available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Enhanced visible light photocatalytic activity of Ag₂S-graphene/TiO₂ nanocomposites made by sonochemical synthesis

Ze-Da Meng, Lei Zhu, Kefayat Ullah, Shu Ye, Qian Sun, Won-Chun Oh *

Department of Advanced Materials Science and Engineering, Hanseo University, Chungnam 356-706, Korea

ARTICLE INFO

Article history:

Received 30 March 2013

Accepted 2 May 2013

Published 20 August 2013

Keywords:

Silver sulfide

Graphene

Titanium dioxide

UV-Vis absorption spectroscopy

Visible light

Rhodamine B

ABSTRACT

Ag₂S-graphene/TiO₂ composites were synthesized by a facile sonochemical method. The products were characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy, and UV-Vis diffuse reflectance spectrophotometry. During the synthesis reaction, the reduction of graphene oxide and loading of Ag₂S and TiO₂ particles were achieved. The Ag₂S-graphene/TiO₂ composites possessed a large adsorption capacity for dyes, an extended light absorption range, and efficient charge separation properties. Hence, in the photodegradation of rhodamine B, a significant enhancement in the reaction rate was observed with the Ag₂S-graphene/TiO₂ composites as compared to pure TiO₂. The generation of reactive oxygen species was detected by the oxidation of 1,5-diphenyl carbazide to 1,5-diphenyl carbazone. The high activity was attributed to the synergetic effects of high charge mobility and the red shift in the absorption edge of the Ag₂S-graphene/TiO₂ composites.

© 2013, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Graphene is a new star, after the carbon nanotube and C₆₀, in condensed matter physics, electronics, and material science [1]. Graphene is a single-atom thick sheet of *sp*²-bonded carbon atoms in a hexagonal lattice, which shows outstanding mechanical, thermal, optical, and electrical properties. Therefore, graphene-based composite materials have attracted much attention, and recent studies have shown their usefulness in electronics, photocatalysis, and photovoltaic devices [2–4]. Nanocarbon materials such as carbon nanotubes (CNT) and C₆₀ have beneficial effects on the photocatalytic activity of homogeneous and heterogeneous semiconductors by their effect on electron transfer and interaction effects [5–7].

Among the various semiconductors, titanium dioxide (TiO₂) is a good catalyst for the degradation of environmental contaminants due to its high photocatalytic activity [8,9]. A TiO₂-nanocarbon composite exhibited higher photocatalytic

performance than the bare TiO₂. However, problems still hinder the efficiency of TiO₂-nanocarbon composites, such as the weakening of the light intensity on the surface of the catalysts and the lack of reproducibility in the preparation and sample treatment [10]. In comparison to CNT and C₆₀, graphene has a perfect *sp*²-hybridized two-dimensional carbon structure with better conductivity and larger surface area. It seems reasonable to envision that a graphene-TiO₂ nanocomposite with large interfacial contact area would be more promising for improving the photocatalytic performance of TiO₂ [11,12]. Furthermore, graphene is easy to produce from inexpensive natural graphite through the intermediate graphite oxide product [13]. The presence of oxygen-containing functional groups in graphene oxide and reduced graphene oxide makes them excellent support on which to anchor TiO₂ nanocrystals for the synthesis of graphene-TiO₂ [14].

An important feature of a coupled semiconductor system is that the photoresponse of a large band gap semiconductor can

* Corresponding author. Tel: +82-41-660-1337; Fax: +82-41-688-3352; E-mail: wc_oh@hanseo.ac.kr

DOI: 10.1016/S1872-2067(12)60611-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 8, August 2013

be extended into the visible region by coupling it with a short band gap semiconductor [15,16]. Metal selenides have attracted much attention in the past few years for their special electronic and optical properties and potential applications [17]. In the last few years, narrow band gap semiconductor quantum dots such as CdS, CdSe, PbS, InAs, and InP have been used as photocatalysts [18]. Among these photocatalysts, Ag₂S is an important material for photocatalysis and electronic devices. Ag₂S has a large absorption coefficient and a direct band gap of 0.9 to 1.05 eV, which makes it an effective semiconductor material for photovoltaic applications [19].

1,5-Diphenyl carbazide (DPCI) can be oxidized by oxidizing substances into 1,5-diphenyl carbazone (DPCO), which can be extracted by organic solvents. It displays absorbance in a certain range of wavelength [20]. In this work, we present our studies on the preparation of the Ag₂S-graphene/TiO₂ (denoted Ag₂S-GR/TiO₂) composite using a facile sonochemical method. The catalyst samples were irradiated with visible light and their catalytic activity was compared. The catalytic efficiency of the Ag₂S-GR/TiO₂ composite was evaluated by measuring the photodegradation of rhodamine B (RhB) and DPCI. The reasons for the improved photocatalytic activity of the Ag₂S-GR/TiO₂ composite were also discussed.

2. Experimental

2.1. Preparation of Ag₂S particles

The Ag₂S nanoparticles were prepared by a precipitation process using AgNO₃ and Na₂S·5H₂O (supplied by Duksan Pure Chemical Co., Ltd., Korea) as precursors. First, 1.02 g of AgNO₃ was dissolved in 100 ml of distilled water, and 0.003 mol of Na₂S·5H₂O solution was added dropwise into the above solution with sonication at room temperature for 30 min. Then, the mixture was vigorously stirred for 6 h. For purification, the mixture was centrifuged and rinsed several times with acetone and distilled water. After filtration and drying under vacuum at 80 °C, Ag₂S was obtained as a black powder.

2.2. Preparation of Ag₂S-GR/TiO₂ nanocomposite

The Ag₂S-GR/TiO₂ composite was synthesized by an ultrasonic-assisted hydrothermal method with minor modification using titanium(IV) *n*-butoxide (C₁₆H₃₆O₄Ti, purchased from Kanto Chemical Company, Japan) as titanium source. Graphene oxide was synthesized according to the modified Hummers-Offeman method from purified natural graphite in our previous work [21]. A typical experiment for the synthesis of the Ag₂S-GR/TiO₂ nanocomposite is as follows. First, 20 mg graphene oxide and 22 mg AgNO₃ were dispersed into a solution with the molar ratio of ethanol:H₂O:titanium *n*-butoxide = 35:15:4. The suspension was sonicated at room temperature for 1 h using a controllable Serial-Ultrasonic apparatus (Ultrasonic Processor, VCX 750, Korea). Then, Na₂S·5H₂O solution was added dropwise into the above solution with sonication at room temperature for 30 min. The reaction mixture was allowed to cool to room temperature and the precipitate was

filtered, washed with distilled water five times, and dried in a vacuum oven at 80 °C for 12 h before heat treatment at 500 °C for 3 h. For comparison, other photocatalysts, TiO₂, Ag₂S-graphene (denoted Ag₂S-GR), and Ag₂S-TiO₂, were prepared using similar procedures.

2.3. Characterization of the photocatalysts

The crystallographic structure of the composite photocatalysts was obtained by X-ray diffraction (XRD, Shimadzu XD-D1, Japan) at room temperature with Cu K α radiation (λ = 0.154056 nm) and a graphite monochromator operated at 40 kV and 30 mA. The BET surface area of the photocatalysts was determined by nitrogen adsorption at -196 °C using a BET analyzer (Monosorb, USA). The morphology of the photocatalysts was analyzed by scanning electron microscopy (SEM, JOEL JSM-5200, Japan) at 3.0 keV. Transmission electron microscopy (TEM, JEOL JEM-2010, Japan) with an accelerating voltage of 200 kV was used to examine the size and distribution of the photocatalysts. Energy dispersive X-ray spectroscopy (EDX) was used for the elemental analysis of the samples. Raman spectroscopy was performed to detect possible structural defects in the graphene flakes. The measurements were carried out by a Horiba Jobin Yvon Lab Ram system with a 100 $\times$ objective lens and 532 nm laser excitation. To analyze the light absorption of the photocatalysts, UV-Vis absorption spectra were obtained by a scan UV-Vis spectrophotometer (Scinco Neosys-2000, Korea) equipped with an integrating sphere assembly.

2.4. Measurement of photocatalytic activity

The photocatalytic experiments were performed at ambient temperature to test the activity of the composites (pure TiO₂, Ag₂S-GR, Ag₂S-TiO₂, and Ag₂S-GR/TiO₂) in the degradation of RhB (purchased from Samchun Pure Chemical Co., Ltd., Korea). The visible light source (λ > 420 nm, LED lamp) was used at a distance of 100 mm from the solution in a darkness box. The initial concentration of RhB (c_0) was 2.0×10^{-5} mol/L. The photocatalyst powder (0.03 g) was dispersed in a 100 ml glass photoreactor containing 100 ml of dye solution. The mixture was sonicated for 10 min and stirred for 30 min in the dark in order to ensure adsorption-desorption equilibrium. At set time intervals, a sample of 3.5 ml was taken from the mixture and immediately centrifuged to remove the dispersed photocatalysts. The concentration of the clean transparent solution was analyzed by measuring the absorbance at 554 nm for RhB with the UV-Vis spectrophotometer. The reproducibility was checked by repeating the measurements at least three times, and it was found to be within the acceptable limit ($\pm 5\%$).

2.5. Evaluation of reactive oxygen species

First, six 10.00 ml DPCI stock solutions (0.01 mol/L) were added into three 80 ml volumetric flasks. Then 50 mg of the three photocatalysts, Ag₂S-GR, Ag₂S-TiO₂, and Ag₂S-GR/TiO₂, were added to above DPCI solutions. All of the three solutions

were diluted to 50 ml with double distilled water. For all three solutions, the final DPCI concentration and photocatalyst amount were 0.001 mol/L and 1.00 g/L, respectively. The reactors were put into a visible light apparatus directly under visible light irradiation. After 180 min irradiation, 10.00 ml solution was taken and extracted with benzene. All extracted solutions were diluted to 10.00 ml with benzene solution and their UV-Vis spectra were determined.

3. Results and discussion

3.1. Physicochemical properties

XRD analysis results used to determine the phase purity and average crystalline properties of the photocatalysts are shown in Fig. 1. The TiO_2 in the as-prepared photocatalysts was anatase phase, while the Ag_2S was predominantly the crystalline acanthite phase. In Fig. 1, the main sharp peaks, which were assigned to (111), (112), (121), (103), (031), (200), (213), and (134) crystal planes, originate from the acanthite Ag_2S phase [22]. For these three samples, the (101), (004), (211), and (204) crystal planes originated from the anatase TiO_2 phase. No impurity phase was detected. The broadening of these diffraction peaks indicated that the sample was nm-sized. The crystalline size of the samples was estimated to be 15 nm from the Scherrer equation. The peak appearing at 25.88° corresponded to the (002) diffraction peak of graphite from the graphene, which partially overlapped with the (101) crystal plane of anatase TiO_2 . This was because the intensity of the (002) diffraction peak was relatively weak, indicating that the graphene oxide has been reduced to graphene, which was in agreement with an earlier report [14].

The EDX spectra of Ag_2S -GR, Ag_2S - TiO_2 , and Ag_2S -GR/ TiO_2 composites are shown in Fig. 2. These spectra indicated that TiO_2 and Ag_2S with high purity were successfully synthesized. The C element was from the graphene sheets. The O and Ti elements mainly come from the TiO_2 nanopowder. The strong K_α and K_β peaks from Ti appeared at 4.51 and 4.92 keV, respectively, while a moderate K_α peak of O appeared at 0.52 keV. Figure 2 shows the presence of C, O, and S, which were the ma-

Fig. 2. EDX elemental microanalysis of Ag_2S -GR (1), Ag_2S - TiO_2 (2), and Ag_2S -GR/ TiO_2 (3).

ior elements, along with strong Ag peaks. There were small amounts of impurities, which were attributed to the use of full-ene without purification. In most samples, C, Ag, and S were the major elements with small quantities of O in the composite. The elemental microanalyses of the samples are shown in Fig. 3. According to a previous study [23], a high concentration of dopant in the TiO_2 matrix can be detrimental to the formation of hole/electron recombination centers and an increase in negative charges.

The microscopic surface structure and morphology of the composites were characterized by SEM and TEM. The morphology of graphene oxide was observed to be a flake texture, reflecting its layered microstructure, as shown in Fig. 4(a). The larger interlayer spaces and the thinner layer edges of graphene oxide can be clearly observed. Simultaneously, it is worth noting that the use of the sonochemical method to synthesize the control sample and Ag_2S -GR/ TiO_2 composite gave the prepared nanoscale TiO_2 observed in Fig. 4(d), which showed a favorable morphology and little tendency to agglomerate. Comparing Fig. 4(b) with (c) indicated that very uniform Ag_2S particles and TiO_2 particles were obtained and it can be suggested that the graphene contributed to the high dispersion of TiO_2 and Ag_2S particles on graphene and it made these particles uniform. It is reasonable to suppose that this structure would enable easy charge transfer between the Ag_2S particles

Fig. 1. XRD patterns of Ag_2S -GR (1), Ag_2S - TiO_2 (2), and Ag_2S -GR/ TiO_2 (3).

Fig. 3. Element content of Ag_2S -GR, Ag_2S - TiO_2 , and Ag_2S -GR/ TiO_2 .

Fig. 4. SEM images of graphene (a), Ag₂S-GR (b), Ag₂S-TiO₂ (c), and Ag₂S-GR/TiO₂ (d).

with TiO₂ particles and the graphene sheets.

Typical TEM images of the graphene, Ag₂S-GR, Ag₂S-TiO₂, and Ag₂S-GR/TiO₂ composites are displayed in Fig. 5. The morphology of graphene oxide, consisting of thin stacked flakes and with well-defined few-layer structure at the edge, can be clearly seen in Fig. 5(a). The nm-scale Ag₂S displayed well dispersed nanoparticles with average size of 10 to 15 nm, which can be clearly seen in Fig. 5(b). The nm-scale TiO₂ and Ag₂S displayed well dispersed nanoparticles with average size of 10 to 15 nm, as shown in Fig. 5(c). Fig. 5(d) revealed a homogeneous dispersion of TiO₂ and Ag₂S nanoparticles attached on the almost transparent graphene sheets, which played a support role in helping the TiO₂ and Ag₂S crystals grow. The average size of the well dispersed TiO₂ nanoparticles was 25 to 30 nm. The formation mechanism of the TiO₂ and Ag₂S particles and the exact role of the graphene sheets in this process is still planned in further studies.

The FT-IR spectrum of graphene was rather simple and it suggested extensive oxidation. The spectra of the crystalline material showed well distinguished and sharp bands, while the spectra of amorphous sample were less resolved. The hydration results established the importance of defined conditions for FT-IR (Fig. 6). They also suggested that this type of study can be performed on oxidized graphene. Figure 6 shows the FT-IR spectra of oxidized graphene, Ag₂S-GR, and

Fig. 5. SEM images of graphene (a), Ag₂S-GR (b), Ag₂S-TiO₂ (c), and Ag₂S-GR/TiO₂ (d).

Ag₂S-GR/TiO₂.

In Fig. 6(1), the peak at 995 cm⁻¹ was assigned to the alkane bending vibration, which occurs between 650 and 1000 cm⁻¹. The peak at 806 cm⁻¹ was assigned to aromatic symmetric stretching modes, which occur in the range 690–900 cm⁻¹. Strong C–O bands at 1102 cm⁻¹ and a strong C=C band at 1538 cm⁻¹ were observed. The functional groups, C=O and C–OH, are indicated in the spectrum at 1685 and 1091 cm⁻¹, respectively. Meanwhile, the –OH vibration was also observed at 1407 cm⁻¹.

This confirmed that artificial aging had actually occurred on the surface, and that the types of structural changes inferred from the spectra are consistent with the mechanism proposed in the literature: the formation of O–H bonds from the oxidation of the hydrocarbon triterperenic molecules by the direct binding of O· and O–O radicals, followed by further oxidation to carbonylic functional groups.

In Fig. 6(2), the weak peaks at 1052 and 1180 cm⁻¹ were assigned to the C–OH and C–O bands, respectively. The C–O and C=C functional groups were observed at 1427 and 1594 cm⁻¹, respectively, while C=O was indicated in the spectrum at 1712

Fig. 6. FT-IR spectra of oxidized graphene (1), Ag₂S-GR (2), and Ag₂S-GR/TiO₂ (3).

cm^{-1} . Comparing the spectrum curves (1) and (2), the peak intensity of the functional group on oxidized graphene was weak and decreased. This was because some of the functional groups had bonded with the Ag_2S particles. The Ag_2S particles were bonded to graphene by different functional groups.

In Fig. 6(3), the weak peaks at 1224 and 1367 cm^{-1} were assigned to the C–OH and C–H bands, respectively. C=O functional groups were observed at 1739 cm^{-1} . Comparing the spectrum curves, the peak intensity of the functional group on oxidized graphene was weak and decreased. This is because some of the functional groups had bonded with Ag_2S and TiO_2 particles. The Ag_2S and TiO_2 particles were bonded to graphene by different functional groups [24].

Nitrogen adsorption isotherms for the original graphene, Ag_2S -GR, and Ag_2S -GR/ TiO_2 composites are shown in Fig. 7. The type IV adsorption isotherms confirmed the presence of mesopores in the samples. The characteristic features of the type IV isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake in the range of high p/p_0 . The initial part of the type IV isotherm is attributed to monolayer-multilayer adsorption because it follows the same path as the corresponding part of a type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form. Type IV isotherms are observed with many mesoporous industrial adsorbents [25,26]. This indicates that the Ag_2S -GR and Ag_2S -GR/ TiO_2 composites studied were mainly mesoporous with some wider pores where capillary condensation occurred. All of the isotherms were of a similar type for all samples. The surface area and pore volume of Ag_2S -GR were reduced due to the deposition of TiO_2 compounds and increased with increasing graphene content. The BET surface areas of the samples are shown in Table 1. The value was decreased from 151.95 m^2/g for Ag_2S -GR to 73.47 m^2/g for Ag_2S -GR/ TiO_2 . This was because TiO_2 and Ag_2S nanoparticles were introduced into the pores of the graphene, which decreased the BET surface area. Ag_2S -GR has the largest area, which could affect the adsorption reaction. The BET surface area of $\text{Ag}_2\text{S}/\text{TiO}_2$ was lower than that of Ag_2S -GR/ TiO_2 because graphene enhanced the surface area of the latter.

Fig. 7. Nitrogen adsorption isotherms obtained from oxidized graphene (1), Ag_2S -GR (2), and Ag_2S -GR/ TiO_2 (3).

Table 1

BET surface area of pure TiO_2 and catalysts.

Sample	$A_{\text{BET}}/(\text{m}^2/\text{g})$
Pure TiO_2	11.59
Ag_2S	17.78
Ag_2S -GR	151.95
Ag_2S - TiO_2	48.32
Ag_2S -GR/ TiO_2	73.47

3.2. Photocatalytic activity of the samples

Figure 8 shows RhB degradation versus time using pure TiO_2 , Ag_2S -GR, Ag_2S - TiO_2 , and Ag_2S -GR/ TiO_2 under visible light. The spectra for the RhB solution after visible light irradiation showed the relative degradation yields at different irradiation time. The dye concentration continuously decreased with a gentle slope, which was due to visible light irradiation. The concentration of RhB was $5.0 \times 10^{-5} \text{ mol/L}$, and the absorbance for RhB decreased with increasing visible light irradiation time. Moreover, the RhB solution increasingly lost its color as the RhB concentration continued to decrease. Two steps are involved in the photocatalytic decomposition of dyes: adsorption of dye molecules and their degradation. After adsorption in the dark for 30 min with magnetic stirring, the samples were at adsorption-desorption equilibrium. In the adsorption step, pure TiO_2 , Ag_2S -GR, Ag_2S - TiO_2 , and Ag_2S -GR/ TiO_2 composites showed different adsorption capacity, with Ag_2S -GR having the highest adsorption capacity. The adsorptive capacity of Ag_2S -GR was better than that of Ag_2S -GR/ TiO_2 and Ag_2S - TiO_2 because the added graphene enhanced the BET surface area, which increased the adsorption capacity. Pure graphene has the largest BET surface area, which enhanced the adsorption capacity. In the degradation step, the Ag_2S -GR/ TiO_2 composite showed good degradation activity. The Ag_2S -GR/ TiO_2 composite showed good adsorption and degradation activities. A comparison of the decoloration of the different catalysts showed that the degradation activity was increased by graphene modification.

Fig. 8. Degradation of RhB under visible light irradiation with magnetic stirring over pure TiO_2 , Ag_2S -GR, Ag_2S - TiO_2 , and Ag_2S -GR/ TiO_2 . c is the concentration of RhB solution, and c_0 is the initial concentration.

Fig. 9. UV-Vis spectra of 1,5-diphenyl carbazone extract liquors (1) and of the liquors from the solutions with Ag₂S-GR/TiO₂ composites under visible light irradiation of 60 min (2), 90 min (3), and 120 min (4).

Figure 9 is the UV-Vis spectra of the DPCO extract liquors obtained from the solution with the presence of the Ag₂S-GR/TiO₂ composite under visible light irradiation. DPCI can be oxidized by oxidizing substances into DPCO. Under visible light irradiation, the Ag₂S-GR/TiO₂ sample gets excited into an excited state. That is, some electrons are excited from the valence band (VB) to the conduction band (CB). Electron-hole pairs are formed on the surface or in the bulk of the Ag₂S-GR/TiO₂ sample. The electrons and holes react with the molecular oxygen (O₂) dissolved in the aqueous solution and H₂O molecules adsorbed on the surface of the Ag₂S-GR/TiO₂ particles, producing superoxide radical anions (O₂^{•-}) and hydroxyl radicals (OH[•]), respectively. OH[•] can oxidize DPCI into DPCO. The DPCO can be extracted by the benzene solvent and it has an absorbance at 560 nm wavelength. The production and yield of OH[•] can be easily detected, and the photodegradation activity can be easily detected. Figure 9 shows that under visible light irradiation, the absorption peak of DPCO at 560 nm showed an obvious increase as compared with no radiation [24]. For different irradiation time of the Ag₂S-GR/TiO₂ sample under visible light, the DPCO solution exhibited different absorbance intensity. This indicates that the photodegradation activity of Ag₂S-GR/TiO₂ was good.

The excitation and charge transfer processes among Ag₂S, TiO₂, and graphene nanosheet under visible light irradiation are shown in Fig. 10. The band gap of the Ag₂S/TiO₂ nanocomposite is smaller than that of pure TiO₂. The narrower band gap allows Ag₂S/TiO₂ to absorb more photons, which enhances the photocatalytic efficiency of TiO₂ under visible light irradiation. Due to the overlapping of the CB, VB, and band gap of the two semiconductors, when the Ag₂S/TiO₂ nanocomposite is irradiated under visible light, the photogenerated electrons can be excited from the VB of Ag₂S and then be transferred to the CB of TiO₂. Photogenerated holes are left in the VB of Ag₂S. In addition, the graphene nanosheet acting as a good electron acceptor accepts the electrons from the light irradiation, and the electrons excited in the CB of Ag₂S are also transferred to the surface of graphene [25,26]. Thus the lifetimes of the excited electrons (e⁻) and holes (h⁺) are prolonged in the transfer process, inducing a higher quantum efficiency. The electrons can react

Fig. 10. Excitation and charge transfer processes among TiO₂ particles, Ag₂S particles, and graphene nanosheet.

with O₂ to generate O₂^{•-}, and the holes can migrate to the surface and react with OH⁻ or H₂O to generate OH[•]. These radicals can react with adsorbed pollutants. The reactions can be expressed as follows:

Ag₂S-GR/TiO₂ has the best degradation and adsorption activity of all the composites because of the high photosensitivity of Ag₂S and high adsorption capacity of graphene.

4. Conclusions

The synthesis and characterization of Ag₂S-GR/TiO₂ composite by a facile sonochemical method was presented. The Ag₂S-GR/TiO₂ composite has high surface area and excellent structural, electrical, and optical properties. FT-IR results illuminated that the Ag₂S and TiO₂ bands transfer electrons to graphene, on which they were attached by functional groups. The adsorption and surface properties such as structural and chemical composition of the Ag₂S-GR/TiO₂ composite were investigated. The surface area and adsorption capacity of the samples were reduced due to the deposition of Ag₂S and TiO₂. The amounts of generated hydroxyl radicals can be analyzed by 1,5-diphenyl carbazide degradation. The results demonstrated that the photocatalytic oxidation of RhB causing its concentration in the aqueous solution to decrease can be attributed to electron-assisted photocatalytic decomposition by Ag₂S and graphene. The Ag₂S-GR/TiO₂ composite catalyst prepared by the sonochemical method demonstrated higher photocatalytic activity than pure Ag₂S or TiO₂.

Acknowledgements

This work was supported by Research Foundation from Hanseo University in 2012. The authors are grateful to the staff at the University for the financial support.

References

- [1] Zhu Y W, Murali S, Cai W W, Li X S, Suk J W, Potts J R, Ruoff R S. *Adv Mater*, 2010, 22: 3906

Graphical Abstract

Chin. J. Catal., 2013, 34: 1527–1533 doi: 10.1016/S1872-2067(12)60611-1

Enhanced visible light photocatalytic activity of Ag₂S-graphene/TiO₂ nanocomposites made by sonochemical synthesis

Ze-Da Meng, Lei Zhu, Kefayat Ullah, Shu Ye, Qian Sun, Won-Chun Oh*
Hanseo University, Korea

This paper presents the research of synthesized Ag₂S-graphene/TiO₂ by the sonochemical method. The generation of reactive oxygen species was detected through the oxidation reaction from 1,5-diphenyl carbazide to 1,5-diphenyl carbazole.

- [2] Wang X R, Li X L, Zhang L, Yoon Y, Weber P K, Wang H L, Guo J, Dai H J. *Science*, 2009, 324: 768
- [3] Xia J L, Chen F, Li J H, Tao N J. *Nat Nanotechnol*, 2009, 4: 505
- [4] Chen F, Qing Q, Xia J L, Li J H, Tao N J. *J Am Chem Soc*, 2009, 131: 9908
- [5] Meng Z D, Zhu L, Choi J G, Chen M L, Oh W C. *J Mater Chem*, 2011, 21: 7596
- [6] Wang S, Shi X L, Shao G Q, Duan X L, Yang H, Wang T G. *J Phys Chem Solids*, 2008, 69: 2396
- [7] Oh W C, Jung A R, Ko W B. *Mater Sci Eng C*, 2009, 29: 1338
- [8] Silva C G, Wang W D, Faria J L. *J Photochem Photobiol A*, 2006, 181: 314
- [9] Shah V, Verma P, Stopka P, Gabriel J, Baldrian P, Nerud F. *Appl Catal B*, 2003, 46: 287
- [10] Meng Z D, Zhang K, Oh W C. *Korean J Mater Res*, 2010, 20: 228
- [11] Zhang Y H, Tang Z R, Fu X Z, Xu Y J. *ACS Nano*, 2010, 4: 7303
- [12] Liang Y Y, Wang H L, Casalongue H S, Chen Z, Dai H J. *Nano Res*, 2010, 3: 701
- [13] Hummers W S Jr, Offeman R E. *J Am Chem Soc*, 1958, 80: 1339
- [14] Akhavan O, Abdollah M, Esfandiar A, Mohatashamifar M. *J Phys Chem C*, 2010, 114: 12955
- [15] Vogel R, Hoyer P, Weller H. *J Phys Chem*, 1994, 98: 3183
- [16] Lee H, Leventis H C, Moon S J, Chen P, Ito S, Haque S A, Torres T, Nuesch F, Geiger T, Zakeeruddin S M, Grätzel M, Nazeeruddin M K. *Adv Funct Mater*, 2009, 19: 2735
- [17] Xie Y, Heo S H, Kim Y N, Yoo S H, Cho S O. *Nanotechnology*, 2010, 21: 015703
- [18] Neves M C, Nogueira J M F, Trindade T, Mendonca M H, Pereira M I, Monteiro O C. *J Photochem Photobiol A*, 2009, 204: 168
- [19] Kryukov A I, Stroyuk A L, Zińchuk N N, Korzhak A V, Kuchmii S Y. *J Mol Catal A*, 2004, 221: 209
- [20] Wang J, Guo Y W, Liu B, Jin X D, Liu L J, Xu R, Kong Y M, Wang B X. *Ultrason Sonochem*, 2011, 18: 177
- [21] Oh W C, Chen M L, Zhang K, Zhang F J, Jang W K, Zhang F J. *J Korean Phys Soc*, 2010, 56: 1097
- [22] Reid M, Punch J, Ryan C, Franey J, Derkits G E Jr, Reents W D Jr, Garfias L F. *IEEE Trans Components Packaging Technol*, 2007, 30: 666
- [23] Zhu L, Meng Z D, Oh W C. *Chin J Catal* (催化学报), 2011, 32: 926
- [24] Meng Z D, Ghosh T, Zhu L, Choi J G, Park C Y, Oh W C. *J Mater Chem*, 2012, 22: 16127
- [25] Meng Z D, Peng M M, Zhu L, Oh W C, Zhang F J. *Appl Catal B*, 2012, 113-114: 141
- [26] Sing K S W. *Pure Appl Chem*, 1982, 54: 2201
- [27] Kitova S, Eneva J, Panov A, Haefke H. *J Imaging Sci Technol*, 1994, 38: 484
- [28] Tubtintae A, Wu K L, Tung H Y, Lee M W, Wang G J. *Electrochem Commun*, 2010, 12: 1158