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Low-temperature synthesis of hexagonal transition metal ion doped ZnS nanoparticles by a simple colloidal method

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ABSTRACT

A general route to synthesize transition metal ions doped ZnS nanoparticles with hexagonal phase by means of a conventional reverse micelle at a low temperature is developed. The synthesis involves *N*,*N*-dimethylformamide, $Zn(AC)_2$ solution, thiourea, ammonia, mercaptoacetic acid, as oil phase, water phase, sulfide source, pH regulator, and surfactant, respectively. Thiourea, ammonia and mercaptoacetic acid are demonstrated crucial factors, whose effects have been studied in detail. In addition, the FT-IR spectra suggest that mercaptoacetic acid may form complex chelates with Zn^{2+} in the preparation. In the case of Cu^{2+} as a doped ion, hexagonal ZnS:Cu^{2+} nanoparticles were synthesized at 95 °C for the first time. The X-ray diffraction (XRD) and transmission electron microscope (TEM) measurements show that the ZnS:Cu^{2+} nanoparticles are polycrystalline and possess uniform particle size. The possible formation mechanism of the hexagonal doped ZnS is discussed.

1. Introduction

ZnS, a II–VI intrinsic semiconductor with good electroluminescent properties, has attracted much research interest in decades [1]. It is well known that ZnS has two crystal lattices, zinc blende (cubic) and wurtzite-type (hexagonal), which both have a wide bandgap. The bandgap of wurtzite ZnS (3.77 eV) is higher than that of cubic one (3.68 eV). Thus, wurtzite ZnS has large potential applications in electronics and optoelectronics such as ultraviolet light-emitting diodes [2].

ZnS nanoparticles (NPs) doped with transition metal ions have different optical properties compared with conventional bulk materials. ZnS:Cu^{2+} NPs, for example, exhibit good blue-green fluorescence properties in the 400 – 500 nm range [3], and ZnS:Mn nanocrystals have a high intensity and short-lived orange fluorescence [4]. The doping effect on ZnS semiconductor nanocrystals, however, is not only confined to alternate the optical and electrical properties, but also to promote the structural transformation. It is demonstrated that Mn^{2+} and Cl^- ions in the ZnS nanocrystals play an important role in the phase transition mechanism from cubic to hexagonal phase [5]. The transformation of ZnS from cubic to hexagonal phase normally occurs at 1296 K [6]. Synthesis at such a high temperature is, obviously, quite energy-consuming, which may involve complicated anti-oxidation equipment. Therefore, research for a simple energy-saving method to synthesize hexagonal ZnS at low temperature is highly desired.

In fact, it is possible to synthesize hexagonal ZnS at a relatively low temperature ranging from 110 to 280 °C via microwave or hydrothermal route with some precursors [7,9]. Furthermore, hexagonal ZnS was synthesized even in absence of precursors by using solvothermal and a new colloidal route at 100 and 150 °C, respectively [10,11]. In the above cases where hexagonal ZnS was prepared at low temperature, however, special equipments such as Teflon-lined autoclave or microwave oven are involved, making the synthetic procedures somewhat complicated and expensive.

In the present work, we developed, for the first time, a simple colloidal approach for the synthesis of hexagonal ZnS:Cu^{2+} NPs at a relatively low temperature with *N*,*N*-dimethylformamide (DMF) as the oil phase, $Zn(Ac)_2$ aqueous solution as the water phase, thiourea as the sulfide source, ammonia as the pH regulator, and mercaptoacetic acid as a surfactant. It is worth to stress that the method may also be applied to transition metal ions doped ZnS other than ZnS:Cu^{2+} NPs under appropriate condition.

2. Experiment

2.1. Materials

Mercaptoacetic acid (MPA) was of 97+% purity. $Zn(CH_3COO)_2{\cdot}6H_2O$, $Cu(CH_3COO)_2{\cdot}2H_2O$, thiourea ($NH_2CSNH_2$), ammonia, and *N*,*N*-dimethylformamide (DMF) were of analytical

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grade, and all chemical reagents were used without further purification.

2.2. Synthesis

Typical synthetic process of the ZnS:Cu^{2+} NPs is as follows. A 3 mL water solution containing of $Zn(CH_3COO)_2{\cdot}2H_2O$ (2.3 mol) and $Cu(CH_3COO)_2{\cdot}2H_2O$ (n_{Zn2+}:n_{Cu2+} = 50:1) was firstly put into a three-necked flask, followed by pouring 22 mL DMF. A 0.6 mL mercaptoacetic acid (MPA) was then added into the mixture, making the solution milky. After stirring for 5 min, ammonia solution was added dropwise into the mixture to regulate the pH until it was 10, during which the mixture changed from milky to clear. Subsequently, after stirring for 5 more minutes, a 3 mL thiourea DMF solution (with 0.1 mmol thiourea) was quickly added into the above pH-regulated solution, and the reaction mixture was finally refluxed at 95 °C for 14 h with magnetic stirring. By adding excessive ethanol, the product was precipitated and centrifuged at 6000 rpm and dried in vacuum at 50 °C for 10 h. The dried product, which can be dissolved in ethanol, is used for further characterization.

2.3. Characterization

The phase of as-synthesized products was characterized by using a Shimadzu XRD-6000 X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5406 Å) at a scanning rate of 10° min^{-1} in the 2θ range of 10–80°. X-ray tubes were operated with an electric current of 150 mA and a voltage of 40 kV. The morphology and size of the products were examined by high-resolution JEOL-2010 transmission electron microscopy (TEM). Samples were prepared by drying a droplet of nanoparticle dispersion on an amorphous carbon-coated copper grid. The scanning electron microscopy (SEM) measurement was carried out on Hitachi S-4800N. The energy dispersive spectroscopy (EDS) was carried out on HORIBA 7593-H. X-ray photoelectron spectroscopy (XPS) analysis was carried out on AXIS ULTRA^{DLD} (Kratos). The UV–visible (UV–vis) absorption spectrum was recorded on a JASCO V-570 UV–vis–NIR spectrophotometer. The infrared (IR) absorption spectrum was recorded on a PerkinElmer Spectrum One FT-IR spectrometer. All measurements were performed at ambient temperature.

3. Results and discussion

3.1. The crystal structure and size of the ZnS:Cu^{2+} NPs

The XRD pattern of the ZnS:Cu^{2+} shown in Fig. 1 is consistent with that of standard hexagonal ZnS (JCPDS Card No. 36–1450, shown as vertical bars). The seven broadened diffraction peaks from the left to the right corresponds to those from the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), and (1 1 2) lattice, respectively [11]. No diffraction peak of copper related compounds was observed, which may be due to the small amount of doping concentration. The calculated average crystallite size of ZnS:Cu^{2+} NPs is around 3.6 nm, according to Scherrer equation $D = k\lambda/\beta\cos\theta$, where D is the mean crystalline size, k is a geometric factor (equal to 0.94), λ is the wavelength of the X-rays, β is the half-width of diffraction peak, and θ is the degree of the diffraction peak. Meanwhile, the (0 0 2) peak (at $2\theta = 28.3°$) is the highest one among the seven peaks, which slightly differs from the standard one. It is known that there are three diffraction peaks at 28.6, 47.5, and 56.3° for standard cubic ZnS (JCPDS No. 5-566), which might be somewhat superimposed with the (0 0 2), (1 1 0), and (1 1 2) of hexagonal ZnS, since each of them appears at almost the same region. Moreover, the peak at 28.6° is dominant in the standard XRD pattern of cubic ZnS, which may cause the intensity deviation of the (0 0 2) peak in Fig. 1. Therefore, the presence of cubic ZnS:Cu^{2+}, herein, might not be completely excluded.

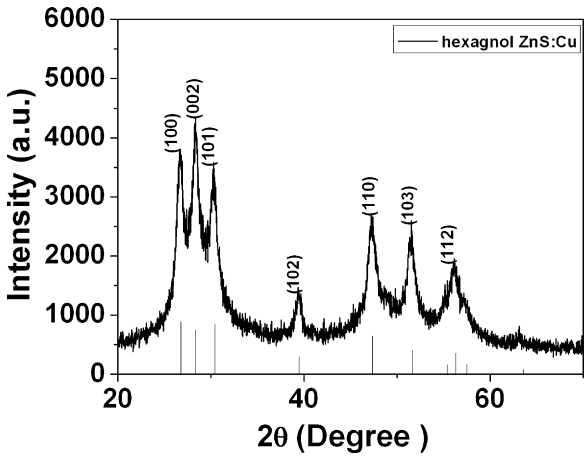

Fig. 1. (a) The XRD pattern of the 2% Cu^{2+}, and (b) Ag^{+}, Mn^{2+} and Co^{2+} doped ZnS NPs prepared at 95 °C.

Fig. 2(a) shows that the ZnS:Cu^{2+} NPs are nearly spherical with an average particle size of around 35–40 nm in the TEM image. The nanoparticles are connected to such extent that they form a coral-like shape. This phenomenon might be due to the presence of coated MPA. On the contrary, the crystalline size is around 4 nm in the high-resolution transmission electron microscopy (HRTEM) image, as shown in Fig. 2(b). This result indicates that the obtained ZnS:Cu^{2+} NPs are polycrystalline, composed of many tiny crystalline spheres. The crystal structure of the sample is hexagonal, which agrees with the result obtained from the XRD analysis. Fig. 2(c) reveals that there are Cu^{2+} ions in the sample, suggesting that Cu^{2+} ions have been successfully doped into ZnS. The result obtained from Fig. 2 indicates the product synthesized is hexagonal ZnS:Cu^{2+} NPs. To further investigate whether the Cu exists as Cu^{2+} or not, XPS is carried out and the XPS profile of Cu^{2+} is presented in Fig. 3. The well-behaved Cu $2p_{1/2}$ (949 eV) and Cu $2p_{3/2}$ (928 eV) lines verify that the Cu definitely exists as Cu^{2+} [12].

To investigate doping effect on the ZnS crystal structure, other transition metal ions with radius larger or smaller than that of Zn^{2+} ion (0.074 Å), Ag^{+} (0.115 Å), Mn^{2+} (0.067 Å) and Co^{2+} (0.065 Å) were used as dopants in the synthesis, and the XRD patterns in the same doping concentration as Cu^{2+} are shown in Fig. 4. The curves show six characteristic diffraction peaks of the hexagonal ZnS, two of which appear as slight shoulders of the highest peak, although not very evident. This result implies that the hexagonal crystal structure of the Ag^{+}, Mn^{2+} and Co^{2+} doped ZnS NPs is not distinctive, but may be so under optimum synthetic conditions. The obvious difference between the former ions and Cu^{2+} is probably owing to the differences in radius. It is known that Cu^{2+} (0.073 Å) has nearly the same radius as Zn^{2+} (0.074 Å). The Cu^{2+} ions can, therefore, readily substitute the Zn^{2+} ions in the host matrix, which makes the formation of hexagonal ZnS much easier in the low-temperature condition.

3.2. Influencing factors and possible mechanism of the formation of hexagonal ZnS:Cu^{2+} NPs

It is interesting that hexagonal ZnS:Cu^{2+} can be synthesized at such a low temperature by means of colloidal method. To investigate the formation mechanism of the hexagonal ZnS:Cu^{2+} NPs, series of experiments were carried out. Many factors were considered, including the influence of surfactants, doping concentration, sulfide sources, pH-regulating reagents, solvents, and reaction temperature.