Hydrothermal Synthesis and Visible Light Photocatalytic Behaviour of Ag2S and Ag2S-TiO2 Nanoparticles

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A simple route to syntheisze nanocrystalline Ag2S-modified TiO2 photocatalyst by a hydrothermal method was developed. The visible light photocatalytic activity of the obtained samples for the degradation of methyl orange was studied. The products were characterized by XRD, EDX SEM, TEM, BET and UV-VIS absorption spectroscopy. The materials characterization showed that the presence of Ag2S onto TiO2 surface results in a blue shift of the material band edge when compared with the initial semiconductor. The introduction of Ag2S can lead to a shift in the absorption band of the Ag2S/TiO2 composite into the visible light region due to the excellent photoelectric characteristics of Ag2S. The material with the best catalytic activity towards the photodecolorization of methyl orange was the 30 mg of TiO2 modified with Ag2S nanoparticles.

Key Words: Sliver sulphide, Titanium dioxide, Visible light photocatalytic properties, Methyl orange.

INTRODUCTION

Dyes are a kind of organic compounds with a complex aromatic molecular structure that can bring bright and firm colour to other substances. However, the complex aromatic molecular structures of dyes make them more stable and more difficult to biodegrade. The extensive use of dyes often poses pollution problems in the form of coloured wastewater discharged into environmental water bodies[1,2]. Advanced oxidation technologies (AOTs) are alternative methods to conventional methods for effective and complete oxidation of various organic pollutants into carbon dioxide and water. The use of nanocrystalline semiconductors as photocatalysts, to initiate interfacial redox reactions, have generated great interest, due to their unique physicochemical properties, caused by their nanosized dimensions and large surface/volume ratios. The most commonly referenced semiconductors for waste degradation are TiO2, ZnO, CdS, *etc.*[3]. Titanium dioxide is a promising material for photoelectrochemical solar energy conversion and photocatalytic hazardous waste treatment because of its superior photoreactivity, nontoxicity, long-term stability and low price[4]. However, the main drawback of TiO2 is its relatively large bandgap (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 irradiation[5]. Therefore, modifying TiO2 photocatalysts to enhance light absorption and photocatalytic activity under

visible light irradiation becomes the main research direction in recent years.

Recently, there are many reports about the modification of TiO2 by non-metal such as nitrogen. Since Sato[6] reported that the calcination of NH4Cl or NH4OH with titanium hydroxide caused the photocatalytic sensitization of TiO2 into the visible light region. Xu *et al.*[7] prepared N-TiO2 photocatalysts with visible light response *via* a low-temperature precipitation treatment of TiCl4 by ammonia with the presence of glacial acetic acid. In this synthesis route, TiCl4 was used as the inorganic Ti precursor and there was not much organic solvent. The doping of nitrogen has reduced the energy band gap efficiently. Xu *et al.*[8] prepared a series of rare earth metal ions doped TiO2 by sol-gel method. The results showed that rare earth ions doping enhanced the photocatalytic activity of TiO2. However, there are still some shortcomings, for instance, the transition metals are easy to become the recombination centers of the photo-electron-hole pairs, the photosensitizers are easy to fall off. In contrast, the compounding semiconductors[9] are considered to be an effective method. For the 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[10,11]. Li *et al.*[12] reported TiO2 nanotube-supported CdS and ZnS hetero structure synthesized *via* a simple wet chemical process and investigated the photocatalytic performance for decomposition of methyl

oange. Kim *et al.*[13] synthesized a new composite material consisting of CdS nanoparticles and TiO$_2$ nanotube and employed a bi-functional organic molecule to bind CdS strongly to TiO$_2$ surface.

However, there were few reports on the Ag$_2$S modifying of TiO$_2$ *via* hydrothermal method by precipitation and use the silver nitrate, sodium sulphide-5-hydrate and titanium(IV) *n*-butoxide as the precursor of silver sulphide and titanium due to nanocrystalline Ag$_2$S is a good candidate for the modifing of TiO$_2$ catalysts. Indeed, Ag$_2$S has a direct band gap of 0.9-1.05 eV, its conduction band (-0.3 eV) is less anodic than the corresponding TiO$_2$ band (-0.1 eV) and the valence band (+0.7 eV) is more cathodic than the TiO$_2$ valence band (+3.1 eV)[14,15].

Herein we report a simply and effective route to synthesize Ag$_2$S/TiO$_2$ photocatalyst with Ag$_2$S on the surface of TiO$_2$ by simple ion change and followed by sulfurization process at a moderate temperature for Ag$_2$S incorporation. The prepared Ag$_2$S/TiO$_2$ composites were characterized by BET, XRD, EDX, TEM and UV-VIS DRS. The photocatalytic degradiation of methyl orange solution photodegradation under visible light radiation over nanosized Ag$_2$S/TiO$_2$ photocatalyst was investigated and discussed.

EXPERIMENTAL

Silver nitrate (AgNO$_3$) and sodium sulphide-5-hydrate (Na$_2$S·5H$_2$O) were supplied by Duksan Pure Chemical Co., Ltd, Korea. The titanium(IV) *n*-butoxide (TNB, C$_{16}$H$_{36}$O$_4$Ti) as a titanium source was purchased from Kanto Chemical Company (TOKYO, Japan). Benzene (99.5 %) and ethyl alcohol were purchased as reagent-grade from Duksan Pure Chemical Co. (Korea) and Daejung Chemical Co. (Korea) and used as received. Methyl orange (C$_{14}$H$_{14}$N$_3$NaO$_3$S) was used as analytical grade which purchased from Samchun Pure Chemical Co., Ltd, Korea. Titanium oxide nanopowder (TiO$_2$, < 25 nm, 99.7 %) with anatase structure used as control sample was purchased from Sigma-Aldrich Chemistry, USA. All the used reagents are of analytical grade without further purification and the deionized water is employed to prepare the solutions in our experiments.
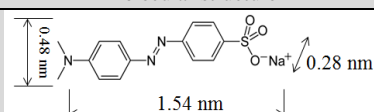
Ag$_2$S/TiO$_2$ photocatalyst preparation: In this work, Ag$_2$S/TiO$_2$ microemulsion colloids were formed during microemulsion process. 4 mL of titanium *n*-butoxide was dissoloved in a sol containing of 50 mL benzene and 5 mL ethyl alcohol, homogenized at 343 K for 0.5 h using a shaking water bath (Lab house, Korea) at a shaking rate of 120 rpm. And amount of AgNO$_3$ and 2.59 mmol Na$_2$S·5H$_2$O were added during vigorously stirring. In the process, the TiO$_2$ was amorphous and it was generated *via* gradual hydrolysis and condensation of titanium *n*-butoxide, while the Ag$_2$S was formed *via* coprecipitation of AgNO$_3$ and Na$_2$S·5H$_2$O in the water nano droplets. In order to obtain photo-active anatase TiO$_2$, the colloids was dried at 393 K and after heating at 773 K for 1 h, the Ag$_2$S/TiO$_2$ photocatalyst was obtained.

Catalysts characterization: Crystallographic structure of the composites photocatalysts were obtained by XRD (Shimatz XD-D1, Japan) at room temperature with CuK$_\alpha$ radiation (λ = 0.154056 nm) and a graphite monochromator, operated at 40 KV and 30 mA. Transmission electron micro-

scopy (TEM, JEOL, JEM-2010, Japan) with an accelerating voltage of 200 kV was used to examine the size and distribution of the photocatalysts. The EDX spectra were also used for elemental analysis of the samples. The BET surface area of the photocatalysts was determined through nitrogen adsorption at 77 K using a BET analyzer (Monosorb, USA). All the samples were degassed at 623 K before the measurement. To analyze the light absorption of the photcatalysts, UV-VIS diffuse reflectance spectra (DRS) were obtained using a scan UV-VIS spectrophotometer (Neosys-2000) equipped with an integrating sphere assembly, while BaSO$_4$ was used with wavelength in the 300-800 nm range. The UV-VIS adsorption parameters for dye solution degraded by anatase TiO$_2$, Ag$_2$S/TiO$_2$ composites photocatalysts under visible light irradiation were recorded using a UV-VIS (Optizen Pop Mecasys Co. Ltd., Korea) spectrometer.

Photocatalytic activity test: The photocatalytic activities of samples were evaluated in terms of the degradation of methyl orange (C$_{14}$H$_{14}$N$_3$NaO$_3$S) decomposition in aqueous solution under visible light illumination. The molecular structure and λ_{max} of organic dyes are shown in Table-1. The photodegradation reactions were carried out with a homemade photoreactor. For visible light irradiation, the reaction beaker was located axially and held in a visible lamp (8W, halogen lamp, KLD-08L/P/N, Fawoo Technology, Korea) box. The luminous efficacy of the lamp is 80lm/W and the wavelength is 400 nm to approximately 790 nm. The distance between the light and the reaction tube was fixed at 100 mm. The initial concentration of methyl orange (c$_0$) was 1.0×10^{-5} mol/L. The photocatalyst powder (0.05 g) was dispersed in a 100 mL glass photoreactor containing 50 mL of dye solution. The mixture was sonicated for 10 min and stirred for 0.5 h in the dark in order to reach the adsorption-desorption equilibrium. At the given time intervals the 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 checking the absorbance at 467 nm for methyl orange with the UV-VIS spectrophotometer.

TABLE-1
MOLECULAR STRUCTURE AND ABSORBANCE
MAXIMUM (λ_{max}) OF ORGANIC DYES

Organic dyes	Molecular structure	λ_{max}
Methylene orange (MO)		465 nm

RESULTS AND DISCUSSION

Physicochemical characterization of the Ag$_2$S/TiO$_2$ nanocomposites: The crystal phase structures of as-prepared Ag$_2$S, anatase TiO$_2$, Ag$_2$S/TiO$_2$ composites photocatalysts were characterized by X-ray diffraction measurements (Fig. 1). It can be confirmed that the TiO$_2$ in three as-prepared photocatalysts is anatase-phase, while the Ag$_2$S is as the predominant crystalline phases of acanthite. For these three samples, (101), (004), (200), (105), (211) and (204) crystal planes are originated from the anatase TiO$_2$ phase while (111), (112), (121),
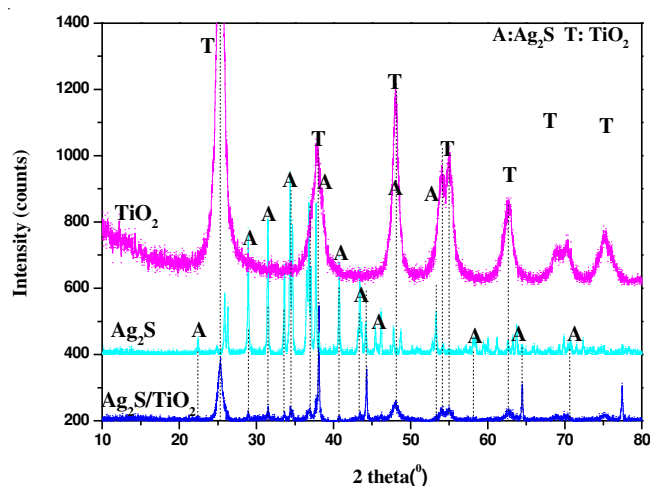
Fig. 1. XRD analysis of acanthite Ag₂S and Ag₂S/TiO₂ composite

(103), (031), (200), (213) and (134) crystal planes are originated from the acanthite Ag$_2$S phase[16]. After refinement, the cell constants are calculated to a = 4.2261 Å, b = 6.9238 Å, c = 7.8547 Å (JCPDS card No. 14-0072). No impurity phase is detected. The broadening of these diffraction peaks indicates that the sample is nanosized. The crystalline size of the sample is estimated to be 25 nm from the Scherrer equation.

SEM provides information on the morphology, crystallinity and chemical composition of the prepared samples were shown in Fig. 2. Very uniform particles can be observed from the low magnification of SEM (Fig. 2(a, c)) and the particles Ag$_2$S were dispersed on the TiO$_2$ particles regularly. For the obtaining of detailed and high magnification, the surface nanostructures and particle sizes of Ag$_2$S/TiO$_2$ composites were studied by TEM in Fig. 3. From the low and high magnification TEM images, it is observed that the anatase TiO$_2$ and all of the Ag$_2$S/TiO$_2$ particles exhibit uniform size distribution. The black dots in TiO$_2$ matrix should be attributed to the accumulation and the high electron density of Ag$_2$S nanoparticles. They are uniformly dispersed in the TiO$_2$ matrix and exhibit a spherical shape and a small monodisperse size around 10-12 nm.
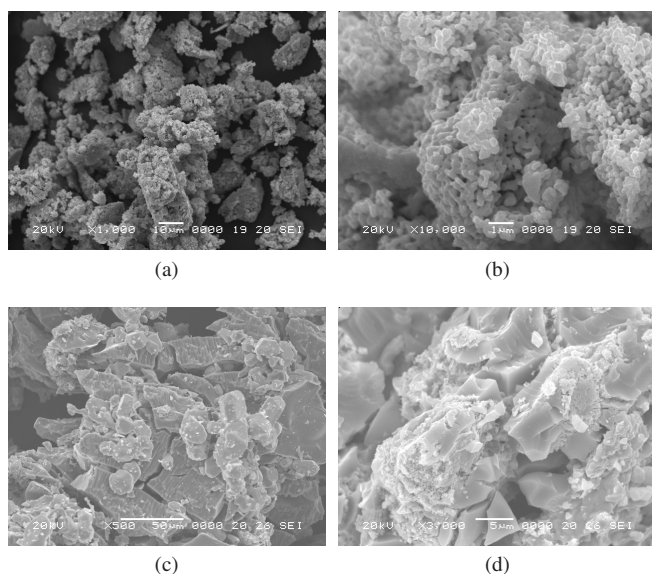

Fig. 2. SEM micrographs of Ag₂S and Ag₂S/TiO₂ composite: (a, b) Ag₂S; (c, d) Ag₂S/TiO₂
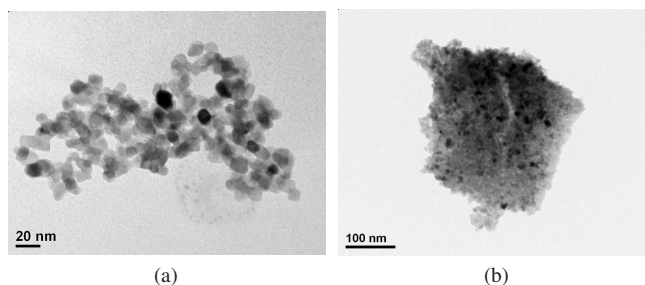
Fig. 3. TEM micrographs of TiO₂ and Ag₂S/TiO₂ composite: (a) TiO₂, (b) Ag₂S/TiO₂

Moreover, these nanocomposite particles were further analyzed by EDX which showed the expected peaks for Ag and S, as well as the peak of Ti due to TiO$_2$. From the Fig. 4, we can see that the main elements such as Ti, O, Ag and S are existed and other impure elements such as Na and C are also existed which might get from the experimental process. However, the content of main elements is much more than that of impure elements. It can be indicated that the Ag$_2$S/TiO$_2$ composite with high purity has been successfully synthesized in this study. The elemental contents of Ag$_2$S/TiO$_2$ composite photocatalysts were listed in Table-2.

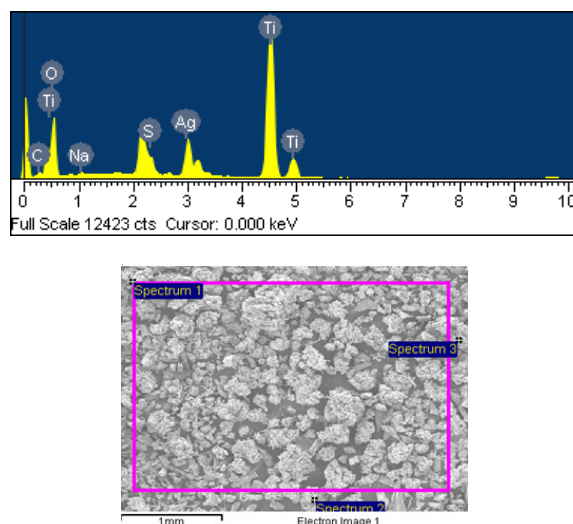Fig. 4. EDX analysis of Ag₂S/TiO₂ composite composite

TABLE-2
EDX ELEMENTAL MICROANALYSIS OF Ag₂S/TiO₂ COMPOSITE

Samples	Elements (wt %)				
	Ti	O	Ag	S	Others
Ag₂S/TiO₂	50.89	35.42	8.85	4.43	0.41

Nitrogen adsorption isotherms and pore size distributions of Ag$_2$S/TiO$_2$ composites were shown in Fig. 5. The BET surface area, total pore volumes and average pore diameters are also listed in Table-3. All the Ag$_2$S/TiO$_2$ composites gave Type I isotherms characterized by plateau that is nearly horizontal to the p/p$_0$ axis in the middle region with increasing of adsorbed volume in low relative pressure region. The data showed that using Ag$_2$S as a modified material the porous distribution of Ag$_2$S/TiO$_2$ composites was improved. Compared with pure TiO$_2$, the surface area and pore volume of Ag$_2$S/TiO$_2$ photocatalysts increased slightly, while the average pore
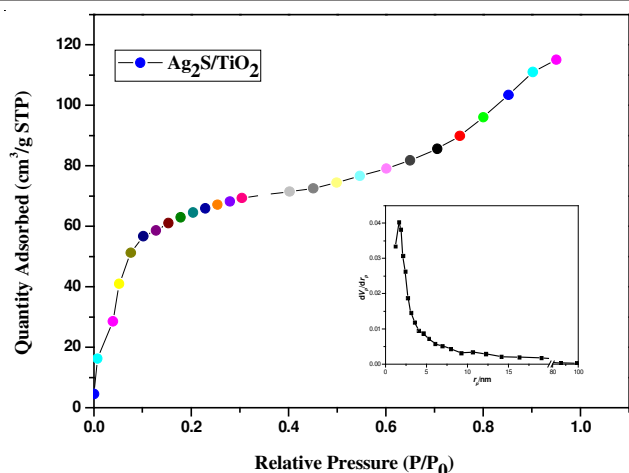
Fig. 5. Nitrogen adsorption isotherms obtained from the Ag₂S-modified TiO₂ composites. The inset is the pore size distribution of Ag₂S-modified TiO₂ composite
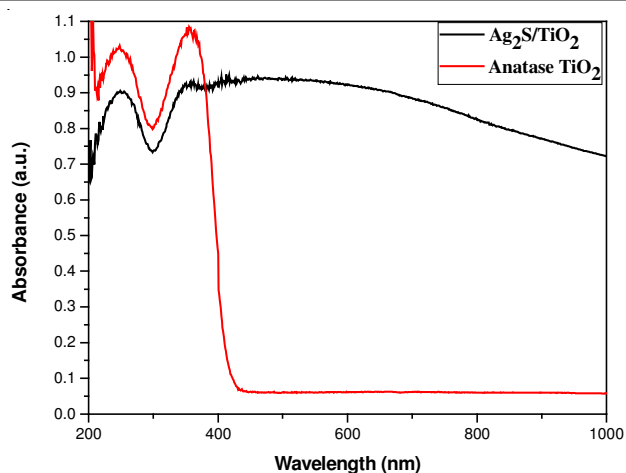
TABLE-3
MICROSTRUCTURES OF ORIGINAL TiO₂
AND COMPOSITE PHOTOCATALYSTS

Samples	TiO_2	Ag_2S/TiO_2
BET surface area (m²/g)	24.78	112.74
Total pore volume (cm³/g)	0.0132	0.2096
Average pore diameter (nm)	2.1289	7.4367

diameter was not changed. The reason was that rich micropores of Ag₂S were distributed on the outer surface of the TiO₂ and no inside pores of TiO₂ were filled and only parts of the outside pores of TiO₂ were covered, in addition, the small clusters of Ag₂S particles on the external surface of TiO₂ formed a certain amount of mesopores and macropores, therefore Ag₂S loaded on the TiO₂ did not change the microstructure of original TiO₂, on the contrary its surface area and pore volume were increased.

As-prepared Ag₂S/TiO₂ nanocomposites exhibit new optical properties concerning about the absorption. The diffuse reflectance UV-VIS absorption spectra of the different samples are presented in Fig. 6. As expected, we can find TiO₂ and Ag₂S/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). Due to Ag₂S nanoparticles can effectively absorb light and trap electrons on the conduction band, so Ag₂S has good adsorption at visible region. Compared with TiO₂ and Ag₂S/TiO₂, it is noticeable that there is an obvious correlation between the Ag₂S, Ag₂S/TiO₂ composites and the UV-VIS spectrum change. These observations might suggest an increase of surface electric charge of the oxides in the composite catalysts due to Ag₂S. Compared with the bulk TiO₂, the blue shift of the UV absorption band happened for the Ag₂S/TiO₂ composites. This blue shift is obviously caused by the strong quantum confinement effect, suggesting that the sizes of Ag₂S/TiO₂ composites are in the nanoscale.

Visible-light photodegradation of methyl orange: The visible-light photocatalytic activity of as-prepared Ag₂S/TiO₂ nanocomposites was studied *via* degradation and mineralization of an aqueous methyl orange. From the results of UV/VIS spectra for the methyl orange solution after photolysis, we attempted a comparison of the relative yields of the photo-

Fig. 6. UV-VIS diffuse reflectance spectra of pure TiO₂, Ag₂S/TiO₂ composite

products formed at different irradiation times. The UV/VIS spectra of methyl orange concentration against the anatase TiO₂ and as-prepared Ag₂S/TiO₂ composite derivatives at various times are also studied. According to a previous study[17], electrons in the conduction band are generated on the surface of TiO₂ when it is irradiated with light with an energy equal to or exceeding its band gap energy. Theoretically, pure TiO₂ cannot be excited by visible light irradiation. However, in this study, the photocatalytic activity of TiO₂ under visible light was improved by introducing of Ag₂S nanoparticles.

As shown in Fig. 7, the absorbance values decreased with an increase in visible light irradiation time. The Ag₂S/TiO₂ composite showed a marked and fast adsorption of methyl orange. An effect of the high crystallinity of the anatase phase on photocatalytic degradation of methyl orange has been shown. Moreover, it is shown that the absorbance of anatase TiO₂ is lower than that of Ag₂S composites due to pure TiO₂ cannot be excited by visible light irradiation, similar results have also been observed by Yu *et al.*[18]. The effect of the catalyst amount on the methyl orange photodecolorization (Fig. 7) was investigated for the nanocomposite Ag₂S/TiO₂ (30, 50 and 70 mg), in order to demonstrate which sample was the material with the best photoactivity, concerning the decolorization of methyl orange. During light-off (first 0.5 h needed to reach the adsorption-desorption equilibrium), an increase of the percentage of the methyl orange adsorbed was observed with the increase on the amount of the nanocomposite, as expected. The photocatalytic degradation of methyl orange using 50 mg of Ag₂S/TiO₂ composite is better than that of the other composites. These results can be explained by two main reasons: first and taking into account the 30 and 50 mg experiments, it must be considered that increasing the catalyst concentration the number of dye molecules adsorbed will increase and the number of photons absorbed will also increase. As a result of the high density of molecules in the area of illumination, the decolorization rate will be increased. However for a very high particles concentration (in this case 70 mg) the suspensions turbidity increases. In this situation the light penetration decreases, as a result of an enhanced light scattering effect and consequently the photodecolorization will be less effective.
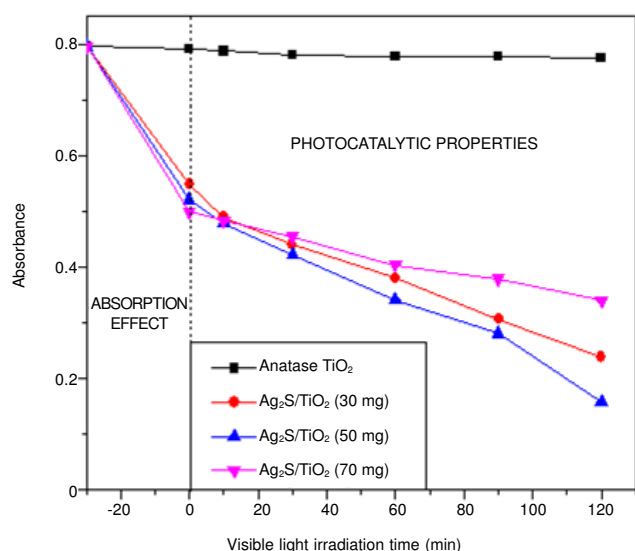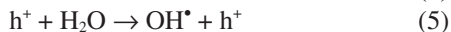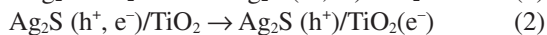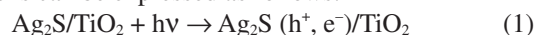
Fig. 7. Effect of photocatalyst amount on the MO decolorization process in presence of Ag$_2$S/TiO$_2$ (50 mL of MO solution)

Furthermore, when the Ag$_2$S/TiO$_2$ composite was irradiated with visible light, the photogenerated electrons can be excited from the valence band of Ag$_2$S and be transited rapidly to the conduction band of TiO$_2$, whereas the photogenerated holes would be left in the valence band of Ag$_2$S. The electrons can react with O$_2$ to generate O$_2^{\bullet-}$ and the holes theoretically migrate to the surface and react with OH$^-$ or H$_2$O to generate OH$^\bullet$. These radicals can then react with adsorbed pollutants. The reactions can be expressed as follows:

$$\text{Ag}_2\text{S/TiO}_2 + h\nu \rightarrow \text{Ag}_2\text{S (h}^+, \text{e}^-)/\text{TiO}_2 \qquad (1)$$
$$\text{Ag}_2\text{S (h}^+, \text{e}^-)/\text{TiO}_2 \rightarrow \text{Ag}_2\text{S (h}^+)/\text{TiO}_2(\text{e}^-) \qquad (2)$$
$$\text{e}^- + \text{O}_2 \rightarrow \text{O}_2^{\bullet-} \qquad (3)$$
$$\text{h}^+ + \text{OH}^- \rightarrow \text{OH}^\bullet \qquad (4)$$
$$\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{OH}^\bullet + \text{h}^+ \qquad (5)$$

Therefore, the Ag$_2$S/TiO$_2$ composites have a narrower band gap and can increase the level of absorption in the visible-light region. The departed holes can migrate to the surface of the Ag$_2$S particles. Therefore, the rate of the photodecomposition under visible light irradiation is enhanced.

Conclusion

In this study, we present the preparation and characterization of Ag$_2$S and Ag$_2$S/TiO$_2$ composite photocatalysts synthesized by a sol-gel method. The structural variations and surface states were investigated through preparation of Ag$_2$S and Ag$_2$S/TiO$_2$ composites. In the XRD patterns for the Ag$_2$S/TiO$_2$ composites, it showed that the Ag$_2$S/TiO$_2$ composite contained a typical single and clear anatase phase and acanthite Ag$_2$S phase. The surface properties seen by SEM and TEM present a characterization of the texture of Ag$_2$S/TiO$_2$ composites with homogenous compositions in the particles for the titanium sources used. The photocatalytic results showed that the decrease of methyl orange concentration should be considered to both the effects between photocatalysis of the supported TiO$_2$ and charge transfer of the Ag$_2$S nanoparticels. Furthermore, the introduction of Ag$_2$S can lead to a shift in the absorption band of the Ag$_2$S/TiO$_2$ composite into the visible light region due to the excellent photoelectric characteristics of Ag$_2$S.

REFERENCES

1. W.C. Oh, F.J. Zhang and M.L.Chen, *J. Ind. Eng. Chem.*, **16**, 299 (2010).
2. W.C. Oh, *J. Photocataly. Sci.*, **1**, 29 (2010).
3. A.L. Linsebigler, G. Lu and J.T. Yates. Jr, *Chem. Rev*., **95**, 735 (1995).
4. L. Zhu, Z.D. Meng, M.L. Chen, F.J. Zhang, J.G. Choi and J.Y. Park, *J. Phys. Chem. Sci.*, **1**, 69 (2010).
5. M. Romero, J. Blanco, B. Sanchez, A. Vidal, S. Malato, A.I. Cardona and E. Garcia, *Sol. Energy*, **66**, 169 (1999).
6. S. Sato, *Chem. Phys. Lett*., **123**, 126 (1986).
7. J.H. Xu, W.L. Dai, J. Li, Y. Cao, H. Li, H. He and K. Fan, *Catal. Commun.*, **9**, 146 (2008).
8. A.W. Xu, Y. Gao and H.Q. Liu, *J. Catal*., **207**, 151 (2002).
9. R. Brahimi, Y. Bessekhouad, A. Bouguelia and M. Trari, *J. Photochem. Photobiol. A*, **194**, 173 (2008).
10. R. Vogel, P. Hoyer and H. Weller, *J. Phys. Chem.*, **98**, 3183 (1994).
11. A.I. Kryukov, S.Y. Kuehmii and V.D. Pokhodenko, *Theor. Exp. Chem.*, **36**, 63 (2000).
12. H. Li, B. Zhu, Y. Feng, S. Wang, S. Zhang and W. Huang, *J. Solid State Chem.*, **180**, 2136 (2007).
13. J.C. Kim, J.K. Choi, Y.B. Lee, J.H. Hong, J.I. Lee, J.W. Yang, W.I. Lee and N.H. Hur, *Chem. Commun.*, **48**, 5024 (2006).
14. A.I. Kryukov, S.Y. Kuehmii and V.D. Pokhodenko, *Theor. Exp. Chem.*, **36**, 63 (2000).
15. D. Robert, *Catal. Today*, **122**, 20 (2007).
16. W.X. Zhang, L. Zhang, Z.H. Hui, X.M. Zhang and Y.T. Qian, *Solid State Ionics*, **130**, 111 (2000).
17. T.Y. Han, C.F. Wu and C.T. Hsieh, *J. Vac. Sci. Technol. B*, **25**, 430 (2007).
18. X.D. Yu, Q.Y. Wu, S.C. Jiang and Y.H. Guo, *Mater. Character.*, **57**, 333 (2006).