Chalcogenide Letters Vol. 16, No. 8, August 2019, p. 387 - 393

REFUXING SYNTHESIS AND CHARACTERIZATION OF ZnS NANOPARTICLES AND THEIR PHOTOCATALYTIC PROPERTIES

A. PHURUANGRAT[a,*], K. KARTHIK[b], B. KUNTALUE[c] ,
P. DUMRONGROJTHANATH[d], S. THONGTEM[e,f] , T. THONGTEM[f,g]
[a]Department of Materials Science and Technology, Faculty of Science,
Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
[b]Department of Physics, Bharathidasan University, Tiruchirappalli 620 024,
Tamil Nadu, India
[c]Electron Microscopy Research and Service Center, Faculty of Science,
Chiang Mai University, Chiang Mai 50200, Thailand
[d]Rajamangala University of Technology Lanna Chiang Rai,
Chiang Rai 57120, Thailand
[e]Department of Physics and Materials Science, Faculty of Science,
Chiang Mai University, Chiang Mai 50200, Thailand
[f]Materials Science Research Center, Faculty of Science, Chiang Mai University,
Chiang Mai 50200, Thailand
[g]Department of Chemistry, Faculty of Science, Chiang Mai University,
Chiang Mai 50200, Thailand

ZnS nanoparticles were synthesized by refluxing of $Zn(NO_3)_2{\cdot}6H_2O$ and CH_3CSNH_2 as zinc and sulfur sources in ethylene glycol at 60-100 °C for 2-6 h. Phase, atomic vibration and morphology of ZnS products were investigated by X-ray powder diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM). The results show that all the as-synthesized samples are cubic ZnS nanoparticles with different orientations. The particle size of ZnS nanoparticles is controlled by the reaction time and temperature. The photocatalytic degradation of as-synthesized ZnS nanoparticles was investigated through photodegradation of methylene blue (MB) and methyl orange (MO) under UV light irradiation. According to the photocatalytic results, ZnS nanoparticles synthesized by refluxing method at 100 °C for 6 h have the highest photocatalytic degradation of 96.73% for MB and 94.68% for MO under UV radiation within 120 min.

(Received May 22, 2019; Accepted August 7, 2019)

Keywords: ZnS; Nanoparticles; Photocatalysis; Spectroscopy

1. Introduction

Metal sulfides such as CdS, ZnS, $ZnIn_2S_4$, $AgGaS_2$ and $CdIn_2S_4$ have been attracting a great deal of research interest for hydrogen production by water splitting and wastewater treatment due to their high chemical stability and photocatalytic activity [1-5]. Among them, zinc sulfide (ZnS) with a wide band gap of ~3.6 eV and a large exciton binding energy of 40 meV has been applied in semiconducting photocatalyst, H_2 evolution, bio-imaging, flat-panel displays and light emitting diodes (LEDs) because of its good thermal stability, high electronic mobility, nontoxicity, water insolubility and inexpensive cost [1, 2, 6, 7, 8]. ZnS has been used for photocatalytic reaction under radiation with wavelength below 380 nm due to its relatively wide band gap and high negative value of conduction band potential [1, 6, 7, 9]. According to Ye et al. cubic phase of ZnS nanoparticles was synthesized by simple chemical precipitation method. The photocatalytic activities of ZnS nanoparticles used for degradation of methylene blue (MB), xylenol orange (XO), methyl orange (MO) and methyl red (MR) as model dyes were studied [1]. Pure ZnS nanoparticles exhibited an obviously enhanced photocatalytic activity for degradation of

---

*Corresponding author: phuruangrat@hotmail.com

MO and MR dyes better than the degradation of MB and XO dyes because ZnS nanoparticles can easily degrade the -N=N- bond. Jacob et al. succeeded in biosynthesizing of ZnS quantum dots from Zn tolerant Penicillium sp. under ambient reaction conditions for photodegradation of MB dye [6].

In this research, cubic phase of ZnS nanoparticles synthesized by refluxing method was used for photodegradation of MB and MO dyes. The crystal structure, atomic vibration and morphologies of as-synthesized ZnS samples were characterized by different techniques. The photocatalytic activities of as-synthesized ZnS nanoparticles were investigated through photodegradation of MB and MO dyes under UV light irradiation. A possible photocatalytic mechanism of as-synthesized ZnS nanoparticles was also proposed according to the experimental results.

2. Experiment

All chemicals with analytical grade were used without further purification. In a typical experimental procedure, 0.005 mole $Zn(NO_3)_2{\cdot}6H_2O$ and 0.006 mole thioacetamide (CH_3CSNH_2) were dissolved in 100 ml of ethylene glycol under vigorous stirring at room temperature for 30 min. Then, the solution was transferred to a 250 ml round-bottom flask and refluxed in a silicon oil bath at 60-100 °C for 2-6 h. The precipitates were filtered, washed with distilled water and absolute ethanol, and dried in an oven at 80 ^{o}C for 24 h for further characterization.

X-ray powder diffraction (XRD) patterns of the products were recorded on a Philips X'Pert MPD X-ray powder diffraction analyzer with a graphite monochromator and Cu K_α line at a scanning rate of 0.02 deg/s ranging from 10^o to 80^o. Raman spectra of samples were recorded on a HORIBA Jobin Yvon T64000 Raman spectrometer of 50 mW and 514.5 nm wavelength Ar green laser. Scanning electron microscopic (SEM) images of the products were taken on a JEOL JSM-6335F FE-scanning electron microscope at an accelerating voltage of 35 kV.

The photocatalytic measurement of as-synthesized ZnS samples was investigated by photodegradation of methyl blue (MB) and methyl orange (MO) as model dyes under UV light illumination. The 0.2 g of as-synthesized ZnS sample was added to 200 ml of $1x10^{-5}$ M MB and MO solutions under vigorous stirring. The solutions were kept in the dark for 30 min. Subsequently, the suspension solutions were exposed to a UV radiation from three black light lamps. Approximately 5 ml of suspension solution was collected at different time intervals and centrifuged at a speed of 6000 rpm to remove the residual photocatalyst from the MB and MO solutions. In the end, the residual contents of MB and MO were measured by UV-visible spectrophotometer (PerkinElmer Lambda 25) at λ_{max} = 664 nm for MB and λ_{max} = 465 nm for MO. The degradation was calculated by the following equation

$$\text{Decolorization efficiency (\%)} = (C_o - C_t)/C_o \times 100 \qquad (1)$$

C_o is the initial dye concentration and C_t is the dye concentration at time t.

3. Results and discussion

Fig. 1 shows the XRD patterns of ZnS nanomaterials synthesized by refluxing method with different holding time and reaction temperature. All as-synthesized ZnS samples show diffraction peaks at $2\theta = 28.56^o$, 33.09^o, 47.58^o, 56.34^o, 59.12^o, 69.45^o, 76.75^o and 79.18^o which can be indexed to the (111), (200), (220), (311), (222), (400), (331) and (420) planes of cubic ZnS structure (JCPDS file no. 05-0566 [10]), respectively. No impurities were detected in these XRD patterns, indicating that the as-synthesized ZnS samples are high purified and homogenous phase. Moreover, the intensities of diffraction patterns were increased with increasing in the holding time and reaction temperature, indicating that the crystalline degree of cubic ZnS structure was increased. Among them, the as-synthetized ZnS nanomaterials synthesized by refluxing method at 100 ^{o}C for 6 h show the diffraction intensity higher than other samples. The results indicate that the crystalline degree of cubic ZnS structure synthesized at 100 ^{o}C for 6 h is the highest. The crystallite size of as-synthesized ZnS nanostructure can be calculated by the following formula.

$$D = k\lambda/\beta\cos\theta \tag{2}$$

D is the crystallite size of ZnS nanoparticles, k is a dimensionless shape factor (k = 0.89), λ is the Cu K_α line (1.54056 Å), β is the full width at half maximum (FWHM) of the (111) diffraction peak and θ is the Bragg angle of the (111) plane [1, 11, 12]. The calculated crystallite sizes of as-synthesized ZnS nanoparticles are 7.87 nm, 15.32 nm, 28.48 nm, 32.85 nm and 39.45 nm for the refluxing synthesis at 60 ^{o}C for 2 h, 60 ^{o}C for 4 h, 60 ^{o}C for 6 h, 80 ^{o}C for 6 h and 100 ^{o}C for 6 h, respectively. It can be seen that the crystallite sizes of as-synthesized ZnS nanoparticles were increased with increasing in the holding time and reaction temperature. The lattice parameter of ZnS nanoparticles can be estimated by the following equations.

$$1/d^2 = (h^2+k^2+l^2)/a^2 \tag{3}$$

$$2d\sin\theta = n\lambda \tag{4}$$

, where d is the interplanar spacing of ZnS nanoparticles, h, k and l are the Miller indices, a is the lattice parameter, λ is the Cu K_α line (1.54056 Å) and θ is the Bragg angle [1, 13, 14]. The calculated lattice parameters of ZnS nanoparticles are 5.4339 ± 0.0042 Å, 5.4275 ± 0.0098 Å, 5.4158 ± 0.0034 Å, 5.4105 ± 0.0025 Å and 5.4089 ± 0.0014 Å for the refluxing synthesis at 60 ^{o}C for 2 h, 60 ^{o}C for 4 h, 60 ^{o}C for 6 h, 80 ^{o}C for 6 h and 100 ^{o}C for 6 h, respectively.

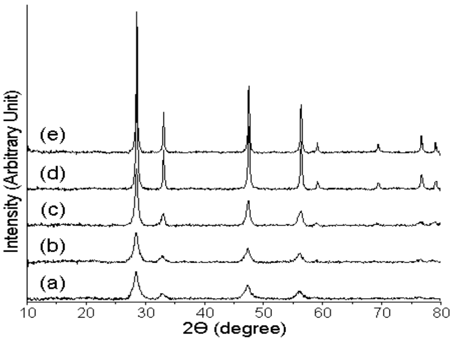


Fig. 1. XRD patterns of ZnS products synthesized by refluxing method at (a) 60 ^{o}C for 2 h, (b) 60 ^{o}C for 4 h, (c) 60 ^{o}C for 6 h, (d) 80 ^{o}C for 6 h and (e) 100 ^{o}C for 6 h.

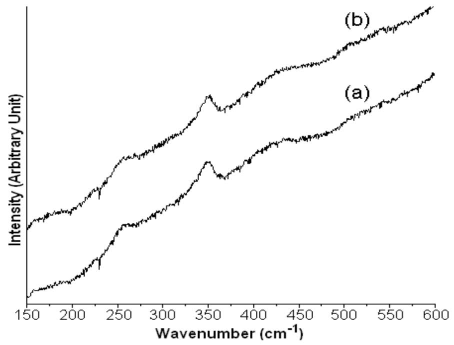
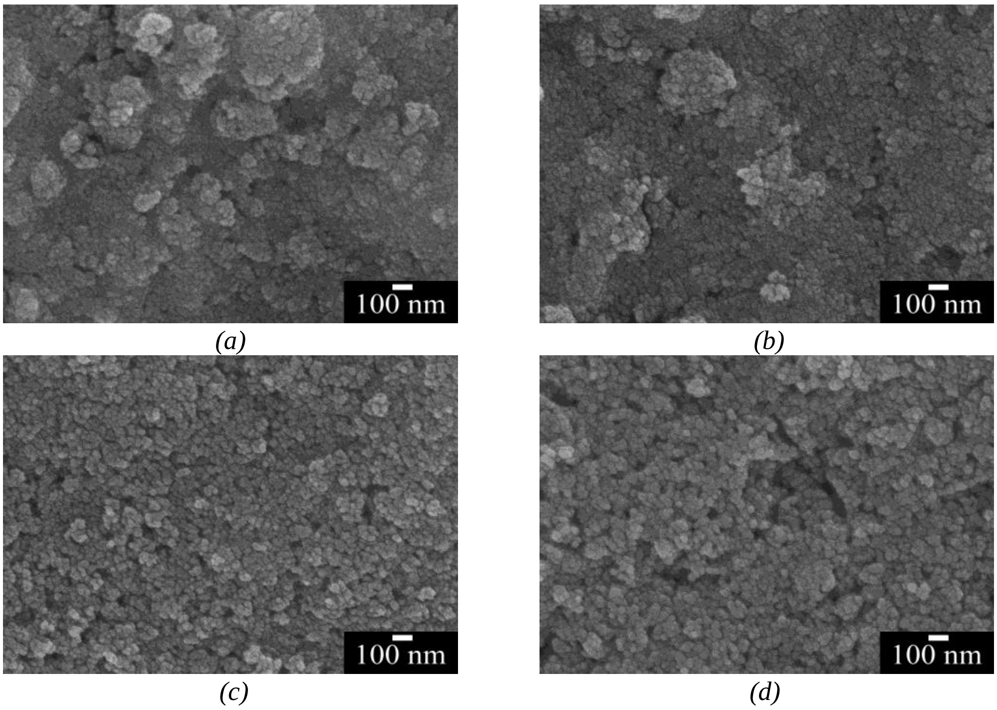


Fig. 2. Raman spectra of ZnS products synthesized by refluxing method at (a) 60 ^{o}C for 6 h and (e) 100 ^{o}C for 6 h.

Cubic ZnS belongs to the space group C_{6v} (6mm) within the primitive cell. The zone-center optical phonons can be classified as the following irreducible representation: Γ_{opt} =

$A_1+E_1+2E_2+2B_1$. The B_1 modes are silent, A_1 and E_1 are polar and are both Raman and infrared (IR) active, and E_2 vibrations are nonpolar and Raman active only [1, 15]. Fig. 2 shows Raman spectra of ZnS nanoparticles synthetized by refluxing method at 60 °C for 6 h and 100 °C for 6 h. The Raman peaks at 258.34 cm^{-1} and 349.02 cm^{-1} can be assigned to the A_1(TO) and E_1(LO) of Raman vibration modes [1, 6, 15, 16]. The XRD and Raman results indicate that no impurities were detected in the ZnS products.



(a) *(b)*

(c) *(d)*

Fig. 3. SEM images of ZnS products synthesized by refluxing method at (a) 60 °C for 2 h, (b) 60 °C for 6 h, (c) 80 °C for 6 h and (d) 100 °C for 6h.

The morphologies of as-synthesized ZnS nanostructures were investigated by SEM as the results shown in Fig. 3. Clearly, the as-synthesized ZnS nanostructures are uniformly distributed nanoparticles with different orientations controlled by reaction time and temperature. The particle sizes of ZnS nanoparticles are 10-15 nm, 12-25 nm, 18-25 nm and 20-30 nm for the refluxing synthesis at 60 °C for 2 h, 60 °C for 6 h, 80 °C for 6 h and 100 °C for 6 h, respectively. Therefore, the particle sizes of as-synthesized ZnS nanoparticles are controlled by the holding time and reaction temperature.

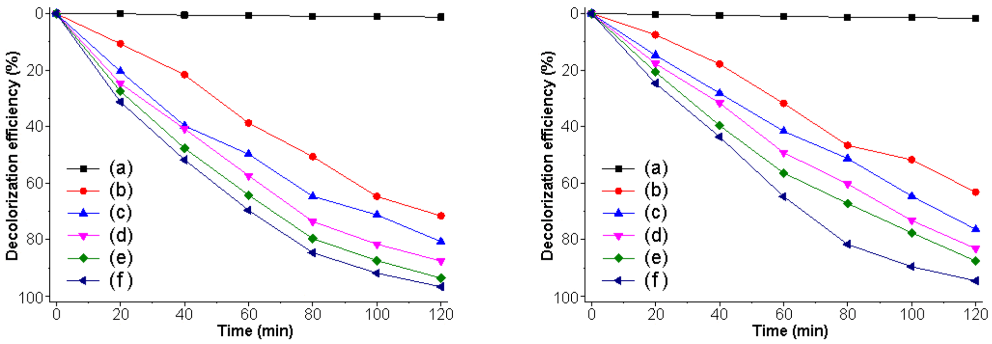


Fig. 4. Decolorization efficiency of MB(left) and MO(right) for the (a) blank solution and the solutions containing ZnS products synthesized by refluxing method at (b) 60 °C for 2 h, (c) 60 °C for 4 h, (d) 60 °C for 6 h, (e) 80 °C for 6 h and (f) 100 °C for 6 h under UV light irradiation.

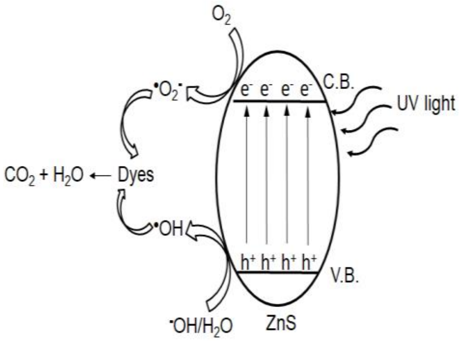


Fig. 5. Schematic diagram for photocatalysis of ZnS nanoparticles induced by UV light irradiation.

The photocatalytic activities of ZnS nanoparticles were investigated by photodegradation of MB and MO as dye models under UV light irradiation within 120 min as the results shown in Fig. 4. The photocatalytic activities of ZnS nanoparticles were tested with respect to the pure MB and MO solutions without ZnS nanoparticles under UV light irradiation. Clearly, both pure MB and MO solutions show negligible photodegradation under UV light, indicating that both MB and MO molecules are very high stability under UV light irradiation. The photocatalytic efficiencies of MB are 63.25%, 76.41%, 83.25%, 87.65% and 96.73%, and those of MO are 56.12%, 71.62%, 80.75%, 87.65% and 94.68% over ZnS nanoparticles synthesized by refluxing method at 60 ^{o}C for 2 h, 60 ^{o}C for 4 h, 60 ^{o}C for 6 h, 80 ^{o}C for 6 h and 100 ^{o}C for 6 h under UV light irradiation within 120 min, respectively. Clearly, the photocatalytic efficiencies of ZnS nanoparticles were controlled by the crystalline degree of cubic ZnS structure. Cubic ZnS with the highest crystalline degree shows the highest photocatalytic efficiency under UV light irradiation, in accordance with those of the previous reports [17, 18]. Based on the above experiment, a possible photocatalytic mechanism for photodegradation of dyes over ZnS nanoparticles was proposed as the schematic diagram shown in Fig. 5. The photo-induced electron-hole pairs were generated on the valence and conduction bands and transferred to the surface of ZnS nanoparticles under UV radiation. Subsequently, the photo-induced electrons and photo-induced holes were reacted with dissolving oxygen molecules and water molecules adsorbed on the surface of ZnS nanoparticles to form superoxide anion radicals ($^{\bullet}O_2^-$) and hydroxyl radicals ($^{\bullet}OH$) as strong oxidants for degradation and mineralization of organic dye molecules and transformed them into CO_2, H_2O and degraded products [1, 6, 9, 18]. The above explanation can be written as the following equations.

$$ZnS + h\nu \rightarrow h^+ + e^- \quad (5)$$

$$e^- + O_2 \rightarrow {}^{\bullet}O_2^- \quad (6)$$

$$4{}^{\bullet}O_2^- + 2H_2O \rightarrow 3O_2 + 4OH^- \quad (7)$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \quad (8)$$

$${}^{\bullet}O_2^- + {}^{\bullet}OH + \text{dyes} \rightarrow CO_2 + H_2O + \text{degraded products} \quad (9)$$

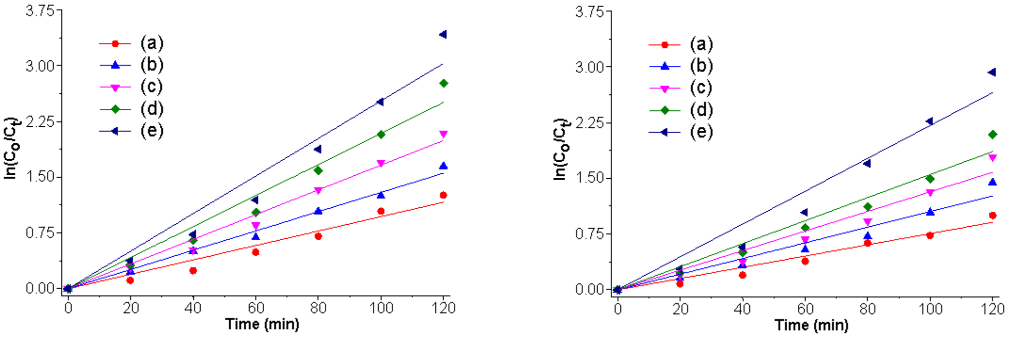
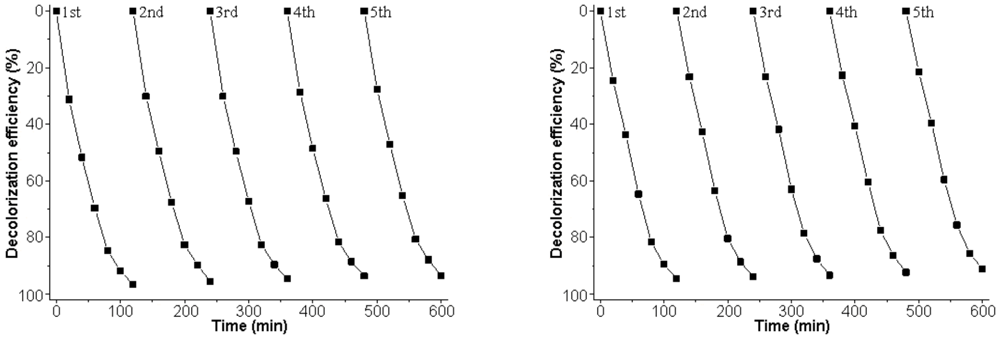


Fig. 6. Pseudo-first-order plots of MB(left) and MO(right) solutions photocatalyzed by ZnS synthesized by refluxing method at (a) 60 °C for 2 h, (b) 60 °C for 4 h, (c) 60 °C for 6 h, (d) 80 °C for 6 h and (e) 100 °C for 6 h under UV light irradiation.

The photocatalytic reaction rates of degraded MB and MO over ZnS nanoparticles can be expressed through the pseudo-first-order model as follows.

$$\ln(C_o/C_t) = K_{app}t \tag{10}$$

C_o and C_t are the absorbance of dye solutions at time 0 and t, respectively. K_{app} is the apparent photocatalytic reaction rate constant and t is the UV irradiation time [1, 4, 9, 18]. Fig. 6 shows the plots of $\ln(C_o/C_t)$ versus irradiation time for photodegradation of MB and MO by ZnS nanoparticles under UV light irradiation within 120 min. The potting curves of $\ln(C_o/C_t)$ versus irradiation time for photodegradation of MB and MO over ZnS nanoparticles obey the pseudo-first-order kinetics [4, 9]. The first-order rate constants of the photodegradation reaction over ZnS nanoparticles were calculated through the slopes of straight lines. The photodegradation rates of MB over ZnS nanoparticles synthesized by refluxing method at 60 °C for 2 h, 60 °C for 4 h, 60 °C for 6 h, 80 °C for 6 h and 100 °C for 6 h are 0.0097, 0.0121, 0.0168, 0.0211 and 0.0253 min^{-1}, respectively. The photodegradation rates of MO over ZnS nanoparticles synthesized by refluxing method at 60 °C for 2 h, 60 °C for 4 h, 60 °C for 6 h, 80 °C for 6 h and 100 °C for 6 h are 0.0076, 0.0105, 0.0132, 0.0156 and 0.0220 min^{-1}, respectively. ZnS nanoparticles synthesized by refluxing method at 100 °C for 6 h show the highest first-order rate constants for both MB and MO solutions under UV light irradiation within 120 min.



(a) *(b)*

(b)

Fig. 7. Recyclability of ZnS nanoparticles synthesized by refluxing method at 100 °C for 6 h used for photodegradation of (a) MB and (b) MO solutions under UV light irradiation.

The photocatalytic stability of the re-used ZnS nanoparticles was investigated for five cycles. For each of the cyclic run, the re-used ZnS nanoparticles as photocatalyst were centrifuged, washed with double distilled water and 95% ethanol, and dried at 60 °C for 24 h. Then, the re-used

ZnS nanoparticles were tested for photocatalysis at the same condition. Fig. 7 shows the photocatalytic stability of the re-used ZnS nanoparticles under UV radiation. Clearly, photodegradation performance of the re-used ZnS nanoparticles decreased from 96.73% to 93.47% for MB and 94.68% to 91.05% for MO at the end of the fifth cycle. These results certify that the as-synthesized ZnS nanoparticles possess high photocatalytic activity and good stability for wastewater treatment.

4. Conclusions

ZnS nanoparticles were synthesized by a refluxing method at 60-100 °C for 2-6 h. ZnS nanoparticles synthesized by a refluxing method at 100 °C for 6 h showed photocatalytic degradation of MB for 96.73% and of MO for 94.68% under UV light irradiation within 120 min. At the end of the fifth cycle, the re-used ZnS nanoparticles show very little reduction in the photodegradation performance. In summary, the as-synthesized ZnS nanoparticles as a UV-light-driven photocatalyst have very good photocatalytic activity and are considered as a promising photocatalyst for wastewater treatment.

Acknowledgment

We wish to thank the Prince of Songkla University, Hat Yai, Songkhla, Thailand for providing financial support.

References

[1] Z. Ye, L. Kong, F. Chen, Z. Chen, Y. Lin, C. Liu, Optik **164**, 345 (2018).
[2] B. Barrocas, T. J. Entradas, C. D. Nunes, O. C. Monteiro, Appl. Catal. B **218**, 709 (2017).
[3] M. Antoniadou, V. M. Daskalaki, N. Balis, D. I. Kondarides, C. Kordulis, P. Lianos, Appl. Catal. B. **107**, 188 (2011).
[4] A. Phuruangrat, P. Dumrongrojthanath, O. Yayapao, T. Thongtem, S. Thongtem, Mater. Sci. Semicond. Process. **26**, 329 (2014).
[5] K. Zhang, L. Guo, Catal. Sci. Technol. **3**, 1672 (2013).
[6] O. Sacco, V. Vaiano, D. Sannino, R. A. Picca, N. Cioffi, J. Colloid Interf. Sci. **537**, 671 (2019).
[7] J. M. Jacob, R. Rajan, M. Aji, G. G. Kurup, A. Pugazhendhi, Ceram. Inter. **45**, 4857 (2019).
[8] Y. Piña-Pérez, O. Aguilar-Martínez, P. Acevedo-Peña, C. E. Santolalla-Vargas, S. Oros-Ruíz, F. Galindo-Hernández, R. Gómez, F. Tzompantzi, Appl. Catal. B **230**, 125 (2018).
[9] A. Eyasu, O. P. Yadav, R. K. Bachheti, Int. J. Chem. Tech. Res. **5**, 1452 (2013).
[10] Powder Diffract. File, JCPDS-ICDD, 12 Campus Boulevard, Newtown Square, PA 19073-3273, U.S.A. (2001).
[11] B. Arunkumar, S. J. Jeyakumar, M. Jothibas, Optik **183**, 698 (2019).
[12] P. Baláž, E. Boldižárová, E. Godočíková, J. Briančin, Mater. Lett. **57**, 1585 (2003).
[13] S. I. Sadovnikov, A. A. Rempel, Phys. Solid State **51**, 2375 (2009).
[14] E. Yücel, Y. Yücel, Ceram. Inter. **43**, 407 (2017).
[15] Y. C. Cheng, C. Q. Jin, F. Gao, X. L. Wu, W. Zhong, S. H. Li, P. K. Chu, J. Appl. Phys. **106**, 123505 (2009).
[16] T. Liu, W. J. Kong, M. Qiao, Y. Cheng, Result. Phys. **11**, 822 (2018).
[17] J. Hu, Y. Cao, K. Wang, D. Jia, RSC Adv. **7**, 11827 (2017).
[18] N. Soltani, E. Saion, M. Z. Hussein, M. Erfani, A. Abedini, G. Bahmanrokh, M. Navasery, P. Vaziri, Int. J. Mol. Sci. **13**, 12242 (2012).