Hydrothermal Synthesis of Porous Ag₂S Sensitized TiO₂ Catalysts and Their Photocatalytic Activities in the Visible Light Range

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Abstract: Porous Ag₂S sensitized TiO₂ catalysts were synthesized by the hydrothermal process. The crystallization and porous structure of the Ag₂S/TiO₂ composite photocatalysts were investigated by X-ray diffraction, scanning electron microscopy with energy dispersive X-ray analysis, UV-Vis diffuse reflectance spectroscopy, and N₂ adsorption. The Ag₂S/TiO₂ composites were mainly composed of anatase TiO₂ and acanthite Ag₂S. The absorption edge wavelengths of TiO₂ and the Ag₂S/TiO₂ composite prepared with 3 mmol Na₂S·5H₂O were 400 and 800 nm, respectively, that is, the absorption edge of the composite had a pronounced red shift. The photocatalytic activity under visible light was investigated by the degradation of methylene blue with a UV-Vis spectrophotometer. The photocatalytic activities under visible light of the Ag₂S/TiO₂ photocatalysts were much higher than that of TiO₂.

Key words: silver sulfide; titanium dioxide; visible light; photocatalytic activity; methylene blue

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The treatment of industrial wastewaters to remove organic pollutants is a very important aspect of environmental technology. Heterogeneous photocatalysis as an advanced oxidation technique has been developed for it [1,2]. Nanocrystalline semiconductors are used as photocatalysts to initiate interfacial redox reactions because of their unique physicochemical properties resulting from their nanosized dimensions and large surface/volume ratios. The most common semiconductors for waste degradation are TiO₂, ZnO, and CdS [3].

Titanium dioxide (TiO₂) has the advantages of high activity, good stability, and low cost, and it is fairly harmless to humans. However, the main drawback of TiO₂ is its relatively large band gap (anatase: 3.2 eV, rutile: 3.0 eV). As a consequence, TiO₂ shows photocatalytic activity only in the near-ultraviolet region and can harvest only a small fraction (< 5%) of incident solar radiation [4]. Therefore, modifying TiO₂ photocatalysts to enhance light absorption and photocatalytic activity under visible light has been a main research direction in recent years.

The development of a visible light-responsive photocatalyst based on TiO₂ coupled with a visible light sensitizer is an important goal. Metals [5], non-metallic elements [6], and adsorbed dyes [7] have been used as sensitizers. However, these have shortcomings. For instance, transition metals easily become the recombination centers of photoelectron-hole pairs, and the photosensitizers easily fall off. In

contrast, compound formation with a semiconductor [8] is considered an effective method. With nanoscale coupled semiconductors, it can be expected that the TiO₂ photocatalytic activity will be significantly improved by the enhancement of charge separation and minimization or inhibition of charge-carrier recombination [9,10]. Ag₂S is useful for this because it is a direct, narrow band gap semiconductor [11] with good chemical stability and excellent optical limiting properties, and its optical responses to nanosecond laser pulses at 532 nm are much stronger than those of C₆₀ fullerene and chloro-aluminum phthalocyanine [12]. It has been used in optical and electronic devices such as photovoltaic cells, photoconductors, and infrared (IR) detectors [13,14], and as a superionic conductor [15,16]. It is also used as a photosensitizer for photographic purposes [17]. However, there has been no report on the utilization of a porous Ag₂S/TiO₂ composite photocatalyst system for environmental purification under visible light irradiation.

In this work, visible light-driven Ag₂S/TiO₂ composite photocatalysts for degradation of organic dyes were obtained by a conventional hydrothermal preparation method. The Ag₂S/TiO₂ composites exhibited new characteristics and properties that were different from those of bulk Ag₂S and TiO₂. The enhanced photocatalytic activity of the nanocomposites was assessed by the degradation of methylene blue (MB) in aqueous solutions under visible light irradiation and compared with that of pure anatase TiO₂.

1 Experimental

1.1 Preparation of the photocatalysts

1.1.1 Preparation of Ag₂S nanoparticles

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

1.1.2 Preparation of porous Ag₂S/TiO₂ nanocomposite

Porous Ag₂S sensitized TiO₂ nanocomposites were prepared with different molar concentrations of Na₂S·5H₂O (2, 3, and 4 mmol) by a hydrothermal reaction. The schematic diagram of the synthesis process comprising two parts is shown in Fig. 1. Into 25 ml distilled water containing 0.5 g of titanium oxide, a measured amount of silver nitrate powder was added and ultrasonicated (using a 750 W, Ultrasonic Processor VCX 750, Korea) for 20 min. The Na₂S solution was prepared separately and added dropwise to the solution, which was then stirred for at least 8 h at 80 °C. The above solution was transferred into a Teflon-lined stainless steel autoclave that was then sealed. The contents were then heated at 140 °C for 10 h. After the temperature of the mixture was brought down to room temperature, the mixture was filtered using Whatman filter paper and washed with distilled water and ethanol five times. Finally, it was dried under vacuum at 100 °C. By using different molar concentrations of Na₂S·5H₂O, three composite photocatalysts were obtained, and they were denoted a-Ag₂S/TiO₂, b-Ag₂S/TiO₂, and c-Ag₂S/TiO₂.

The titanium oxide nanopowder (TiO₂, < 25 nm, 99.7%) with the anatase structure that was used as a control sample was purchased from Sigma-Aldrich Chemicals, USA.

1.2 Characterization of the photocatalysts

The morphology of the photocatalysts were analyzed by a scanning electron microscope (SEM, JSM-5200 JOEL, Japan) at 3.0 keV equipped with an energy dispersive analysis system of X-ray analysis (EDX). Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) with an accelerating voltage of 200 kV was used to examine the size distribution of the photocatalysts. The crystallographic structures of the composite photocatalysts were characterized by X-ray diffraction (XRD, Shimadzu XD-D1, Japan) at room temperature with Cu K_α radiation ($\lambda = 0.154056$ nm) and a graphite monochromator, which was operated at 40 kV and 30 mA. To analyze light absorption by the photocatalysts, UV-Vis diffuse reflectance spectra (DRS) were obtained using a scan UV-Vis spectrophotometer (Neosys-2000) equipped with an integrating sphere assembly. BaSO₄ was used with wavelengths in the 300–800 nm range. The BET surface area of the photocatalysts was determined by nitrogen adsorption at −196 °C using a BET analyzer (Monosorb, USA). All the samples were degassed at 350 °C before the measurement. The UV-Vis spectra for the MB solution degraded by TiO₂ and the Ag₂S/TiO₂ composite photocatalysts under UV-Vis light irradiation were recorded using a UV-Vis (Optizen Pop Mecasys Co., Ltd., Korea) spectrometer.

1.3 Photocatalytic activities

In the photocatalytic test performed at room temperature, 0.03 g Ag₂S/TiO₂ composite was added into 50 ml of 2.0×10^{-5} mol/L MB (analytical grade, Samchun Pure Chemical Co., Ltd., Korea) solution that was first kept in the dark for 2 h to ensure the adsorption/desorption equilibrium of the organic dye. Commercial anatase TiO₂ was adopted as the reference with which to compare the photocatalytic activity. For irradiation, a visible light lamp (8 W, $\lambda > 420$ nm, KLD-08L LED lamp) was used at the distance of 100 mm from the solution in a darkness box. The first MB sample was taken at the end of the dark adsorption period (just before the light was turned on) and was treated as the starting point ($t = 0$) of the reaction where the concentration of the MB solution was c_0 . The suspension was irradiated with

Fig. 1. Schematic of the synthesis of the porous Ag₂S/TiO₂ composites.

visible light under magnetic stirring. Samples were then withdrawn regularly from the reactor at 30, 60, 90, 120, and 150 min. These were immediately centrifuged to remove any suspended solid before analysis. The concentration of MB solution (c) during the photocatalytic degradation reaction was monitored by measuring the absorbance of the solution samples with the UV-Vis spectrophotometer (Optizen POP) at $\lambda_{\max} = 665$ nm [18] using a calibration curve. No reaction byproducts absorb at this wavelength.

2 Results and discussion

2.1 Characterization results

The typical microscopic surface structure and morphology of the Ag_2S nanoparticles and $\text{Ag}_2\text{S}/\text{TiO}_2$ composites were investigated by SEM and TEM. Fig. 2(a) is a typical SEM image from the microscopic rod-shaped Ag_2S nanoparticles. These were large scale uniform micro-rods with an average diameter of 1.5 μm . A high magnification SEM image is shown in Fig. 2(b), which showed that the porous Ag_2S nanoparticles had a smooth surface and did not tend to agglomerate. This was attributed to that only crystal particles whose size is very small can easily agglomerate due to the weak attractive forces of the surface. Figure 2(c) and (d) show typical SEM images from a porous Ag_2S sensitized TiO_2 composite. The average size of the particles is in the nanoscale range. The particles were compact, uniform, and had no cracks and no abnormality, which can be attributed to the growth and densification of porous Ag_2S particles on TiO_2 in the composite.

For a more detailed and higher magnification, the surface nanostructure and particle sizes of the $\text{Ag}_2\text{S}/\text{TiO}_2$ compos-

ites were examined by TEM. As shown in Fig. 3, the TEM images revealed that unlike TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$ displayed well dispersed nanoparticles with an average size of 15–20 nm and particle agglomeration was effectively inhibited by the introduction of the porous Ag_2S nanoparticles. A few black dots can be observed in these images that corresponded to deposited Ag_2S nanoparticles. The presence of a distinct junction between the two crystal phases further confirmed the strong interaction between Ag_2S and TiO_2 in $\text{Ag}_2\text{S}/\text{TiO}_2$.

Fig. 3. TEM micrographs of the $\text{Ag}_2\text{S}/\text{TiO}_2$ composite.

The surface area is a very important parameter for the efficiency of a photocatalyst. This was evaluated for TiO_2 and $\text{b-Ag}_2\text{S}/\text{TiO}_2$. The BET surface area, total pore volumes, and average pore diameters are listed in Table 1. Compared with pure TiO_2 , the surface areas, pore volume, and the average pore diameter of the $\text{Ag}_2\text{S}/\text{TiO}_2$ photocatalysts were increased. The reason was that the plentiful micropores of Ag_2S were distributed on the outer surface of the TiO_2 . No inside pores of TiO_2 were filled and only parts of the outside pores of TiO_2 were covered. In addition, the small clusters of Ag_2S particles on the external surface of TiO_2 had formed

Fig. 2. SEM images of different samples. (a, b) Ag_2S ; (c, d) $\text{Ag}_2\text{S}/\text{TiO}_2$.

Table 1 Microstructure of TiO₂ and b-Ag₂S/TiO₂ composite

Sample	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
TiO ₂	24.78	0.0132	2.1289
b-Ag ₂ S/TiO ₂	112.74	0.2096	7.4367

some mesopores and macropores. Therefore, Ag₂S loaded on the TiO₂ did not change the microstructure of the original TiO₂, and on the contrary its surface area and pore volume were increased. The pore size distribution curves calculated from the nitrogen adsorption isotherms by the Barret-Joyner-Halenda (BJH) method and the corresponding isotherm of the Ag₂S/TiO₂ sample is shown in Fig. 4. The Ag₂S/TiO₂ composites gave Type I isotherms characterized by a plateau that was nearly horizontal to the p/p_0 axis in the middle region, with increasing adsorbed volume in the low relative pressure region. The data showed that by using Ag₂S as a modifier material, the pore size distribution of the Ag₂S/TiO₂ composites was improved.

Fig. 4. N₂ adsorption isotherm and BJH pore size distribution for the Ag₂S/TiO₂ composite.

The crystal phase structures of the Ag₂S, anatase TiO₂, and Ag₂S/TiO₂ composite photocatalysts were characterized by XRD measurements (Fig. 5). The TiO₂ in the photocatalysts was the anatase phase, while the Ag₂S was predominantly the crystalline phases of acanthite. For these three samples, the (101), (004), (200), (105), (211), and (204) crystal planes were from the anatase TiO₂ phase while the (111), (112), (121), (103), (031), (200), (213), and (134) crystal planes were from the acanthite Ag₂S phase [19]. The cell constants were calculated to be $a = 0.42261$ nm, $b = 0.69238$ nm, and $c = 0.78547$ nm (JCPDS 14-0072). No impurity phase was detected. The broadening of these diffraction peaks indicated that the sample was nanosized. The crystalline size of the sample was estimated to be 15 nm from the Scherrer equation.

Fig. 5. XRD patterns of different samples. (1) a-Ag₂S/TiO₂; (2) b-Ag₂S/TiO₂; (3) c-Ag₂S/TiO₂; (4) Ag₂S; (5) TiO₂.

These nanocomposite particles were further characterized by EDX, which showed the expected peaks for Ag and S, as well as the peak of Ti due to TiO₂. Impurity elements such as Na and C also existed, which might be from the experimental process. The contents of the main elements were much more than those of the impurity elements. This indicated that a b-Ag₂S/TiO₂ composite with high purity has been successfully synthesized in this study. The elemental compositions of Ti, O, Ag, S, and impurity in the b-Ag₂S/TiO₂ composite photocatalysts are 50.89%, 35.42%, 8.85%, 4.43%, and 0.41%, respectively.

UV-Vis reflectance analysis was carried out on the various systems of interest. The measurements were converted to absorbance spectra using the Kubelka-Munk method. Figure 6 shows the UV-Vis diffused reflectance spectra of TiO₂ and b-Ag₂S/TiO₂. As expected, the spectrum from TiO₂ showed that TiO₂ absorbs mainly ultraviolet light with wavelengths below 400 nm. After the introduction of Ag₂S, the absorption edge was shifted towards the visible region. The b-Ag₂S/TiO₂ sample exhibited its fundamental absorp-

Fig. 6. UV-Vis absorbance spectra of pure TiO₂ and Ag₂S/TiO₂ composite.

tion edge at 800 nm. The diffuse reflectance spectra of b-Ag₂S/TiO₂ were transformed by performing the Kubelka-Munk transformation of the measured reflectance by

$$K = (1-R)^2/2R = F(R)$$

where K is the transformed reflectance, R is the reflectance (%), and $F(R)$ is the Kubelka-Munk function [20].

The band gap E_g and absorption coefficient α are related as

$$ah\nu = A(h\nu - E_g)^{1/2}$$

where α , ν , E_g , and A are the absorption coefficient, light frequency, band gap, and a constant, respectively. If the compound scatters in a perfectly diffuse manner, K becomes equal to 2α . In this case, we can use the following expression:

$$[F(R)h\nu]^2 = A(h\nu - E_g)$$

The estimated E_g value was 1.95 eV for the b-Ag₂S/TiO₂ sample. This value was red shifted from the typical E_g of TiO₂ (3.2 eV). This result suggested the possibility of using this material as a photocatalyst for degradation processes with lower energetic requirements than TiO₂.

2.2 Adsorption and photo-decolorization process

Since a photo-oxidation reaction takes place at the catalyst surface, the adsorption characteristics of the system are important for the photocatalytic process. The adsorption of MB on the nanocomposite surface was tested using suspensions of MB and Ag₂S/TiO₂ under dark conditions. The dye adsorbs onto the Ag₂S/TiO₂ composite and after the first two hours, a clear decrease in the MB solution concentration can be seen (Fig. 7(a) for time zero). After this period, adsorption-desorption equilibrium was achieved and no more decrease in the MB concentration occurred. The ability of the semiconductor phases (Ag₂S and TiO₂) to adsorb MB was also tested using Ag₂S and TiO₂ particles. The MB adsorbed percentage was higher for the materials containing Ag₂S than pure TiO₂. The adsorbed percentage of MB in the presence of b-Ag₂S/TiO₂ was the highest of the samples. These results are in agreement with other works, and suggest that MB photodecomposition occur with the dye adsorbed on the catalyst surface [21].

The photocatalytic efficiency of the Ag₂S/TiO₂ materials on the decolorization of MB solution was tested over 150 min (Fig. 7(a)). The intensity of the absorption peaks corresponding to MB gradually diminished with increasing irradiation time. Figure 7(a) also shows the change in the concentration of MB with different irradiation time in the presence of different photocatalysts. The pure TiO₂ had almost no photocatalytic activity towards the photodegradation of MB solution. The MB solution also degraded only a little on the introducing of Ag₂S particles. However, the MB mole-

Fig. 7. Photocatalytic degradation behavior of MB over TiO₂ and Ag₂S/TiO₂ nanocomposites under visible light. (a) Comparison of the photocatalytic degradation behaviors of MB over different samples; (b) UV-Vis adsorption spectra of MB concentration of the b-Ag₂S/TiO₂ nanocomposites. Reaction conditions: catalyst 30 mg, MB solution 2.0×10^{-5} mol/L, lamp 8 W ($\lambda > 420$ nm).

cules were well degraded in the presence of the Ag₂S/TiO₂ composites. The degradation efficiency of MB under visible light followed the order: b-Ag₂S/TiO₂ > a-Ag₂S/TiO₂ > c-Ag₂S/TiO₂ > Ag₂S > TiO₂. Clearly, the addition of Ag₂S in the b-Ag₂S/TiO₂ nanocomposite should be of an appropriate amount. The photocatalytic activity of b-Ag₂S/TiO₂ was the best, which was attributed to that the introduction of larger amounts of Ag₂S onto the TiO₂ surface resulted in most of the surface being covered, thus the performance for MB decolorization was not as good (Fig. 7 (b)).

The enhanced activity was attributed to the improved optical absorption and the heterostructure, which favored the separation of photo-induced electron-hole pairs in the photosensitized titanium dioxide photocatalysts [22–26]. The scheme of the excitation and charge transfer process between Ag₂S and TiO₂ under visible light irradiation is shown in Fig. 8. Under the irradiation by a visible lamp, electrons in Ag₂S and holes in TiO₂ are generated and migrated to the conduction band (CB) of TiO₂ and valence band (VB) of

Fig. 8. Scheme of excitation and charge transfer process between Ag₂S and TiO₂ particles.

Ag₂S, respectively (corresponding to Eq. (1) and (2)). This transfer process is more thermodynamically favorable because both the CB and VB of Ag₂S lie above that of TiO₂. Meanwhile, generated electrons react with dissolved oxygen molecules and produce oxygen peroxide radicals O₂^{•-} (Eq. (3) and (4)). The positively charged holes (h⁺) react with the OH⁻ derived from H₂O to form hydroxyl radicals OH[•] (Eq. (5) and (6)). O₂^{•-} and OH[•] are powerful oxidizing agents capable of degrading most pollutants [27,28]. MB molecules can be photodegraded by the oxygen peroxide radicals O₂^{•-} and hydroxyl radicals OH[•] to CO₂, H₂O, or other mineralization (Eq. (7)).

2.3 Recyclability of the photocatalyst

For investigating the long term stability of the Ag₂S/TiO₂ nanocomposites under visible light irradiation, recycling experiments were carried out using the b-Ag₂S/TiO₂ nanocomposite. For each new cycle, the sample was collected and vacuum dried at 100 °C for 5 h keeping the other reaction conditions constant. As shown in Fig. 9, after five cycles the decolorization rate decreased only 8%, from 60% to 52%. The slight decrease indicated that the photocatalytic activity of the Ag₂S/TiO₂ nanocomposites was reproducible. The reduction in the degradation efficiency during the cycles can be explained by the formation of byproducts and their accumulation in the cavities and on the active surface sites of the photocatalysts. The result was probably due to the decrease of the surface area for both photon absorption and MB adsorption.

Fig. 9. Effect of reuse of the b-Ag₂S/TiO₂ nanocomposite on the degradation efficiency of MB in aqueous solution.

3 Conclusions

A hydrothermal method with the precipitation reaction of AgNO₃ and Na₂S·5H₂O was used to prepare Ag₂S sensitized TiO₂ composite photocatalysts. The composites were composed of an anatase phase and an acanthite Ag₂S phase. The absorption edge of Ag₂S/TiO₂ in the UV-Vis absorbance spectra had a pronounced red shift. The Ag₂S/TiO₂ nanocomposites had a high surface area, excellent structure, and good optical properties. The visible light photodegradation rates of MB with the Ag₂S/TiO₂ composites were markedly higher than that of TiO₂, which was due to the excellent effects of the Ag₂S semiconductor.

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