Research Article

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The Photocatalytic Activity of ZnS-TiO₂ on a Carbon Fiber Prepared by Chemical Bath Deposition

<https://doi.org/10.1515/chem-2019-0011>

received July 7, 2018; accepted December 4, 2018.

Abstract: This research prepared a TiO₂, ZnS, and ZnS-TiO₂ film on a carbon fiber, to produce TiO₂/C-fiber, ZnS-C-fiber, and ZnS-TiO₂/C-fiber by Chemical Bath Deposition (CBD). Results show that TiO₂/C-fiber consist of anatase at 2θ 25.3 ° and 54.6 °, rutile at 2θ 43.5 ° and a carbon characteristic peak at 2θ of 24.5 °. Meanwhile, the characteristic peaks of ZnS on ZnS-TiO₂/C-fiber present at 2θ of 27.91 ° and 54.58 °. TiO₂/C-fiber has a band gap energy of 3.60 eV, the ZnS/C-fiber of 3.73 eV; when those two catalyst combine, the gap energy is 3.15 eV indicating the interface charge transfer between ZnS-TiO₂. Photocatalytic treatment of an isopropanol solution with TiO₂/C-fiber as a catalyst and under UV light radiation present results peaks at 222- 224 nm and 265 nm, indicating the electronic transition of acetone. Meanwhile, the isopropanol degradation with ZnS-TiO₂/C-fiber produced a new peak at 234-237 nm. The Quantum Yield, QY, of ZnS-TiO₂/C-fiber is 6.96 x 10⁻⁴, higher than TiO₂/C-fiber, i.e., 0.42 x 10⁻⁴. It indicates that ZnS provides a significant role in the photocatalytic activity through a red shift of light response and decreasing electron-hole recombination.

Keywords: carbon fiber; TiO₂/C-fiber; ZnS-TiO₂/C-fiber; photo catalytic activity.

1 Introduction

Photocatalysis is a combination between photochemistry and a catalytic reaction to produce chemical

transformation. Photocatalysis is a potential method to overcome many problems in chemical pollution such as organic waste degradation and dye molecules degradation. TiO₂ is a well-known photocatalyst used either as a single photocatalyst powder, or in a composite form such as TiO₂/carbon [1], ZnS-CdS/TiO₂ [2], and nano-CdS/TiO₂ [3]. Titanium dioxide (TiO₂) or titania is a very well-known and well-researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties [4]. The anatase phase shows higher photocatalytic activity than other TiO₂ phases in water disinfection and pollutant compound degradation [5].

Coating TiO₂ or the photocatalyst layer on a substrate was conducted. Its goal was to develop the reliability of a TiO₂ application, such as the possible increase of reactivation to reduce the cost of post-process separation. Some substrates that were used were glass substrate [6,7], Porous Vycor glass [8], cellulose acetate [9], graphite powder [10], graphite disc [11], graphite oxide intercalated by TiO₂ [12], and also a composite of CdS-graphene/TiO₂ [13]. Our previous research on a graphite substrate found that TiO₂/G had a quantum yield of 1.96 x 10⁻³ at 380 nm of a light source, and that the value increased to 6.0 x 10⁻² when the ZnS layer was coated on TiO₂/G. the graphite substrate proved to contribute to the photocatalytic activity [14]. Low-density carbon material, which is known as exfoliated graphite, also showed a good performance on the electrochemical degradation of *p*-nitro phenol [15]. Graphite is a low cost and stable carbon material to aggressive media, which develops a specific surface, compatibility, and flexibility [16]. However, the graphite substrate is hard, brittle, and difficult to produce on a large scale. Therefore, in this research, a carbon fiber was used as a substrate for the TiO₂ deposition as well as for the ZnS and ZnS-TiO₂ deposition. This carbon fiber was more flexible and appropriate for a large scale production.

A chemical bath deposition, CBD, was chosen because of its simplicity and because of its inexpensive cost while requiring less energy than other methods such as magnetron sputtering and vapor phase deposition. Some

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research on the preparation of a ZnS thin film also used the CBD method [17–19]. CBD also successfully produced a TiO₂/CdS/ZnS layer [20], a ZnS multilayer film [18].

TiO₂ anatase with gap energy 3.2 eV is known to have a high photocatalytic activity. However, the QY is still low due to the recombination of excited electrons back to the hole. Many efforts to inhibit the recombination have been investigated by some researchers such as metal deposition. ZnS is a high band gap semiconductor with E_g of 3.7 eV [17]. Only high UV light will activate ZnS to produce excited electrons to the conduction band. This kind of high gap energy may become a good electron trapper due to its empty conduction band. The addition of ZnS at 0.5% and 0.2% proved to increase the photocatalytic of nano TiO₂ to degrade methylene blue dye [21].

This research will deposit TiO₂, ZnS, and ZnS-TiO₂ on carbon fiber, analyzing their optical properties (energy gap, reflectance spectrum), X-ray diffraction patterns to ensure the existence of the targeted compound, and test their photocatalytic activity through a degradation test on 2-isopropanol. The 2-isopropanol was chosen due to its inactivity with UV-Vis light as it would eliminate the possibility of degradation only by light. Therefore, isopropanol is ideal for studying a photocatalyst activity without considering the contribution of photolysis. In addition, severe isopropanol poisoning results in respiratory depression and circulatory collapse. Isopropanol is also rapidly absorbed with a peak plasma concentration within 30 min [22].

2 Methods

2.1 Synthesis of TiO₂/C-fiber

The synthesis method is based on previous research [23] on the synthesis of the semiconductor film on a graphite substrate. A 100 mL of synthesis solution was prepared by dissolving 1.1 mL of TiCl₄ into 100 mL of HCl 1 M and then adding 0.583 g of cetyl trimethyl ammonium bromide. The solution was stirred for 2 minutes at room temperature and cured for 5 minutes to stabilize the interface between solution-air. The carbon fiber or carbon cloth was procured from the Fuel cell store, USA which was used as the substrate. The carbon fiber area was 1.0 cm² which was analytically balanced to record the accurate weight. A cotton fiber hung the carbon fiber into the synthesis solution, and kept it at 60°C in the oven for four days. The treated carbon fiber was then pulled, washed with distilled water and heated at 450°C for four h.

2.2 Synthesis of ZnS-TiO₂/C-fiber

The ZnS solution was prepared in ten mL of 0.16 M of ZnSO₄ aqueous solution and mixed with 5.6 mL of 7.5 M ammonia solution, and ten mL of 0.6 M thiourea at 80°C. The carbon fiber was dipped three times into the ZnS solution for 15 minutes each. This dipping method has been studied by previous research [23]. The ZnS was also deposited on the prepared TiO₂/C-fiber, the prepared ZnS/C-fiber and the ZnS-TiO₂/C-fiber. The prepared materials were washed with distilled water and dried at room temperature.

All prepared materials were investigated for their content by analyzing the characteristic peaks present in their X-ray diffraction (Bruker D8) pattern and comparing the pattern with a standard diffraction pattern of anatase ICSD#9852, rutile ICSD#23697, carbon ICSD#28419, and ZnS ICSD#157133. A Scanning Electron Microscope (JEOL-JED-2300) analysis was also conducted to investigate their surface morphology, equipped with EDX to analyze their elemental content. A UV Vis diffuse reflectance (UV 1700 *Pharmaspec* Shimadzu) analysis was used to investigate their optical properties by analyzing the reflectance data into a Tauc plot to obtain the gap energy (eV) values.

2.3 Photocatalytic Activity test

The photocatalytic activity test was conducted by applying the prepared materials as a catalyst for isopropanol degradation. Isopropanol was selected based on its inactive properties at UV-Vis range, confirmed by flat absorbance spectra; this would eliminate the possibility of photolysis involvement during isopropanol degradation. The photocatalytic test was conducted in a quartz cuvette with a monochromatic light source coming from the UV Vis spectrophotometer instrument (HR 4000 CG-UV-VIS-NIR Ocean Optic) that was setup in photometric mode. The isopropanol solution was four mL, and the prepared photocatalyst composite was hung up using a cotton fiber. The degradation process was stopped every 10 minutes to take absorbance measurements at 200 – 700 nm of wavelengths. The test was conducted for 30, 60, and 90 minutes. The FTIR (Prestige-21 Shimadzu) analysis detected the change in functional groups at before and after photocatalytic degradation. The QY value was calculated by equation (1).

$$QY = \frac{N_{mol} \left(\frac{mol}{s} \right)}{N_{photon} \left(\frac{E_{Einstein}}{s} \right)} = \frac{reaction\ rate}{rate\ of\ photon\ absorption} \quad (1)$$

In which, 1 Einstein is $\frac{0.1196}{\lambda}$, λ is a wavelength of light radiation (m^{-1}). The reaction rate was calculated based on the production of acetone during photocatalysis in mole s^{-1} . A mole of acetone was calculated from absorbance at the maximum wavelength of acetone, 265 nm. Meanwhile, the molar attenuation coefficient, ε in $\text{L mole}^{-1}\text{cm}^{-1}$, was found by plotting absorbance, A , versus concentration, C , of a series of an acetone solution. The absorbance, A , of the solution after photo catalytic treatment was measured, and then the absorbance value at 265 nm was applied to the Lambert-Beer equation for acetone. Then, a mole of acetone was calculated by multiplying the calculated concentration with the volume of the analyzed solution. Dividing the mole of produced acetone by time of irradiation was the reaction rate, mole s^{-1} . Meanwhile, the rate of photon absorption, N_{photon} , was calculated by equation (2).

$$N_{\text{photon}} = \frac{\text{Total Power Adsorbed (Js}^{-1}\text{)}}{\text{Photon Energy (Jmol}^{-1}\text{)}} \quad (2)$$

Total Power Adsorbed, TPA, is the light adsorbed by the photo catalyst in accordance with irradiation wavelength (300 nm or 380 nm). The absorbance value was calculated from UV Vis DR data. Multiplying absorbance by the power of light source used in the UV Vis DR instrument in accordance with the time of photo catalytic treatment resulted in the TPA value.

3 Result and Discussion

The carbon fiber was cut into 1 cm^2 small squares, as shown in the optical image in Figure 1a. The fiber diameter is around $5.5 \mu\text{m}$ (Figure 1b), and the x-ray diffraction pattern is depicted in Figure 1. The pattern shows a weak characteristic peak at 2θ 24.5° which matches well with the characteristic peak of standard carbon ICSD#28419. The peak is broad indicating amorphous and small particle size.

Meanwhile, the diffraction pattern of TiO_2/C -fiber (Figure 2) provided a peak at 2θ 25.3° and 54.60° indicating an anatase peak with a standard diffraction of ICSD # 9852, and a rutile peak at 2θ 43.5° , based on a rutile standard of ICSD#23697. However, the 2θ 43.5° peak may have overlapped with the carbon peak at 2θ 44° based on the carbon standard diffraction of ICSD#28419. The high intensity of the anatase peak indicated anatase as a dominant phase. It provided an advantage because

Figure 1: The XRD pattern of C fiber along with its optical image (a), and its SEM image (b).

Figure 2: The XRD pattern of TiO_2/C along with its SEM images (insert) under different magnification. Marker ● refers to the anatase peak, in which a high peak of 25.3° overlaps with the carbon peak of 24.5° . Marker ○ signifies a rutile TiO_2 overlap with carbon.

anatase has a higher photocatalytic activity than another TiO_2 phase [24].

The SEM image of TiO_2/C under high magnification as depicted in Figure 2 (insert) shows some tiny particles attached to the carbon fiber. A mapping analysis was conducted to ensure the existence of the TiO_2 particle; the result is depicted in Figure 3 along with its elemental composition.

The ZnS deposition on carbon fiber and TiO_2/C -fiber was conducted three times, dipping each for 15 minutes. The ZnS formation followed the reaction depicted in the equations (3)-(8). ZnSO_4 is the Zn^{2+} source. Meanwhile,

Figure 3: The EDX analysis result of TiO₂/C along with its elemental mapping and elemental composition.

thiourea is the S²⁻ source [25]. XRD patterns of ZnS/C fiber is depicted in Figure 4a. The ZnS characteristic peak presented at 27.91 ° and 54.58 ° matched well with ICSD # 15477. These results corroborated with other researchers' results who found a broad peak at 2θ 20 – 35 ° confirming the presence of a small size of ZnS grains [6]. Meanwhile, a peak at around 44 ° refers to the characteristic peak of carbon. Therefore, the similar peak at 44 ° that is presented in Figure 3, tends to be the characteristic peak of carbon rather than that of rutile. The SEM image along with the EDX elemental and mapping analysis are depicted in Figure 4(b) and 4(c).

The diffraction pattern of the ZnS-TiO₂/C-fiber as shown in Figure 5, show some peaks at 2θ 27.91 ° and 54.58 °. As the patterns of ZnS-TiO₂/C-fiber are compared with the diffraction patterns of ZnS/C and TiO₂/C (Figure 5), it was concluded that the ZnS peaks seemed to overlap with the rutile peak at 2θ 27.9187 ° and the anatase peak at 2θ 54.60 °. Meanwhile, the carbon peak at 14.88 ° matched well with ICSD# 88812. The ZnS peak was similar to the ZnS peak on ZnS/C fiber as well as with the peak found on the ZnS layer that was prepared from the zinc chloride as precursor [18].

When ZnS was deposited on TiO₂/C producing the XRD pattern in Figure 5, the deposit form (Figure 6 a and b) was different than with the ZnS on the carbon fiber substrate directly (Figure 4b). The EDX analysis confirmed the presence elements Zn and Ti (Figure 6). This indicated the reliability of the CBD method to deposit ZnS and TiO₂ on a carbon fiber. Another method of homogeneous hydrolysis was also successfully preparing ZnS/TiO₂ as titania and ZnS sphalerite [26]. The higher amount of ZnS was deposited on the TiO₂/C rather than on the C fiber. It was 0.7 wt% on C fiber, and 13.09% on TiO₂/C. The polarity of TiO₂ was the important parameter for the growth of the hetero structure ZnS-TiO₂, as it was also explained in a

Zinc ammonia complex and the sulfide ions migrate to the surface and react to form ZnS through equation (7).

Figure 4: The XRD pattern (a) of ZnS/C along with its SEM image (b) and its elemental mapping and composition (c). Marker ⊗ refers to ZnS peak and ▲ refers to carbon peak.

Figure 5: XRD patterns of ZnS/C, TiO₂/C, and ZnS-TiO₂/C.

TiO₂ capped ZnS heterostructure The TiO₂ growth further in the direction of the polar ZnS [0001] [27].

Tauc plots of the prepared materials, depicted in Figure 7, confirmed that the TiO₂/C-fiber had a gap energy of 3.60 eV. It was higher than a single TiO₂ anatase or rutile, i.e., 3.2 eV and 3.0 eV, respectively [20]. The carbon substrate which becomes active at about 4.0 -5.0 eV may have been the reason for this gap energy shift. ZnS/C-fiber showed a gap energy of 3.73 eV. It was close to the homogeneous layer ZnS which was also 3.76 eV [18]. Due

to the ZnS layer covering the carbon fiber better than TiO₂, the ZnS might dominate more than the TiO₂ deposit on the carbon fiber. Meanwhile, the ZnS-TiO₂/C-fiber had a gap energy of 3.13 eV. The value was close to the E_g value of the ZnS/TiO₂ composite prepared by mechano-chemical synthesis with zinc acetate, sodium sulfide, and TiO₂ Degussa P25 as precursors [28]. A study on the interfacial charge transfer mechanism in a nanostructured TiO₂-ZnS coupled network, found a situation when a bias voltage was applied until it reached a saturation current at a particular biasing voltage of ~3.6 V, close to the band gap of ZnS. The situation itself indicates the electronic activity of the composite at a voltage of under ~3.6 V, which compares to the ZnS band gap. The charge transfer from the trap center of ZnS into the surface states, or the conduction band of TiO₂ may be a proper explanation because of its favorable energy under the suitable bias voltage[29]; this is comparable to the photon energy under 3.6 eV. The trap center refers to the energy levels in the physical locality due to a crystal defect where the charge carrier, such as electrons, can be trapped. Table 1 lists the gap energies of the prepared materials.

The photocatalytic activity test through isopropanol degradation resulted in the absorbance plots as described in Figure 8. It showed that the degradation with TiO₂/C under 300 nm (Figure 8a), and 380 nm (Figure 8b) light source, at 30, 60, and 90 minutes produced new peaks at 222 – 224 nm and 265 nm. Those peaks indicated the

Figure 6: SEM images of ZnS-TiO₂/C-fiber at different magnification (a), (b), its EDX analysis (c), and its elemental mapping (d).

Figure 7: Tauc plots of (a) TiO₂/C-fiber, (b) and (c) ZnS-TiO₂/C-fiber, and (d) ZnS/C-fiber.

presence of acetone. The peak at 265 nm referred to $n \rightarrow \pi^*$ transition. Meanwhile, peaks at 222-224 nm might be a $\pi \rightarrow \pi^*$ transition of acetone. Kumar states [30], that the ketone functional group will show electronic transition at 180 – 195 nm for $\pi \rightarrow \pi^*$ transition and at 270 – 295 nm for $n \rightarrow \pi^*$ transition. However, in a more polar solvent, in

Table 1: The gap energy values of the prepared materials.

Materials	E _g (eV)
ZnS /C-fiber	3.73
TiO ₂ /C-fiber	3.60
ZnS-TiO ₂ /C-fiber	3.15

which the production of acetone increases the polarity of the solvent, the electronic transition of $\pi \rightarrow \pi^*$ transition might shift to a longer wavelength. Other research on isopropanol photo catalytic degradation also found acetone as a product [8]. A photocatalytic degradation of isopropanol with TiO₂-LnPc₂ hybrid powder also produced propanone (acetone) and acetaldehyde [31]. Some works of literature agree that the main products of isopropanol or 2-PROH photocatalytic oxidation in a gas–solid system are propanone, CO₂, and H₂O, with selectivity versus propanone or CO₂ depending strongly on the experimental conditions [30]. In a solid-liquid system such as in this research, propanone or acetone is reported as the primary intermediate [30], [31].

Isopropanol degradation with ZnS/C and ZnS-TiO₂/C produced a new peak at 234-237 nm, as described

Figure 8: The absorbance of isopropanol and its degradation results during 30, 60, and 90 minutes with TiO_2/C as catalyst under 300 nm (a) and 380 nm (b) of a light source.

Figure 9: The absorbance of 2-propanol and its produced solution after 30, 60, 90 minutes degradation with ZnS/C under 300 nm (a), and $\text{TiO}_2\text{-ZnS}/\text{C}$ under 300 nm (b) and 380 nm (c) of light sources.

Figure 10: FTIR spectrum of isopropanol before (a) and after degradation with TiO₂/C as catalyst (b).

Figure 11: FTIR spectrum of isopropanol at before (a) and after photo degradation with ZnS-TiO₂/C-fiber as a catalyst.

in Figure 9a, b, and c. It indicated a different photo-degradation result. The peak at 234-237 nm was probably mesityl oxide, C₆H₁₀O [35] as it was also found in other results while degrading isopropanol with TiO₂/PVG as the photocatalyst to produce acetone and mesityl oxide with a chemical shift at 205 ppm in its proton-decoupled ¹³C CP/MAS NMR spectra [8]. Mesityl oxide may be produced from 2-propanol photo-oxidation, in which 2-propanol undergo two parallel paths. The first path is an acetone formation from the H-bonded 2-propanol species, and the second path is the aldol condensation of acetone to form mesityl oxide [8]. Initially, UV light radiation and the presence of oxygen allowed isopropanol to become acetone. Further UV light radiation, especially under a high energy of 300 nm UV light, increased the possibility of aldol condensation to produce mesityl oxide. As seen in Figure 8a 300 nm UV light radiation produced higher peaks of 234-237 nm, which points to a high mesityl oxide concentration. 300 nm of UV light radiation has sufficient energy to activate ZnS valence band electrons to jump into the conduction band and to contribute to the reaction

Table 2: The QY values of each material as calculated by equation (1) from isopropanol degradation data at photon radiation of 300 and 380 nm.

Materials	l photon (nm)	Quantum Yield
TiO ₂ /C-fiber	300	0.99×10^{-4}
	380	0.42×10^{-4}
ZnS-TiO ₂ /C-fiber	300	0.57×10^{-4}
	380	6.96×10^{-4}
ZnS/C-fiber	300	3.96×10^{-4}

other than to become an electron sink for excited TiO₂ electrons. It might produce more acetone molecules and a more likely possibility for aldol condensation to occur.

FTIR analysis (Figure 10 and 11) showed the same functional groups of C-O at 1162 cm⁻¹, C-H aliphatic at 2981 cm⁻¹ and C-H bending at 1383 cm⁻¹ which disappeared after photocatalytic degradation, which indicated a significant catalytic activity. The nanocomposite of TiO₂/ZnS also proved to have a higher visible photocatalytic activity to degrade the Orange II dye compared to the bulk TiO₂ or ZnS or even to compare to the commercial P25 anatase TiO₂ [26].

The QY values of each material as calculated by equation (1) are depicted in Table 2. The higher energy of photon radiation produced a higher QY value as illustrated for the TiO₂/C-fiber. However, ZnS-TiO₂/C-fiber provided a higher QY value with a lower energy of photon radiation or a longer wavelength of light at 380 nm (Table 2). Because of the 380 nm UV light which was comparable to 3.2 eV, it could activate TiO₂ by moving electrons from the valence band to the conduction band. However, that energy was not high enough to promote electrons from the ZnS valence band to the conduction band. It allowed the empty conduction band orbitals to act like the electrons sink for the excited electrons from TiO₂ valence band. It allowed a larger separation between the excited electrons with the hole, h⁺, and inhibited the recombination process providing the holes and electrons to migrate to the surface and to serve as oxidation and reduction agents.

4 Conclusion

The C-fiber can be used as the substrate for the TiO₂, ZnS, and ZnS-TiO₂ layer. The deposition of that layer was successfully conducted through a chemical bath deposition, CBD, as a very simple method without any requirements for specific tools or a high temperature. All

of the prepared composites had photocatalytic activity under UV light irradiation of 300 nm and 380 nm. The ZnS-TiO₂/C-fiber had a lower gap energy even to the TiO₂/C-fiber, i.e., 3.13 eV. An interface charge transfer mechanism may properly explain the advantage of the composite, including its photocatalytic activity as seen on the highest QY value even under low UV energy of 380 nm.

Acknowledgement: This research is a part of Hibah Mandatory that was funded by PNPB Universitas Sebelas Maret 2016. Authors express gratitude for this financial support.

Conflict of interest: Authors declare no conflict of interest.

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