Photocatalytic Performance of ZnS and TiO₂ Supported on AC Under Visible Light Irradiation

Ze-Da Meng, Sun-Bok Cho, Trisha Ghosh, Lei Zhu,
Jong-Geun Choi, Chong-Yeon Park and Won-Chun Oh^{*†}

Department of Advanced Materials Science & Engineering, Hanseo University, Seosan-si,
Chungnam-do 356-706, Korea

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Abstract AC and ZnS modified TiO₂ composites (AC/ZnS/TiO₂) were prepared using a sol-gel method. The composite obtained was characterized by Brunauer-Emmett-Teller (BET) surface area measurements, X-ray diffraction (XRD), energy dispersive X-ray (EDX) analysis, scanning electron microscope (SEM) analysis, and according to the UV-vis absorption spectra (UV-vis). XRD patterns of the composites showed that the AC/ZnS/TiO₂ composites contain a typical single and clear anatase phase. The surface properties as observed by SEM present the characterization of the texture of the AC/ZnS/TiO₂ composites, showing a homogenous composition in the particles showing the micro-surface structures and morphology of the composites. The EDX spectra of the elemental identification showed the presence of C and Ti with Zn and S peaks for the AC/ZnS/TiO₂ composite. UV-vis patterns of the composites showed that these composites had greater photocatalytic activity under visible light irradiation. A rhodamine B (Rh.B) solution under visible light irradiation was used to determine the photocatalytic activity. The degradation of Rh.B was determined using UV/Vis spectrophotometry. An increase in the photocatalytic activity was observed. From the photocatalytic results, the excellent activity of the Y-fullerene/TiO₂ composites for the degradation of methylene blue under visible irradiation could be attributed to an increase in the photo-absorption effect caused by the ZnS and to the cooperative effect of the AC.

Key words ZnS, TiO₂, visible light, UV-Vis, Rh.B.

1. Introduction

Semiconductor oxides have been widely used in optical coating and microelectronics devices, the application to purify contaminants in air and water has been recognized recently.¹⁻⁴⁾ Photocatalytic reactions of semiconductors such as splitting of water and decomposition of waste materials have received special attention because of their possible application to the conversion of solar energy into chemical energy and pollution control using solar energy.^{5,6)} In these investigations, various semiconductor materials such as TiO₂, CdS, ZnS, ZnO and WO₃ have been employed to study photocatalytic reduction of pollution in water,⁷⁻¹¹⁾ among which TiO₂ was proved to be the most efficient photocatalyst due to its exceptional optical, electronic properties, chemical stability, non-toxicity, and low cost.¹²⁻¹⁴⁾ TiO₂ shows the highest quantum yield among the popular semiconductors. However, in many cases, the photocatalytic activity of TiO₂ is not enough to be useful for industrial purposes.¹⁵⁻¹⁷⁾

The general photocatalytic process of a semiconductor

involves the formation of photoinduced electrons at the conduction band and holes at the valence band, and the subsequent chemical reactions with the surrounding media after photostimulated 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 crystal lattice, which would lower the probability for electron-hole recombination.¹⁸⁻²⁰⁾

ZnS is an important II-VI semiconductor and can be applied in cathode-ray tubes (CRTs),²¹⁾ luminescence materials,²²⁾ infrared windows,²³⁾ and photocatalysis.²⁴⁻²⁶⁾ In recent years, ZnS nanocrystals (NCs) have been extensively studied due to their unique properties and are reported to have potential as photocatalysts in environmental contaminant elimination, CO₂ reduction, and H₂ evolution.^{27,28)} For the sake of improving the photocatalytic efficiency of ZnS or TiO₂, nanoscale ZnS coupled TiO₂ photocatalyst have attracted a great deal of attention for potential applications such as purification of water or organic dyes.^{29,30)} However, as other powder photocatalysts, ZnS/TiO₂ nanoparticles have some disadvantages, such as low photoca-

[†]Corresponding author
E-Mail : wc_oh@hanseo.ac.kr (W. -C. Oh)

talysis efficiency in the visible light region, low utilization rate in practical applications owing to the fact that the generated electron/hole (e^-/h^+) pairs are easily recombined, meanwhile there are some dispersion problems because this nanoparticles are easy to cohere. Thus one way of improving these defects is choosing an appropriate catalyst support.

Active carbon (AC) is an excellent alternative because it can concentrate pollutants through adsorption around loaded TiO_2 , leading to an increase in the degradation of pollutants.³¹⁾ Additionally, the interaction between the pollutants and the surface of the AC- TiO_2 was enhanced to promote further degradation.³²⁾ Consequently, the AC/ TiO_2 is a promising photocatalyst with the prospective potential for industrial applications.³³⁾

In the present work, the AC/ZnS/ TiO_2 photocatalyst was prepared from the sol-gel method and the photocatalytic activity for Rh.B solution was investigated under visible light irradiation. The effect of composition will be tested to clarify the mechanism of 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

All chemicals were used as received without further purification. To obtain active carbon, a coconut-based precursor char purchased from Hanil Green Tec was used (Korea). The coconut shell was pre-carbonized first at 773 K, and then activated by steam diluted with nitrogen in a cylindrical quartz tube at 1023 K for 30 minutes. This AC was washed with deionized water and dried overnight in a vacuum drier at over 683 K.

The titanium (IV) n-butoxide (TNB, $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) used as the titanium source for the preparation of the AC/ZnS/ TiO_2 composites was reagent-grade and purchased from Acros Organics (USA). Zinc Chloride (ZnCl_2) and sodium sulfide·5-hydrate ($\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$) were used for the preparation of ZnS supplied by Daejung Chemicals & Metals Co., Ltd, Korea and Yakuri Pure Chemicals Co., Ltd, Japan, respectively. Rhodamine B (Rh.B $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$) was purchased from Samchun Pure Chemical Co., Ltd, (Korea).

2.2 Preparation of AC/ZnS composites

These ACs were washed with deionized water and dried for 24 h at ambient temperature. ACs were pulverized by pulverizer. 20 g of AC 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 (Idar-Oberstein, Frisch, Germany) for 1 h

with ZrO_2 ball (1 mm $\times$ 300 g). H_2SO_4 and H_3PO_4 mixed solution (volume ratio of 70:30, solution A) was used to oxidize the AC particles. 10 g pulverized AC were mixed with 100 ml solution A, stirring 7-8 hours and flush with distilled water for 3 times and dried at 323 K. Oxidized AC were formed.

For ZnS coating, the detailed information of AC/ZnSs (Zn^{2+} - S^{2-} -refluxing) preparation is described as follows: 30 mg ACs were dispersed in 50 mL of ZnCl_2 solution with continuous stirring for 30 mins, and then a stoichiometric amount of 30 ml 2.59 mmol Na_2S solution was prepared separately and injected dropwise into the above mixture with continuous stirring for 3h at 343K. After that, they obtained suspension was heated and refluxed for another 4 h under stirring. The final products were filtered and washed repeatedly with distilled water and ethanol and then vacuum dried at 333K.

2.3 Preparation of AC/ZnS/ TiO_2 composites

AC/ZnS was prepared using pristine concentrations for the preparation of AC/ZnS/ TiO_2 composites. AC/ZnS powder was mixed with 3 ml TNB solution. The mixture was homogenized under reflux at 343 K for 3 hour, while being stirred in a vial. After stirring, the solution transformed to AC/ZnS/ TiO_2 gels and heat treated (N_2 atmosphere) at 773 K to produce the AC/ZnS/ TiO_2 composites.

2.4 Characterization of AC/ ZnS/ TiO_2 compounds

XRD (Shimata XD-D1, Japan) was used for crystal phase identification and to estimate the anatase ratio of TiO_2 and estimate the crystal phase of ZnS. The XRD patterns were obtained at room temperature using Cu $\text{K}\alpha$ radiation. SEM (JOEL, JSM-5200, Japan) was used to observe the surface state and porous structure of the AC/ZnS/ TiO_2 composites. The elemental composition of the AC/ZnS/ TiO_2 composites was examined by EDX. SEM was used to observe the surface state and structure of AC/ZnS/ TiO_2 composites using a scanning electron microscope (JSM-5200 JOEL, Japan). The Brunauer-Emmett-Teller (BET) surface area was determined by N_2 adsorption measurements at 77 K (Monosorb, USA).

2.5 Photocatalytic tests

A specified quantity of the photocatalyst composite was added to a 100 ml Rh.B solution. The reactor was placed in the dark for 2 hours to allow the maximum adsorption of Rh.B molecules to the photocatalyst composite particles. In all experiments, the initial concentration of the Rh.B was 1×10^{-5} mol/L, and the amount of the photocatalyst composite was 0.01 g/(100 ml solution). After adsorption, the photodecomposition of the Rh.B 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 used was an 18 W lamp with the main emission wavelength at 460 nm. Visible light irradiation of the photoreactor was performed for 10 min, 30 min, 60 min, 90 min and 120 min. The experiments were performed at room temperature. In the process of Rh.B degradation, a glass reactor was used and the reactor was placed on a magnetic churn dasher. Samples were then withdrawn regularly from the reactor and the dispersed powders were removed by a centrifuge. The Rh.B concentration in the solution was then determined as a function of the irradiation time from the change in absorbance at a wavelength of 560 nm. After treatment with the centrifuge the centrifugalizations were analyzed using a UV-vis spectrophotometer.

3. Results and Discussion

3.1 Elemental analysis of the preparation

Fig. 1 shows the EDX patterns of the AC/TiO₂ (a), ZnS/TiO₂ (b) and AC/ZnS/TiO₂ (c). The elemental composition

Fig. 1. EDX elemental microanalysis for (a) AC/TiO₂, (c) ZnS/TiO₂ and (d) AC/ZnS/TiO₂.

Table 1. Nomenclature of samples prepared with photocatalysts.

Preparation method	Nomenclatures
AC + MCPBA + 3 ml TNB	AC/TiO ₂
2.59 mmol Na ₂ S·5H ₂ O + ZnCl ₂ + 3 ml TNB	ZnS/TiO ₂
AC + Na ₂ S·5H ₂ O + ZnCl ₂ + 3 ml TNB	AC/ZnS/TiO ₂

of these samples was analyzed and the characteristic elements were identified. Fig. 1 shows strong K α and K β peaks from Ti at 4.51 and 4.92 keV, whereas a moderate K α peak for O appears at 0.52 keV.³⁴⁾ In addition to the above peaks, Zn and S was also observed. Fig. 1 presents the quantitative microanalysis of C, O, Ti, Zn and S 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 AC or ZnCl₂ and Na₂S. In the case of most 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 ZnS particles were coated uniformly over the AC 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.³⁵⁾ The surface roughness appears to be high due to some grain aggregation. We cannot find AC particles from the SEM image, this is because the content of AC is so small (shown in Table 2). Figs. 2(a), (b)

Fig. 2. SEM images of (a) AC/TiO₂, (b) ZnS/TiO₂ and (c) AC/ZnS/TiO₂.

Table 2. EDX elemental microanalysis and BET surface area.

Sample name	C (%)	O (%)	Zn	S	Ti (%)	Impurity (%)	BET (m ² /g)
TiO ₂	—	—	—	—	99.99	0.01	18.95
AC/TiO ₂	20.72	44.11	—	—	34.05	1.12	83.25
ZnS/TiO ₂	—	31.67	27.66	7.67	21.59	0.04	32.20
ZnS/AC/TiO ₂	45.36	26.53	6.19	2.67	18.51	0.74	52.11

and (c) show the SEM images of AC/TiO₂, ZnS/TiO₂ and AC/ZnS/TiO₂, respectively. The level of aggregation increased with an increasing amount of addition. Comparing Figs (a), (b) and (c), we can find that when TiO₂ was added, the aggregation became strong. 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 AC/TiO₂, ZnS/TiO₂ and AC/ZnS/TiO₂, were 18.95 m²/g, 83.25 m²/g, 32.20 m²/g and 52.11 m²/g, respectively. The TiO₂ and ZnS particles were introduced to the pore of the AC, which decreased the BET surface area. The AC/TiO₂ sample had the largest area, which can affect the adsorption reaction. The BET surface area of the photocatalyst AC/ZnS/TiO₂ was decreased by 37.40% when AC/TiO₂ particles were doped by ZnS. This is because ZnS particles fill the pores of the AC/TiO₂ particles,³⁶⁾ thereby reducing the pore size and pore volume of AC/TiO₂ particles (showed in Table 2).

3.3 Structural analysis

Fig. 3 shows XRD patterns of the AC/TiO₂, ZnS/TiO₂ and AC/ZnS/TiO₂ composites. 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), (211), and (204) planes of anatase, indicating that the prepared TiO₂ is anatase. These results suggest that AC/ZnS/TiO₂ also has a pure anatase phase structure with the current preparation conditions. The XRD

Fig. 3. The XRD patterns of AC/TiO₂, ZnS/TiO₂ and AC/ZnS/TiO₂.

pattern shows the characteristic peaks of ZnS, while (111), (220), and (311) crystal planes are originated from the cubic ZnS phase (JCPDS files, No. 5-0566, 77-2100 and 02-0564). The peaks of TiO₂ were also observed in the XRD pattern of AC/ZnS/TiO₂ compound at 37.9° (2θ). In the ZnS/TiO₂ and AC/ZnS/TiO₂ composite's XRD pattern the intensity of the peaks about TiO₂ was decreased. This is because of the content of TiO₂ was decreased, and the peaks of ZnS have affect TiO₂ peak. There are few other peaks which are believed to have been introduced from the unpurified Na₂S·5H₂O, ZnCl₂ and TNB.^{37,38)}

3.4 UV-vis diffuse reflectance spectroscopy

The diffuse reflectance UV-vis absorption spectra of the different samples are presented in Fig. 4. As expected, we can find TiO₂, ZnS/TiO₂, AC/TiO₂ and AC/ZnS/TiO₂ composites have great absorption at ultraviolet region, TiO₂ shows the characteristic spectrum with its fundamental absorption sharp edge rising at 400 nm (E_g = 3.2 eV). On the other hand, ZnS/TiO₂, AC/TiO₂ and AC/ZnS/TiO₂ composites have good absorption at the visible region, this is also means that these composites has greater photocatalytic activity under visible light irradiation. Due to ZnS nano particles can effectively absorb light and trap electrons on the conduction band, so ZnS/TiO₂ has good adsorption at visible region. Compared with TiO₂ and ZnS/TiO₂, it is noticeable that there is an obvious correlation between the AC/TiO₂, AC/ZnS/TiO₂ composites and the

Fig. 4. Diffuse reflectance UV-vis spectra of pure TiO₂, AC/TiO₂, ZnS/TiO₂ and AC/ZnS/TiO₂.

UV-vis spectrum change. These observations might suggest an increase of surface electric charge of the oxides in the composite catalysts due to AC introduction, which may lead to modifications of the fundamental process of electron/hole pair formation while applying visible irradiation.^{39,40)}

3.5 Photocatalytic activity of samples

Fig. 5 shows the time series of Rh.B degradation using AC/TiO₂, ZnS/TiO₂ and AC/ZnS/TiO₂ under visible light irradiation. The spectra for the Rh.B solution after visible light irradiation show the 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 Rh.B was 1.0×10^{-5} mol/l, the absorbance for Rh.B decreased with increasing visible light irradiation time. Moreover, the Rh.B solution increasingly lost its color, and the Rh.B 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 hours, the samples reached adsorption-desorption equilibrium. In the adsorptive step, AC/TiO₂, ZnS/TiO₂ and AC/ZnS/TiO₂ composites showed different adsorptive effects with AC/TiO₂ having the best adsorptive effect. The adsorptive effect of pure TiO₂ was the lowest. AC/TiO₂ has the largest BET surface area, which can enhance the adsorptive effect. In the degradation step, the AC/TiO₂, ZnS/TiO₂ and AC/ZnS/TiO₂ composites showed a good degradation effect. A comparison of the decoloration effect of the catalysts showed that AC/ZnS/TiO₂ composites have best degradation effect, which is due to the synergistic reaction of ZnS, AC and TiO₂.

Fig. 6 is the schematic diagram of the separation of the photogenerated electrons and holes on the photocatalytic interface. Both the minimum conduction band and the maximum valence band of ZnS lie above those of TiO₂;

Fig. 5. UV/Vis spectra of the Rh. B concentration against AC/TiO₂, ZnS/TiO₂ and AC/ZnS/TiO₂ composites.

Fig. 6. Schematic diagram of the separation of photogenerated electrons and holes on the photocatalytic interface.

therefore the electrons excited to the conduction band of the TiO₂ would transfer to the ZnS, whereas the holes generated in the valence band in the TiO₂ prefer an opposing transfer to the ZnS. Charge carriers separated in different semiconductors effectively reduce the chance of electron-hole pair recombination and prolong their lifetime, thus increasing their quantum efficiencies. In addition, the working range of the wavelength is extended to a visible region due to reduce of the band gap from ZnS and TiO₂, further enhancing the efficiency of the solar energy transition. Synergistic cooperation of these effects enables the ZnS/TiO₂ system to exhibit great potential for solar cell and photocatalysis applications.⁴¹⁻⁴⁴⁾ AC acts as the adsorb effect, and increases the surface area of the compounds which can increase the adsorption effect for samples, adsorbing more O₂ and dye molecules, and ensuring these systems take full advantage of yield oxidizing species. The positive holes in the valence band can be trapped by OH⁻ or H₂O species adsorbed on the surface of the catalyst, producing reactive hydroxyl radicals in aqueous media. The photo-generated electrons accumulate on the surface of TiO₂ and could be rapidly transferred to molecular oxygen O₂ to form the superoxide radical anion O₂⁻ and hydrogen peroxide H₂O₂. The oxidative degradation of dyes was caused by the attack of hydroxyl radicals and superoxide ions, which are the highly reactive electrophilic oxidants. Due to the efficiency of hydroxyl radicals and superoxide ions, azo dyes decomposed to CO₂, H₂O and small inorganic molecules.⁴⁵⁾

4. Conclusion

This study examined the preparation and characteriza-

tion of AC/TiO₂, ZnS/TiO₂ and AC/ZnS/TiO₂. The BET surface area of AC/TiO₂ was higher than that of the AC/ZnS/TiO₂ composite. XRD revealed the ZnS structure and anatase. AC/TiO₂ has a good photo-degradation effect under visible light irradiation, due to the photosensitivity and enhances the BET surface area effect of AC. The AC/ZnS/TiO₂ composite showed the best photocatalytic degradation activity of the Rh.B solution under visible light irradiation. This was attributed to the three different effects between the photocatalytic reaction of the supported TiO₂, the energy transfer effects of AC and ZnS, such as electrons and light and separation effect in this system.

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