



Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Hydrothermal synthesis of zinc selenide in smectites

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ARTICLE INFO

Article history:

Received 14 June 2016

Received in revised form 2 September 2016

Accepted 2 September 2016

Available online xxxx

Keywords:

Zinc selenide

Montmorillonite

Saponite

Intercalation

ABSTRACT

Nanohybrids of zinc selenide and smectites (a natural montmorillonite and a synthetic saponite) were prepared by a hydrothermal reaction of zinc chloride and sodium selenosulfite in the presence of smectites. The products were characterized by powder X-ray diffraction, scanning and transmission electron microscopies, thermogravimetric analysis, as well as, UV–visible and photoluminescence spectroscopies. The round-shaped zinc selenide nanoparticles with the average diameter of 1–4 nm formed in the interlayer space of smectites, which gave the absorption onsets at 379–456 nm for montmorillonite system and at 475 nm for saponite system. Additional absorption onsets were observed at around 478–665 nm for montmorillonite system and at 609–682 nm for saponite system, suggesting the larger-sized particles formed at the external surfaces. The photoluminescence observed in the wavelength range of 357–360 nm was interpreted to the formation of zinc selenide nanoparticles in smectites. The increase of the photoluminescence intensities of all the products (from 35 for bulk ZnSe to 126–294 for ZnSe(n)-smectites) was thought to be caused by the interactions with smectites and/or size and shape of ZnSe formed in the hybrids.

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1. Introduction

Hybridization of organic and/or inorganic species and inorganic layered solids has drawn much attention because it is a way to obtain ordered organic-inorganic or inorganic-inorganic materials with novel physical and chemical properties controlled by host-guest and guest-guest interactions (Ogawa and Kuroda, 1995, 1997; Ogawa, 1998, 2004; Lagaly et al., 2006; Okada et al., 2012; Ide et al., 2014; Ogawa et al., 2014). Smectite has received a great interest due to their peculiar features such as large surface area, swelling ability, cation exchange property and so on for organizing a wide variety of guest species (Okada et al., 2014).

It is well known that the optical properties of semiconductors could be modified by controlling the size and shape. Zinc selenide (ZnSe) has been used in such optoelectronic applications as blue-emitting device and photocatalysts (Shavel et al., 2004; Fang et al., 2009; Zhang et al., 2009b; Chen et al., 2012). Numerous methods were developed to synthesize highly luminescent ZnSe nanocrystals (Chen and Gao, 2005; Qian et al., 2006; Zhang et al., 2009a; Zhang et al., 2010), while the preparation was complicated and toxic, and/or explosive chemicals were used. Hydrothermal syntheses of nanocrystalline and microcrystalline ZnSe were reported (Quinlan et al., 2000; Peng et al., 2001; Gong et al., 2007, 2008; Li et al., 2010; Chen et al., 2012). The precise control of the optical properties of ZnSe nanoparticle is limited due to the growth

of particles with increasing reaction temperature and time (Quinlan et al., 2000; Peng et al., 2001; Gong et al., 2008; Li et al., 2010). A number of host matrices were used to tune the optical properties and stability of semiconductor nanoparticles (Han et al., 2008; Ontam et al., 2012b; Kabilaphat et al., 2015a, 2015b, 2016). The deposition of ZnSe on SiO₂, carbon and graphene for the improved thermal stability has been reported so far (Hao et al., 2007; Pol et al., 2007; Wang et al., 2009; Chen et al., 2012; Wang et al., 2015). The controlled spatial distribution of the size controlled ZnSe particles is a key to tune the performance of the functional hybrids.

Smectites have been used as supports of semiconductor nanoparticles to encapsulate or protect the particle from aggregation (Enea and Bard, 1986; Yoneyama et al., 1989; Hur et al., 2006; Han et al., 2008; Khaorapong et al., 2010, 2011, 2015; Gao et al., 2011; Ontam et al., 2011, 2012a, 2012b; Khumchoo et al., 2015; Goto and Ogawa, 2015, 2016). Besides the hierarchical structures of the hybrids, the size and the spatial distribution of nanoparticles are parameters to control optical, catalytic, and chemical properties of the resulting hybrids. This paper reports the synthesis and properties of ZnSe-smectite hybrids. The thermal stability and luminescence intensity were modified for the supported ZnSe if compared with bare ZnSe nanoparticles. Because ZnSe with large content of surface atom is very sensitive in ambient condition, *herein*, we report the formation of ZnSe nanoparticles in the interlayer space of montmorillonite and synthetic saponite by hydrothermal reaction of zinc chloride and selenosulfite in the presence of smectites. To the best of our knowledge, the incorporation of ZnSe in the interlayer space of smectites has not been reported so far. The study

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on the optical properties of the stored and heated products was also investigated. This may open a novel way to control the optical properties and thermal stability of the semiconductor particle for the uses in the next generation of the optical and sensing devices.

2. Experimental

2.1. Materials

Two sodium forms of smectites, a natural montmorillonite (Kunipia F, Kunimine Industries, the reference clay sample of the Clay Science Society of Japan; JCSS-3101) and a synthetic saponite (Sumecton SA, the reference clay sample of the Clay Science Society of Japan, JCSS-3501, synthesized hydrothermally by Kunimine Industries, Japan) were used as the host materials. The cation exchange capacities (CEC) of the clay minerals were 1.20 and 0.70 meq/g of montmorillonite and synthetic saponite, respectively. Zinc chloride (ZnCl_2) was obtained by Carlo Erba Reagent. Selenium (Se) powder was purchased from Sigma-Aldrich. Sodium sulfite (Na_2SO_3) was supplied by APS Finechem. All chemicals are reagent grade and were used as received without any further purification.

2.2. Preparation of ZnSe and ZnSe-smectites

ZnSe was obtained by the hydrothermal reaction between the aqueous solutions of zinc chloride (ZnCl_2) and sodium selenosulfite (Na_2SeSO_3) prepared according to the previous report (Yochelis and Hodes, 2004). The aqueous mixture of ZnCl_2 and Na_2SeSO_3 was magnetically stirred for 5 min and transferred into a Teflon-lined autoclave to be heated at 150 °C for 6 h. The molar ratio of $\text{Zn}^{2+}:\text{Se}^{2-}$ was 1:1. After the reaction, the yellow solid was collected by centrifugation, washed several times with deionized water and finally dried at 60 °C for 3 days.

The experimental procedure for the preparation of ZnSe-smectites was the same as that for pure ZnSe except that the aqueous solution of ZnCl_2 was replaced by the aqueous dispersion of Zn^{2+} -montmorillonite (or Zn^{2+} -saponite), which was prepared by the conventional ion exchange reaction of the smectites with aqueous solution of ZnCl_2 (Khaorapong and Ogawa, 2008). The products were designated as ZnSe(*n*)-Mt or ZnSe(*n*)-Sap, where “*n*” in the parenthesis indicated the reaction period (in hour).

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE diffractometer using monochromatic $\text{CuK}\alpha$ radiation. Thermal analysis (TG-DTA) was measured on a Perkin Elmer Pyris Diamond TG-DTA instrument under a dry air at a heating rate of 10 °C min^{-1} using α -alumina ($\alpha\text{-Al}_2\text{O}_3$) as the standard material. Scanning electron micrograph (SEM) was obtained on a SEC Mini-SEM SNE-4500 M. Transmission electron micrograph (TEM) was obtained on a Tecnai G² 20 transmission electron microscope operating at 200 kV (FEI). Diffuse reflectance absorption spectra of the solid samples were conducted in the range of 200–800 nm with a Shimadzu UV–vis-

NIR3101PC spectrophotometer using an integrated sphere. Photoluminescence (PL) spectra of the products were taken on a Shimadzu RF-5301PC spectrofluorophotometer in the wavelength range of 335–480 nm with the excitation wavelength of 300 nm and the slit widths of 3 for the excitation and 5 for the emission.

3. Results and discussion

After the hydrothermal reaction, colored solids were obtained (orange for ZnSe(6)-Mt (Fig. 1a), cream for ZnSe(4)-Mt and ZnSe(2)-Mt (Fig. 1b–c) and brown for ZnSe(*n*)-Sap, (Fig. 1d–f)). The difference in the color of the products was caused by the difference in the size and/or shape of the intercalated ZnSe nanoparticles (the loading amount of ZnSe in all of the products was equal to the CEC of the smectites). The XRD pattern of bulk ZnSe (Fig. 2, inset) shows the reflections located at $2\theta = 27, 45, 54$ and 67° ($d = 0.33, 0.20, 0.17$ and 0.14 nm) that were indexed to the zinc blende ZnSe (JCPDS 37–1463) (Gong et al., 2008). After the hydrothermal reaction, the (001) reflection of ZnSe(*n*)-smectites was ca. 1.26–1.28 nm. Because the products were prepared in aqueous solution, the increase of the basal spacing can be ascribed to the hydration. In order to exclude this possibility, the products were heated at 200 °C for 2 h. The basal spacings (d_{001}) of all the heat treated products maintained the same basal spacings (ca. 1.24–1.26 nm) as listed in Table 1 and shown in Fig. 2, while those of the heated smectites were decreased due to the dehydration (from 1.21 to 1.08 nm for montmorillonite and from 1.22 to 1.07 nm for saponite, Fig. S1). By subtracting the thickness of the silicate layer (0.96 nm) from the observed basal spacings, the expansion of the interlayer spaces was determined to be ca. 0.28–0.30 nm. In addition, there were no other reflections due to any ZnSe form (ZnSeO_3 and/or ZnSeO_4). From the expansion of the interlayer space as well as the change in the color of all products, the formation of ZnSe nanoparticles in the interlayer space of smectites by the present hydrothermal reaction was confirmed.

TG-DTA curves of ZnSe(6)-Mt and ZnSe(6)-Sap are shown in Fig. 3 together with those of bulk ZnSe (Fig. 3, inset). The mass gain owing to the oxidation of ZnSe was seen from 240 to 340 °C for bulk ZnSe, which associated the exothermic peak at around 253 °C, corresponding to the formation of ZnO together with ZnSeO_3 and/or ZnSeO_4 (Liu et al., 2008; Moezzi et al., 2013). The decomposition of ZnSeO_3 and/or ZnSeO_4 took place at around 454 to 680 °C (Jiang et al., 2006). In the TG-DTA curves of all hybrids, dehydration occurred in the temperature below 200 °C, meanwhile, the dehydroxylation of the silicate layer occurred at above 400 and 310 °C for montmorillonite and saponite, respectively. The thermal behavior of ZnSe in smectites is different from pristine ZnSe. The mass gain due to the oxidation of ZnSe was not observed for ZnSe(*n*)-Mt, while, it was seen for ZnSe(*n*)-Sap at higher temperature (290–370 °C) than that observed for pristine ZnSe (240–340 °C). The subsequent mass loss due to the oxidation and thermal decomposition of the intercalated ZnSe and ZnSeO_3 and/or ZnSeO_4 in the ZnSe(*n*)-smectites revealed at the temperature (above 400 °C) higher than that of bare ZnSe, indicating to the protection of the ZnSe particle from the decomposition. This suggested the improvement of the thermal stability of ZnSe in the hybrids.

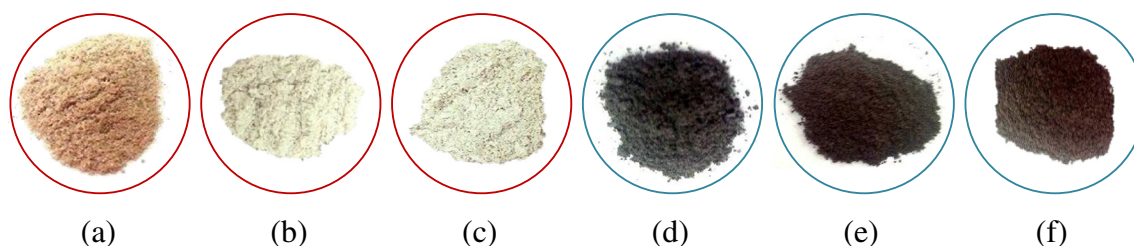


Fig. 1. Colors of ZnSe(6)-Mt (a), ZnSe(4)-Mt (b), ZnSe(2)-Mt (c), ZnSe(6)-Sap (d), ZnSe(4)-Sap (e), ZnSe(2)-Sap (f).

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