Synthesis and optical properties of composites based on ZnS nanoparticles embedded in layered magadiite

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(Received 28 August 2013; revised 7 November 2013; Editor: George Christidis)

ABSTRACT: Composites based on ZnS nanoparticles embedded in layered magadiite were synthesized via a three step process: protonation of Na-magadiite, ion exchange in order to introduce Zn(NH$_3$)$_2^{2+}$ in the interlayer space, and addition of Na$_2$S to form ZnS particles in the interlayer space of magadiite. The composites obtained were characterized by X-ray powder diffraction (XRD), Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS), Transmission Electron Microscopy (TEM), Raman spectroscopy, Photoluminescence spectra (PL), and UV-visible transmission spectra (UV-vis). Results indicated that ZnS nanoparticles embedded in magadiite presented different optical properties and photoluminescence enhancement properties compared with those of uncovered ZnS particles (without host magadiite).

KEYWORDS: magadiite, ZnS, photoluminescence, nanoparticles, composite.

II–IV semiconductor ZnS nanoparticles have been studied extensively because of their potential applications in blue/green light-emitting diodes (LEDs), electroluminescence devices (ELDs), optoelectronic data storage, etc. (Oliver et al., 1970; Manzoor et al., 2004; Rizzo et al., 2007). The most striking feature of ZnS nanocrystallites is that their chemical and physical properties differ dramatically from those of the bulk solids. Moreover, the inherent photoluminescence (PL) properties of ZnS can be improved by controlling particle size and surface defects (Tiwari et al., 2012). Because of the large surface area of nanoparticles, surface defects play an important role in their quantum efficiency.

Nanoparticles easily aggregate because of high surface energy and this characteristic greatly limits their applications. To overcome this difficulty, various approaches have been proposed to control the particle size and surface defects and thus enhance their stability and improve their photoluminescence by using polymers (Lu et al., 2003; Xi et al., 2003; Xie et al., 2008; Ullah et al., 2008; Ummartyotin et al., 2012) and organic molecules (Chatterjee et al., 2007; Unni et al., 2009; Mehta et al., 2011). In addition, studies on ZnS nanoparticles incorporated in inorganic matrices have been carried out. For instance, Khaorapong et al. (2010) have intercalated ZnS and CdS nanoparticles in the interlayer spaces of montmorillonite by solid–solid reactions between Zn(II)- or Cd(II)-montmorillonite and Na$_2$S at ambient temperatures. CdSe/ZnS nanoparticles were coated with silica by a polyvinyl alcohol (PVA) polymer coating (Sung & Lo, 2012). A ZnS-graphene nanocomposite was synthesized by an one-step hydrothermal method (Pan & Liu 2012), ZnS nanoparticles were embedded in SiO$_2$ by coating (Han et al., 2007) or cosputtering (Taghavinia & Yao, 2004) and ZnS nanoparticles have been incorporated in inorganic materials by other methods (W.H. Zhang et al.,...
2001; J. Zhang et al., 2003; Sayle et al., 2006; Kozak et al., 2010; Song et al., 2013). The ZnS nanoparticles exhibit different photoluminescent properties when combined with different organic molecules or incorporated into different inorganic materials or polymers (Ni et al., 2005; Ullah et al., 2008; Chen et al., 2010; Khaorapapong et al., 2010; Ummartyotin et al., 2012; Pan et al., 2012).

Magadiite (Na$_2$Si$_{14}$O$_{29}$·$x$H$_2$O) is an alternative host for controlling the sizes of semiconductor ZnS nanoparticles because of its special structure. It is a layer silicate which is composed of two-dimensional units of host layers and a guest cation between the layers (Brandt et al., 1988; Eypert-Blaison et al., 2001a,b; Aline et al., 2009). It is a useful host material which exhibits a broad range of properties, including adsorption, intercalation, exfoliation, and organization of guest species (Wang et al., 2003; Petrucelli et al., 2006; Díaz et al., 2007; Guerra et al., 2008; Yukutake et al., 2009).

Therefore, layered magadiite can be used as a host for ZnS particles; it will control the sizes of ZnS incorporated in the interlayer space by flexibly adjusting its interlayer distance. In this contribution, we propose a three-step approach to incorporating ZnS in the interlayer space of magadiite which was selected as host material because of its excellent chemical and thermal stability, high optical transparency in the visible region and the layer structure. Moreover, it is more effective to use H-magadiite instead of Na-magadiite to perform ion-exchange with Zn(NH$_3$)$_4^{2+}$ ions. The new composites based on ZnS incorporated into magadiite should have higher stability and antioxidation properties and be more resistant to acids compared with pure ZnS. Furthermore, this study also extends the application of magadiite to the optical field.

**MATERIALS AND METHODS**

**Preparation of Na-magadiite and H-magadiite**

Silica gel (SiO$_2$) solution (40 wt.%) and chemical reagents NaOH, Na$_2$CO$_3$, ZnCl$_2$, NH$_3$·H$_2$O, and Na$_2$S·9H$_2$O of AR grade were purchased from the Chemistry Reagent Corporation of the National Medicine Group. Na-magadiite was prepared by reaction of the SiO$_2$-NaOH-Na$_2$CO$_3$ system under hydrothermal conditions (Kwon, et al., 1995) in a sealed teflon-lined autoclave at 150°C using silica gel solution (15 mL 40 wt.%) and 70 mL of deionized H$_2$O, 0.9739 g NaOH and 2.8693 g Na$_2$CO$_3$ as reactants. After four days, the product was filtered, washed with deionized water and dried at 40°C for 12 h. The magadiite sample obtained was labelled as Na-Mag. The protonation of the Na-Mag (3.7295 g) was performed by soaking in 50 mL 0.2 M HCl aqueous solution for 24 h while stirring. The H-magadiite obtained was filtered, water-washed, dried at 40°C in air and labelled as H-Mag.

**Preparation of composites based on ZnS embedded in magadiite**

The Zn(NH$_3$)$_4^{2+}$ solution (0.2 M) was prepared by the reaction of ZnCl$_2$ (5.4412 g) with NH$_3$ solution (200 mL, 6 M). In order to introduce ZnS nanoparticles into the interlayer space of H-Mag, a three-step process was involved. The first step comprised protonation of Na-mag by HCl and formation of H-mag. The second step involved ion exchange in order to introduce Zn(NH$_3$)$_4^{2+}$ into the interlayer space of H-mag by adding 2.6132 g of H-Mag to Zn(NH$_3$)$_4^{2+}$ aqueous solution (200 mL, 0.2 M) and stirring for three days at room temperature. The pH of the mixed suspension was increased to 11.8 to avoid hydrolysis of Zn(NH$_3$)$_4^{2+}$ (Bases & Mesmer, 1976); then part of the sediment from the mixed suspension was filtered, washed, and dried at 40°C for 12 h. The dried product (Zn-intercalated magadiite) was labelled as Zn-Mag. The remaining sediment was filtered, washed, and quickly dispersed into deionized water (200 mL) to form a new suspension in order to remove excess Zn(NH$_3$)$_4^{2+}$, because it can react with Na$_2$S to form ZnS outside the interlayer space of magadiite (Vorokh et al., 2008). The new suspension (200 mL) was divided into two equal parts. In the third step 10 mL and 25 mL of 0.1 M Na$_2$S solution were gradually added to the two suspensions, respectively, under continuous stirring. The final products (labelled as ZnS-Mag-1 and ZnS-Mag-2) having different ZnS content were filtered, washed with deionized water, and dried at 40°C for 12 h.

In addition to the ZnS-Mag composites, pure ZnS without host magadiite was prepared, by adding 25 mL of 0.1 M Na$_2$S solution to 50 mL of 0.2 M Zn(NH$_3$)$_4^{2+}$ solution while stirring. The ZnS obtained was filtered, washed with deionized water, and dried at 40°C for 12 h.
**Characterization**

X-ray powder diffraction (XRD) patterns were obtained on a Bruker D8 Focus diffractometer using Cu-Kα radiation. The samples were scanned in the 2θ range of 3–70° at a scan rate 2°/min. The Raman spectra were collected with a Renishaw inVia Raman Microscope using a 633 nm line from an argon-ion laser. The optical properties were determined by UV-vis transmission spectrophotometry (U-4100 Spectrophotometer). The data mode was based on transmission with scanning speed of 600 nm/min and slit width of 2.00 nm. The photoluminescent spectra were obtained by a F-7000 FL Spectrophotometer using the emission scanning and fluorescence data modes.

Thermogravimetric (TG) and differential thermal analysis (DTA) data were collected using synchronous thermal analyser (Pyris Diamond, American PE Company) in a dynamic atmosphere using dry nitrogen flux, in the temperature range 25–800°C at a heating rate of 10°C/min. An environmental scanning electron microscope equipped with energy dispersive X-ray analytical facilities (SEM-EDX XL30 ESEM FEG, Philips, Genesis2000, Netherlands) was used for the morphological analysis of the surface structure and to determine Na, Zn, Si, S and O elemental composition of the samples. An accelerating voltage of 20 keV was used for the EDX microanalysis. The Zn content of the samples was determined also by inductively coupled plasma atomic emission spectroscopy (ICP-AES OPTIMA 5300 DV, America). The H and S contents were determined with a CHNS elemental analyser (Elementar Vario EL II, Germany). The chemical formulae were estimated from the results of ICP, EDX, and CHNS element analyses.

**RESULTS AND DISCUSSION**

**Composition and structure of the nanocomposite**

The chemical compositions of Na-Mag, ZnS-Mag-1, and ZnS-Mag-2 are shown in Table 1 and Fig. 1. The Na:Si:O:H molar ratio of Na-mag was 2.0:13.9:36.0:14.4. By combining the analytical data and the charge-balance principle, an empirical structural formula was calculated for the Na-magadiite, namely Na$_2$Si$_{14}$O$_{29}$$\cdot$$x$H$_2$O, which is comparable with the formula Na$_2$Si$_{14}$O$_{29}$$\cdot$H$_2$O suggested in previous works (Lagaly et al., 1975; Garces et al., 1988). The relative errors for Na (−0.4%), Si (0.07%) and O (0.07%) are very small, suggesting that the chemical formula is rational. The relative error for H is higher (2.10%), due to the lower H content and the adsorbed water. Based on the same method, the molar ratios of Zn:Si:O:S:H for the ZnS-Mag-1 and ZnS-Mag-2 composites were estimated at 1.2:13.9:30.4:0.2:3.2 and 1.6:13.8:29.9:0.6:2.6 respectively. The empirical structural formulae of the ZnS-Mag-1 and ZnS-Mag-2 composites were Zn$_{1.0}$Si$_{13.9}$O$_{28.8}$(ZnS)$_{0.18}$$\cdot$1.6H$_2$O and

<table>
<thead>
<tr>
<th>Table 1. Chemical composition of Na-Mag and ZnS-Mag composites.</th>
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<tbody>
<tr>
<td>Samples</td>
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<tr>
<td>Na-Mag</td>
</tr>
<tr>
<td>4.48 (4.46)</td>
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<tr>
<td>Molar ratio: Na: Si: O: H = 2.0:13.9:36.0:14.4</td>
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<tr>
<td>ZnS-Mag-1</td>
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<tr>
<td>Molar ratio: Zn: Si: O: S: H =1.2: 13.9:30.4:0.2: 3.2</td>
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<tr>
<td>ZnS-Mag-2</td>
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<tr>
<td>Molar ratio: Zn: Si: O: S: H =1.6: 13.8:29.9: 0.6: 2.6</td>
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</tbody>
</table>

* Calculated (determined): Si and O analysed by EDX; Na and Zn analysed by EDX and ICP; S obtained from EDX and CHN elemental analysis; H obtained from CHN elemental analysis
Zn$_{1.0}$Si$_{13.8}$O$_{28.6}$(ZnS)$_{0.62}$·1.3H$_2$O, respectively. The calculated and experimental values of Zn, Si, O, S, and H present in the ZnS-Mag-1 and ZnS-Mag-2 composites are comparable, indicating that the structural formulae are rational.

X-ray diffraction patterns of pure ZnS and of Na-Mag, H-Mag, Zn-Mag, ZnS-Mag-1, and ZnS-Mag-2 are shown in Fig. 2. The diffraction lines of ZnS occur at $2\theta = 29.3$, 48.7 and 56.5°, in agreement with previous work (Evans & McKnight, 1959, PDF# 12-0688). Na-Mag showed a $d_{001}$ reflection at 15.4 Å in accordance with previous studies (Schwieger et al., 1985). The cell parameters of Na-Mag were refined as $a = 7.205(4)$, $b = 7.235(8)$, $c = 15.42(2)$ Å; $\beta = 92.40(8)^\circ$, which are similar to values reported in the literature ($a = 7.25$, $b = 7.25$, $c = 15.69$ Å, $\beta = 96.8^\circ$, after Schwieger et al., 1985). After reaction of the Na-Mag with HCl, the $d_{001}$ of Na-Mag decreased to 11.4 Å (H-mag) due to

Fig. 1. EDX spectra of Na-Mag, ZnS-Mag-1 and ZnS-Mag-2.

Fig. 2. XRD patterns of Na-Mag, H-Mag, Zn-Mag, ZnS-Mag-1, ZnS-Mag-2, and pure ZnS.
the loss of the interlayer water following replacement of Na\(^+\) cations by protons. Moreover, except for a strong diffraction maximum at \(\sim 26^\circ\) 2\(\theta\), other peaks were very weak in agreement with previous reports (Kooli & Yan, 2009; Peng et al., 2006). When the H-Mag reacted with Zn(NH\(_3\))\(_4^{2+}\) aqueous solution, the intermediate product Zn-Mag exhibited different XRD patterns. Most reflections originated from Zn-Mag can be indexed as based on the H\(_2\)Si\(_{14}\)O\(_{29}\) 5.4H\(_2\)O phase [PDF# 29-0668] (Fig. 2). The cell parameters of Zn-Mag were refined as \(a = 7.088(4)\) Å, \(b = 7.360(7)\) Å; \(c = 15.12(1)\) Å; \(\beta = 93.7(1)^\circ\). When S\(^2-\) was introduced to Zn-Mag, the final products ZnS-Mag-1 and ZnS-Mag-2 retained the layered structure of original Na-magadiite. Moreover, both the ZnS-Mag-1 and ZnS-Mag-2 have basal spacings similar to the initial Na-Mag (15.0–15.1 Å and 15.4 Å respectively). This may be attributed to two reverse effects; the increasing interlayer spacing caused by the introduction of ZnS to H-Mag and the decreasing interlayer spacing caused by the loss of interlayer water occurred simultaneously, leading to invariable basal spacing. Some reflections attributed to ZnS were observed in the X-ray patterns of ZnS-Mag-1 and ZnS-Mag-2 composites.

The crystal morphologies of Na-Mag, H-Mag, ZnS-Mag-1 and ZnS-Mag-2 are presented in Fig. 3. The morphology of H-Mag is distinct from that of Na-Mag (Feng & Balkus, 2003). This may result from the exchange of Na\(^+\) by H\(^+\) ions. During the process, the layer-by-layer stack for the magadiite may change when the Na\(^+\) ions were exchanged by H\(^+\) ions. However, the XRD patterns of H-Mag were very different from that of the Na-Mag. The structural changes of the samples may lead to morphological changes. The crystal shapes of ZnS-Mag-1 and ZnS-Mag-2 are similar to that of H-Mag, but different from that of Na-Mag, which further suggests that the differences in the morphologies among Na-Mag, H-Mag, and ZnS-Mag composites are mainly attributed to the protonation.

Raman spectra and thermogravimetric analysis

The Raman spectra of H-Mag, Zn-Mag, ZnS-Mag-2 and pure ZnS are shown in Fig. 4. For H-Mag, weak bands at 488 and 464 cm\(^{-1}\) are attributed to Si–O–Si symmetric stretching modes (Huang et al., 1999). With regard to ZnS, the band at 257 cm\(^{-1}\) is assigned to transverse optical (TO) phonons of ZnS nanoparticles. The band at 351 cm\(^{-1}\) is assigned to longitudinal optical (LO) phonon frequency (Schneider & Kirby, 1972; Acharya et al., 2013). After the ion-exchange of H\(^+\) by Zn\(^{2+}\), the band at 464 cm\(^{-1}\) became stronger.
Then a very weak band at 257 cm$^{-1}$ was observed as the ZnS was introduced to the magadiite. These results indicate that the ZnS nanoparticles were intercalated to the host magadiite.

The thermogravimetric analysis (TG) was used to study the thermal decomposition behaviour of Na-Mag, H-Mag, Zn-Mag, ZnS-Mag-2, and pure ZnS (Fig. 5). The TG curve of Na-Mag exhibits three distinct stages of thermal degradation between 25 and 270°C, resulting to 13.5% total weight loss. The first stage (6.6% weight loss) between 25 and 85°C is assigned to physically adsorbed water and interlayer water (Aline & Alexandre, 2009). The second stage, which corresponds to 6.0% weight loss, was observed between 85 and 135°C, and is attributed to interlayer water loss (Aline & Alexandre, 2009). The third thermal stage occurred between 135 and 270°C, and is attributed to silanol condensation to siloxanes (Aline & Alexandre, 2009). At temperatures higher than 270°C, the small mass loss is attributed to silanol condensation.

The thermal decomposition of H-Mag is analogous to that reported in the literature (Macedo et al., 2007; Kooli et al., 2002). H-Mag exhibits initial weight loss of 0.7% below 320°C due to loss of H$_2$O. The 1.6% weight loss in the temperature range 320–400°C is attributed to the elimination of OH groups (Kooli et al., 2002). The thermal decomposition of Zn-Mag is markedly different from those of Na-Mag and H-Mag. It is characterized by four weight loss steps. The first stage ranging from 25 to 142°C (weight loss 5.3%) is assigned to physically adsorbed water and interlayer water loss. The second stage between 142 and 340°C (weight loss 2.7%) is due to hydrolysis of interlayer Zn species. The third stage between 340 and 470°C (weight loss 2.3%) is attributed mainly to decomposition of hydrolysis products such as Zn(OH)$_2$ (Bénard et al., 1994). After intercalation of ZnS in the magadiite interlayer, the mass loss stages of ZnS-Mag-2 became less obvious. This may be due to the effects of ZnS nanoparticles combined with host magadiite. The thermal decomposition of the ZnS-Mag-2 is characteristic of both the H-Mag and the ZnS, confirming the formation of a composite based on ZnS embedded in magadiite.

**UV-visible spectra and photoluminescence spectra**

The UV-vis spectra of Na-Mag, H-Mag, Zn-Mag, ZnS-Mag-1, ZnS-Mag-2, and pure ZnS are shown in Fig. 6. The transmission-edge of pure ZnS appeared at 325–400 nm (Zhu et al., 2001), and the transmission-edge of Na-Mag was observed at 250–300 nm. After protonation and ion-exchange of H$^+$ by Zn species, the transmission-edge of Zn-Mag shifted to 300–330 nm. In comparison, the transmission-edges of ZnS-Mag composites shifted to lower energy as the ZnS was introduced to host magadiite, which are different from those of Na-Mag, H-Mag, Zn-Mag, and pure ZnS. It was clearly observed that the transmission-edges of ZnS-Mag composites occurred between those of the Na-Mag and ZnS. Moreover, the transmission-edge of ZnS-Mag-2 is closer to that of pure ZnS compared with that of ZnS-Mag-1, which may be due to more content and larger size of ZnS particles in the ZnS-
Mag-2 compared to the ZnS-Mag-1. This indicates the formation of ZnS nanoparticles in the host magadiite, which is consistent with the photoluminescence spectra described below.

The photoluminescence (PL) spectra of pure ZnS, ZnS-Mag-1, and ZnS-Mag-2, which were excited under different wavelengths from 260 to 340 nm, with 10–20 nm steps, are shown in Fig. 7. The PL spectra of pure ZnS present two peaks at 395 and 467 nm at excitation wavelengths of 260–280 nm. The violet emission peak at about 395 nm may be attributed to the zinc interstitial ions (Wageh et al., 2013) or the recombination of electrons from the energy level of sulfur vacancies (VSE) with the holes from the valence band (Zhang et al., 2007; Lu et al., 2012), whereas the weak peak at 460 nm may arise from the surface states (Denzler et al., 1998; Yang et al., 2001; Wang et al., 2002; Chai et al., 2007). As the excitation wavelength changed to 300–340 nm, the peak at 395 nm became broad and shifted slightly to ~415 nm. This indicates that there were two emission states with different energies in the excitation range of 260–340 nm. These emission states at 395 and 415 nm are attributed to zinc interstitial ions and sulfur vacancies, respectively (Unni et al., 2009; Wageh et al., 2013). The peak at 467 nm attributed to the surface state hardly shifted with changing excitation wavelengths since the surface state may not change during excitation. After a small content of ZnS was incorporated into magadiite, a strong peak at 415 nm and two weak shoulders at 326–342 nm and 467 nm were found in the PL spectra of ZnS-Mag-1 at excitation wavelength 260–280 nm. The peak at 415 nm present in the ZnS-Mag-1 is obviously stronger than that in the ZnS, but the shoulder at 467 nm was weaker compared to that of pure ZnS. The new shoulder at 326–342 nm corresponds to band-edge emission of ZnS nanoparticles (Lu et al., 2012; Wageh et al., 2013), which is in accordance with the transmission-edge of ZnS-Mag-1. These results suggest that the photoluminescence properties of ZnS nanoparticles incorporated into magadiite may be modified by the host magadiite. Previous studies on the ZnS nanoparticles incorporated in inorganic or organic host materials have reported that ZnS nanoparticles...
incorporated in different inorganic or organic host materials have different photoluminescence properties (Ni et al., 2005; Ullah et al., 2008; Chen et al., 2010; Khaorapapong et al., 2010; Pan et al., 2012; Ummartyotin et al., 2012). The PL spectra of ZnS-Mag-2 are similar to that of pure ZnS, probably because some ZnS particles, which have not been incorporated into the interlayer space of magadiite, may have a larger size and thus exhibit similar photoluminescence as the pure ZnS.

CONCLUSION
Nanocomposites based on ZnS nanoparticles embedded in host magadiite have been synthesized by a three-step process. XRD, TG-DTA, and Raman results indicated the formation of composites containing the ZnS nanoparticles. Photoluminescence and UV-vis transmission spectra proved that the optical properties of ZnS particles can be modified by the host magadiite.

ACKNOWLEDGMENTS
The Project was supported by the National Natural Science Foundation of China (Grant No.51162021).

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