2$O.

### 3.2. Surface Characteristics of the Samples

Figure 3 shows a SEM photograph of the micro-surface structure about the compound. TiO$_2$ and zinc oxide particles are uniformly coated onto the surface of the ACF, which leads to an increase in the size of the antiparticles, reportedly because small particles can provide good dispensability to the reactive sites and aggregated particles of the reactant. Due to the number of grain aggregates, higher surface roughness results. We did not capture a SEM image of the particle, as the ACF content was very low (Table 2). SEM images of the ZnO-ACF/Ti1, ZnO-ACF/Ti2 and ZnO-ACF/Ti3 samples are shown in Figs. 2 (a), (b) and (c), respectively. These figures show that the amount of titanium dioxide increased with an increase in the amount of the organic titanium precursor due to the polymerization reaction which occurred at anchoring site on the ACF surfaces. As shown in Fig. 2, the numerous pores on the ACF surface reduce the pore blocking caused by the titanium dioxide particles. This also explains why the pores of the ACF particles are filled with titanium oxide particles with an increase in the pore size and pore volume (Table 1).

### 3.3 Structural Analysis

Figure 4 shows XRD patterns of the ZnO-ACF/Ti1, ZnO-
ACF/Ti2 and ZnO-ACF/Ti3 composites. After a heat treat-
ment at 873 K, major peaks were observed at 25.3, 37.9, 
48.0, 53.8, 54.9 and 62.5° (2θ), which were correspond-
ingly assigned to the (101), (004), (200), (105), (211) and 
(204) planes of the anatase phase, indicating that the pre-
pared TiO2 is anatase. These results suggest that ZnO-
ACF/TiO2 also has a pure anatase phase structure when 
prepared using the current preparation conditions. The 
XRD pattern shows the characteristic peaks of ZnO. Addi-
tional ZnO diffraction peaks for the (002), (020), (200), (120), 
(112), (022), (202), (202), (122), (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, 
44.66, 45.70, 47.24, 48.25, 49.93, 50.3 and 50.74 ° (2θ), 
respectively. The peaks of TiO2 were also observed in the XRD 
pattern of the ZnO-ACF/Ti1 compound at 37.9° (2θ). In the 
XRD pattern of the ZnO-ACF/Ti2 and ZnO-ACF/Ti3 com-
posites, the intensity of the peaks of TiO2 was decreased. 
There were a few other peaks which were most likely intro-
duced as a results of the unpurified Zn(NO3)2 ·6H2O and 
TNB.

3.4. Photocatalytic Activity of the Samples

Figure 5 shows that ZnO-ACF/Ti1, ZnO-ACF/Ti2 and 
ZnO-ACF/Ti3 underwent MO degradation by visible light 
irradiation. Under visible light irradiation and different 
exposure times, the degradation of the MO solution pro-
ceded. The MO concentration was 5.0 × 10−4 mol/L. In the 
results, the MO concentration was shown to be reduced by 
the physical adsorption of the ZnO-ACF/TiO2 composite 
during the initial reaction time without light irradiation. 
Meanwhile, the MO solution gradually lost its color with 
visible light irradiation with an increase in the reaction 
time. This process has two steps: photocatalytic decomposi-
tion during the adsorption of the dye molecules and degra-
dation. After adsorption for 30 minutes in a dark state, the 
samples reached a point of adsorption-desorption equilib-
rium. In the decomposition steps depending on the time, the 

ZnO-ACF/Ti3 revealed the best decomposition result with adsorption effects. This indicates that the best degradation 
effect is related to a synergistic reaction of ZnO, ACF and 
TiO2 in the ZnO-ACF/TiO2 composite material.

Figure 6 shows a schematic diagram of the energy levels of ZnO, TiO2, and ACF.
application of solar energy with a potential photocatalytic effect. The photocatalytic process is determined on the basis of the bandgap excitation of electron-hole pairs. As an oxidizing agent and a reducing agent of titanium dioxide in the photocatalytic process, a key factor is the photoinduced electron holes in these photocatalysts systems given the impact of the photocatalytic reaction and separation process.

OH· hydroxide ions may trigger a trap hole, resulting in the formation of hydroxyl radicals as strong oxidizing agents. The oxygen species are adsorbed in the electron trap, resulting in the formation of superoxide species (O2·−) that are unstable. These two reactions may separately occur in several ways. The active sites of the catalyst are contaminated with degraded molecules via light absorption. In the ZnO-ACF/TiO2 system, the main principle to maximize the electron-hole production of TiO2 and ZnO as the co-catalyst is the use of optimum amounts of titanium and zinc sources. It is believed that the increase in the loading amounts increases the rate of degradation with a large number of electron holes produced due to the quantity of pollutants generated. However, this can create a catalyst poison on the ACF surface. However, the catalyst suspension is related to the light penetration rate with the particle size depending on the precipitation time. This can be explained on the basis of the surface area of the smaller particles. Accordingly, an increase in the proportion of zinc oxide will lead to a decrease of the surface area of the catalyst particles.

According to the specific surface area obtained by the BET method, it is difficult quantitatively to compare the specific surface areas of the samples. However, it is clear that the ZnO powder was uniformly dispersed on the ACF surfaces in the SEM images. As described above, high photocatalytic effects are related to complex factors such as a highly uniform distribution, a high surface area, the electron-hole recombination effect, and the catalyst dispersion rate. ZnO as the major contributor to the high photocatalytic dispersion is conducive to improve the catalytic reaction, and the adsorption reaction leads to better catalytic performance. The rate of degradation of the pollutants is proportional to the numbers of active sites of the catalyst used and the optical absorption rate.

4. Conclusions

This study examined the preparation and characterization of ZnO-ACF/Ti1, ZnO-ACF/Ti2 and ZnO-ACF/Ti3 by a sol-gel method. The typical anatase TiO2 structure and the ZnO structure were observed in the XRD patterns. According to the SEM morphologies, for the ZnO-ACF/TiO2 samples, ACFs can be easily found. Moreover, the ACFs were noted to be decorated uniformly with ZnO particles and TiO2 particles. The ZnO-ACF/TiO2 exhibited a good photocatalytic degradation effect under visible light irradiation due to the photosensitive and enhancing BET surface area effect of the ACF. The ZnO-ACF/Ti3 composite showed the best photocatalytic degradation activity of a MO solution under visible light irradiation. This was attributed to three different effects: the photocatalytic reaction of the supported TiO2, the energy transfer effects of the ACF, and the ZnO with electron-hole combinations under visible light in this system.

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