Journal of Alloys and Compounds 513 (2012) 506–509

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Facile preparation and visible light photocatalytic activity of $CdIn_2S_4$ monodispersed spherical particles

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ARTICLE INFO

Article history:
Received 25 August 2011
Received in revised form 27 October 2011
Accepted 29 October 2011
Available online 9 November 2011

Keywords:
$CdIn_2S_4$
Monodispersed spherical particles
Preparation
Photocatalysis

ABSTRACT

We developed a facile method to prepare $CdIn_2S_4$ monodispersed spherical particles by using mercaptoacetic acid as capping agent and thioacetamide as sulfur source. The results indicated that the size and morphology of $CdIn_2S_4$ particles were related to reaction time. The $CdIn_2S_4$ spherical particles with an average size of about 236 nm and a narrow size distribution were formed after reacting for 7 h. The photocatalytic activity of as-synthesized $CdIn_2S_4$ spherical particles was evaluated by the photocatalytic degradation of methyl orange under visible light illumination. The results showed that the photocatalytic activity increased with prolonging reaction time in the preparation of $CdIn_2S_4$ spherical particles. The $CdIn_2S_4$ spherical particles prepared after reacting for 7 h exhibited a 98% degradation efficiency of methyl orange after 15 min visible light irradiation.

1. Introduction

Monodispersed particles have been widely used as an ideal model for fundamental research in colloid science [1]. They are also of potential importance as advanced materials for industrial applications such as electromagnetic devices, optical devices, sensors, catalysts, and pigments [2,3]. Especially, the uniform metal chalcogenide particles with precisely controlled sizes are expected to provide us with excellent functional optoelectronic materials, catalysts and so on [4,5]. Now, a lot of efforts have been made to synthesize monodispersed particles of chalcogenide compounds [6–9]. However, it is still an interesting topic in the material world to prepare monodispersed spherical particles by a simple process.

Recently, photocatalytic decomposition of organic pollutants in the presence of semiconductor photocatalysts has been proven to be one of the most promising methods for pollutant decontamination [10]. Among various semiconductor photocatalysts, the wide-band-gap semiconductor metal oxides, such as TiO_2 and ZnO, have been attractive due to low cost and high catalytic efficiency [11–13]. However, they have no photocatalytic activity under visible light irradiation. Therefore, the study of photocatalysts with visible light activity has been a focus in the field of photocatalysis. It is known that the electronic and optical properties of ternary chalcogenide compounds, AB_xC_y (A = Cu, Ag, Zn, Cd, etc.; B = Al, Ga, In; C = S, Se, Te), can be easily tuned [14–21], which is favorable for selecting visible light photocatalysts [22–25]. It can be reasonably expected that ternary chalcogenide compounds might be widely applied to photocatalysis in future.

Up to date, there are many reports about $CdIn_2S_4$ films for structural, optical and electrical properties [26–29]. The reported preparation methods generally involved high temperature, toxic organic solvents and organic precursors, as well as long reaction time, etc. These disadvantages not only make it complex to control the size and morphology of samples, but also cause ineluctably environmental pollution. Soft solution process is a convenient and environmental friendly way to produce shaped, sized and oriented materials in only one step [30–32]. Therefore, a series of studies on the preparation of $CdIn_2S_4$ with controlled size and morphology in soft solutions, such as nanotubes, nanorods, hollow spheres and spherical flower, were successfully done [22,33–35]. Based on these achievements, we aim to develop a facile process to prepare monodispersed $CdIn_2S_4$ spherical particles in a soft solution. In this process, mercaptoacetic acid and thioacetamide (TAA) are used as capping agent and as sulfur source, respectively. In addition, we evaluate the visible light photocatalytic activity of the product for the degradation of methyl orange (MeO).

2. Experimental

2.1. Synthesis of $CdIn_2S_4$

In a typical process, a 200 mL mixture aqueous solution was composed of $Cd(NO_3)_2$ (0.35 mL, 0.2 mol L^{-1}), $In(NO_3)_3$ (0.90 mL, 0.2 mol L^{-1}), mercaptoacetic acid (6.50 mL, 0.2 mol L^{-1}). After stirring for 15 min, 10 mL thioacetamide (0.2 mol L^{-1}) was added into the mixture. After continuous stirring for 10 min, the reaction

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doi:10.1016/j.jallcom.2011.10.105

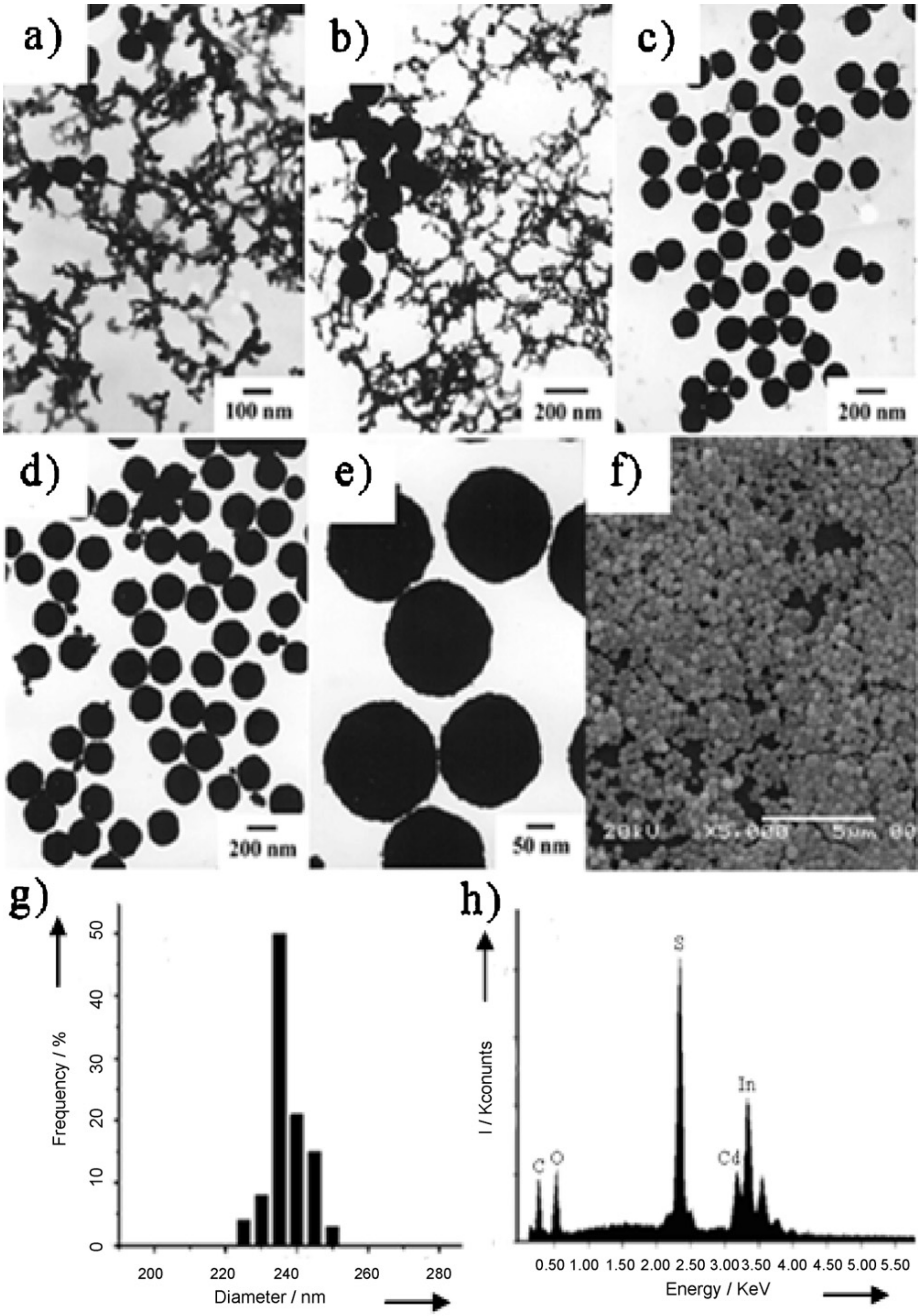

Fig. 1. TEM images of CIS-1 (a), CIS-3 (b), CIS-5 (c) and CIS-7 (d and e). SEM image (f), the size distribution (g) and the EDAX pattern (h) of CIS-7.

mixture was put in water bath and kept at 70 °C for 1–7 h. Then, the reaction system was naturally cooled to room temperature and aged for 12 h. After concentrated with rotary evaporator, the yellow precipitate was washed several times with acetone and subsequently dried for 6 h in a vacuum oven at room temperature. For the sake of description, the samples obtained after reacting for 1 h, 3 h, 5 h, 7 h were labelled as CIS-1, CIS-3, CIS-5, and CIS-7, respectively.

2.2. Characterization

Powder X-ray diffraction (XRD) analysis was made on a Rigaku 2550D/max VB/PC X-ray diffractometer (Japan) using Cu Kα radiation ($\lambda = 0.154056$ nm). TEM images were taken on a JEOL JEM-1200EX II electron microscope (Japan). UV–vis diffuse reflectance spectra (DRS) were measured on a VARIAN Cary 500 Scan UV–vis–NIR spectrophotometer (USA). UV–vis spectra of solution were recorded on a Unico UV-2102 PCS spectrometer (China). SEM images were taken on a JEOL JSM-6360LV electron microscope (Japan). Energy dispersive analysis of X-ray (EDAX) was carried out on a JEOL JSM-6360LV scanning electron microscope (Japan) with a FALCON EDX spectrometer (USA).

2.3. Evaluation of photocatalytic activity

The photocatalytic activity measurement was carried out in a homemade reactor equipped with a water jacket. A 1000 W iodine–tungsten lamp equipped with a cutoff filter ($\lambda > 400$ nm) to remove radiation below 400 nm was used as the visible light source. The distance between the lamp and the reactor was 20 cm. 50 mg of $CdIn_2S_4$ was suspended in the 100 mL methyl orange aqueous solution (2.5×10^{-5} mol L^{-1}) under stirring. The pH of the dispersion was adjusted using HNO_3 or NaOH. At first, the suspension was continuously stirred for 0.5 h in dark to ensure an adsorption–desorption equilibrium prior to irradiation. After irradiation, the residual concentration of MeO was monitored by measuring the absorbance at

464 nm. The photocatalytic degradation efficiency of MeO was calculated according to Eq. (1):

$$C\ \ (\%) = \frac{A_0 - A}{A_0} \times 100 \tag{1}$$

where C is the degradation efficiency, A_0 is the initial absorbance of MeO solution, and A is the absorbance after irradiation.

3. Results and discussion

The morphology and composition of the products were examined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Fig. 1a–d obviously illustrates the growth process of sphere-like $CdIn_2S_4$ particles at different reaction time. As can be seen from Fig. 1a, the sample obtained after reacting for 1 h is mainly composed of very small particles. A few of larger irregular sphere-like particles are also observed. With increasing reaction time, the number of larger sphere-like particles gradually increases and they become more regular. After reacting for 5 h (Fig. 1c), the product obtained is entirely composed of sphere-like particles. As the reaction time reaches 7 h (Fig. 1d and e), these sphere-like particles become rounder and more uniform. SEM image (Fig. 1f) further demonstrates that many spherical $CdIn_2S_4$ particles are formed. Moreover, the size distribution (Fig. 1g) reveals that diameters of more than 75% particles are in the range of 230–240 nm, indicating that the as-synthesized $CdIn_2S_4$ particles are monodispersed.

In fact, the growth mode of nanocrystals strongly depends upon monomer concentration [36]. At low monomer concentration, the number of nucleus of $CdIn_2S_4$ is limited and the growth of $CdIn_2S_4$ particles is slow. On the other hand, Ostwald ripening occurs, and small nanocrystals dissolve to form larger ones. Such growth conditions resulting in the least surface energy favor the formation of spherical particles. Experimentally, during the formation of $CdIn_2S_4$ monodispersed spherical particles, mercaptoacetic acid and thioacetamide (TAA) both played very important roles. On the one hand, mercaptoacetic acid was used as capping agent to promote oriented aggregation and to hinder fast crystal growth by steric effect. On the other hand, thioacetamide (TAA) as sulfur source resulted in slow growth of $CdIn_2S_4$ particles to form the larger ones. As proposed by Matijević [37,38] the formation of such uniform particles is due to the aggregation of preformed small precursors. Thus, on the basis of our experimental results, it can be deduced that with reaction time prolonging, the preformed small $CdIn_2S_4$ particles gradually aggregate and grow to form the uniform and large spherical particles with the help of slow release of sulfur source from TAA and the synergetic effect of mercaptoacetic acid as capping agent.

Energy dispersive analysis of X-ray (EDAX) was carried out to identify the surface elemental composition of as-synthesized $CdIn_2S_4$ particles. As shown in Fig. 1h, the $CdIn_2S_4$ spheres after 7 h growth give the Cd:In:S molar ratio of 1:2:4, illustrating that the stoichiometric ratio of the sample obtained is close to that of $CdIn_2S_4$. Besides the main elements of Cd, In and S, C and O were also detected, which might originate from mercaptoacetic acid and TAA.

Powder X-ray diffraction (XRD) analysis (Fig. 2a) reveals that the diffraction peaks become stronger and narrower with increasing reaction time. At 7 h, the relatively strong and sharp diffraction peaks at 27°, 44° and 51°, could be approximately indexed to the (3 1 1), (5 1 1) and (5 3 1) planes of cubic spinel phase of $CdIn_2S_4$ (JCPDS Card File No. 27-0060). Compared with the standard diffraction pattern of $CdIn_2S_4$, the broadness of the reflections is most probably due to the nanocrystalline nature of the powders.

UV–vis diffuse reflectance spectra (DRS) (Fig. 2b) have been carried out to illustrate the change of the band edge absorption of the $CdIn_2S_4$ obtained at different reaction time. With prolonging reaction time, the red-shift of the absorption can be obviously observed. When the reaction time is 7 h, the band edge absorption red shifts to 529 nm. The spectral change implies that the as-synthesized product after reacting for 7 h has wider visible light response.

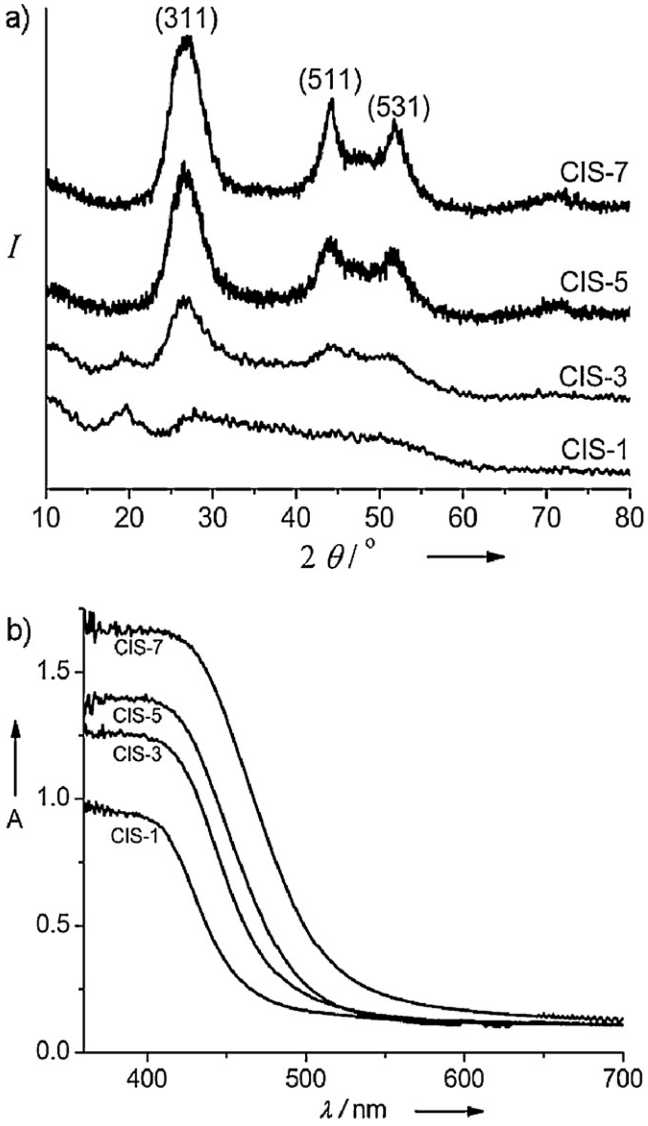

Fig. 2. XRD (a) and DRS (b) of $CdIn_2S_4$ spherical particles obtained after reacting for various time.

Considering the visible absorption of the as-synthesized $CdIn_2S_4$, we try to investigate its visible light photocatalytic activity. In this work, MeO is adopted as a representative organic pollutant in photocatalytic research since it is one of the most stable azo dyes extensively used in textile industry [39]. We evaluate the photocatalytic activity of the $CdIn_2S_4$ particles obtained at different reaction time by determining the MeO degradation efficiency in the presence of $CdIn_2S_4$ under 5 min visible light irradiation (Fig. 3a). The results show that the photocatalytic activity increases with prolonging reaction time in the preparation of $CdIn_2S_4$ spherical particles. The as-synthesized CIS-7 showed highest photodegradation efficiency. Approximately 98% of MeO can be degraded only under 15 min irradiation (Fig. 3b). On the other hand, it can be observed from Fig. 2 that the crystallinity of CIS-1 and CIS-3 is poor, which may lead to their low photocatalytic activity. Next, Fig. 1 shows that the size of CIS-5 is almost same as that of CIS-7. Therefore, the specific surface area has no great effects on the catalytic activities of CIS-5 and CIS-7. This high visible light photocatalytic activity of CIS-7 may be ascribed as follows: (i) the narrow

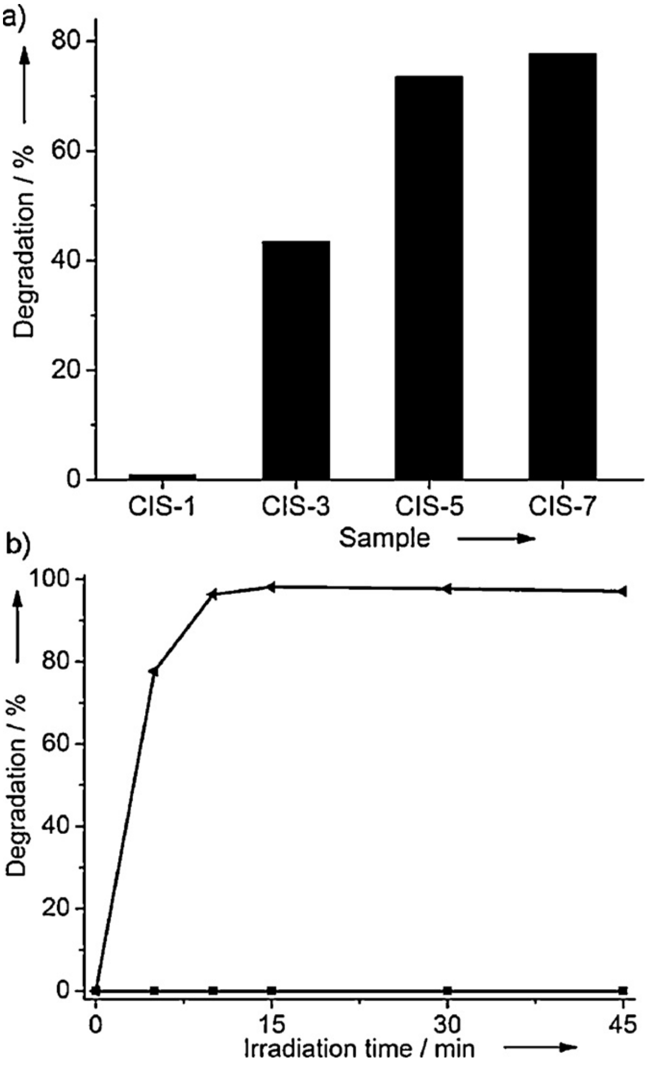

Fig. 3. (a) Visible light photocatalytic degradation efficiency of MeO under 5 min in the presence of $CdIn_2S_4$ spherical particles prepared at different reaction time. (b) Dynamic curves of photocatalytic degradation of MeO under visible light irradiation in the absence of catalyst (■) and in the presence of CIS-7 (◄), respectively (pH = 6, and the dosage of photocatalysts is 0.5 g L^{-1}).

band gap makes it be excited efficiently by visible light irradiation, as indicated in the UV–vis spectra of $CdIn_2S_4$; (ii) the dense spherical structure facilitates the immigration of photogenerated carriers towards the surface.

4. Conclusions

In summary, we have reported a simple method to produce uniform monodispersed $CdIn_2S_4$ spheres with diameters in the range of 230–240 nm by using mercaptoacetic acid as capping agent and thioacetamide as sulfur source. By altering the preparation time of $CdIn_2S_4$, the obtained spheres showed high photocatalytic activity for the MeO degradation under visible light irradiation. The present study indicates that the simple solution method is feasible to prepare the $CdIn_2S_4$ photocatalyst showing potential applications in photocatalysis.

Acknowledgements

This work was financially supported by the Key Project of the National Natural Science Foundation of China (No. 20933007) and the Key Discipline Development Program of Shanghai Municipal Education Commission (No. J51503).

References

[1] S. Libert, V. Gorshkov, V. Privman, D. Goia, E. Matijević, Adv. Colloid Interface Sci. 100–102 (2003) 169–183.
[2] Y. Zhu, W. Zhao, H. Chen, J. Shi, J. Phys. Chem. C 111 (2007) 5281–5285.
[3] C. Wang, Y. Chen, T. Wang, Z. Ma, Z. Su, Adv. Funct. Mater. 18 (2008) 355–361.
[4] I.U. Arachchige, S.L. Brock, Acc. Chem. Res. 40 (2007) 801–809.
[5] L. Shen, N. Bao, P.E. Prevelige, A. Gupta, J. Phys. Chem. C 114 (2010) 2551–2559.
[6] M.B. Sigman Jr., A. Ghezelbash, T. Hanrath, A.E. Saunders, F. Lee, B.A. Korgel, J. Am. Chem. Soc. 125 (2003) 16050–16057.
[7] W. Du, X. Qian, J. Yin, Q. Gong, Chem. Eur. J. 13 (2007) 8840–8846.
[8] P.H.C. Camargo, Y.H. Lee, U. Jeong, Z. Zou, Y. Xia, Langmuir 23 (2007) 2985–2992.
[9] H. Li, D. Chen, L. Li, F. Tang, L. Zhang, J. Ren, CrystEngComm 12 (2010) 1127–1133.
[10] J.-M. Herrmann, Catal. Today 53 (1999) 115–129.
[11] U.I. Gaya, A.H. Abdullah, J. Photochem. Photobiol. C 9 (2008) 1–12.
[12] C. Hariharan, Appl. Catal. A 304 (2006) 55–61.
[13] J. Yu, X. Yu, Environ. Sci. Technol. 42 (2008) 4902–4907.
[14] X. Gou, F. Cheng, Y. Shi, L. Zhang, S. Peng, J. Chen, P. Shen, J. Am. Chem. Soc. 128 (2006) 7222–7229.
[15] H. Zhong, Y. Zhou, M. Ye, Y. He, J. Ye, C. He, C. Yang, Y. Li, Chem. Mater. 20 (2008) 6434–6443.
[16] K.K. Banger, M.H.-C. Jin, J.D. Harris, P.E. Fanwick, A.F. Hepp, Inorg. Chem. 42 (2003) 7713–7715.
[17] D.T.T. Tran, L.M.C. Beltran, C.M. Kowalchuk, N.R. Trefiak, N.J. Taylor, J.F. Corrigan, Inorg. Chem. 41 (2002) 5693–5698.
[18] S.L. Castro, S.G. Bailey, R.P. Raffaelle, K.K. Banger, A.F. Hepp, J. Phys. Chem. B 108 (2004) 12429–12435.
[19] R. Zheng, X. Yang, H. Hu, Y. Qian, Mater. Res. Bull. 39 (2004) 933–937.
[20] S.L. Castro, S.G. Bailey, R.P. Raffaelle, K.K. Banger, A.F. Hepp, Chem. Mater. 15 (2003) 3142–3147.
[21] Y. Jiang, Y. Wu, X. Mo, W. Yu, Y. Xie, Y. Qian, Inorg. Chem. 39 (2000) 2964–2965.
[22] B.B. Kale, J.-O. Baeg, S.M. Lee, H. Chang, S.-J. Moon, C.W. Lee, Adv. Funct. Mater. 16 (2006) 1349–1354.
[23] L. Zheng, Y. Xu, Y. Song, C. Wu, M. Zhang, Y. Xie, Inorg. Chem. 48 (2009) 4003–4009.
[24] K. Cheng, C. Liang, Sol. Energy Mater. Sol. Cells 94 (2010) 1137–1145.
[25] S.K. Apte, S.N. Garaje, R.D. Bolade, J.D. Ambekar, M.V. Kulkarni, S.D. Naik, S.W. Gosavi, J.O. Baeg, B.B. Kale, J. Mater. Chem. 20 (2010) 6095–6102.
[26] K.Y. Rajpure, V.L. Mathe, C.H. Bhosale, Bull. Mater. Sci. 22 (1999) 927–931.
[27] S.N. Baek, T.S. Jeong, C.J. Youn, K.J. Hong, J.S. Park, D.C. Shin, Y.T. Yoo, J. Cryst. Growth 262 (2004) 259–264.
[28] S.H. You, K.J. Hong, T.S. Jeong, C.J. Youn, J.S. Park, B.J. Lee, J.W. Jeong, J. Cryst. Growth 271 (2004) 391–397.
[29] R.R. Sawant, S.S. Shinde, C.H. Bhosale, K.Y. Rajpure, Sol. Energy 84 (2010) 1208–1215.
[30] S.-H. Yu, M. Yoshimura, Adv. Funct. Mater. 12 (2002) 277–285.
[31] S.-H. Yu, M. Yoshimura, Adv. Funct. Mater. 12 (2002) 9–15.
[32] K.-H. Choi, W.-S. Chae, J.-S. Jung, Y.-R. Kin, Bull. Korean Chem. Soc. 30 (2009) 1118–1120.
[33] J. Hu, B. Deng, W. Zhang, K. Tang, Y. Qian, Inorg. Chem. 40 (2001) 3130–3133.
[34] J. Lu, Y. Xie, G. Du, X. Jiang, L. Zhu, X. Wang, Y. Qian, J. Mater. Chem. 12 (2002) 103–106.
[35] L. Fan, R. Guo, J. Phys. Chem. C 112 (2008) 10700–10706.
[36] X. Peng, J. Wickham, A.P. Alivisatos, J. Am. Chem. Soc. 120 (1998) 5343–5344.
[37] D.V. Goia, E. Matijević, Colloids Surf. A 146 (1999) 139–152.
[38] J. Park, V. Privman, E. Matijević, J. Phys. Chem. B 105 (2001) 11630–11635.
[39] N. Bao, X. Feng, Z. Yang, L. Shen, X. Lu, Environ. Sci. Technol. 38 (2004) 2729–2736.