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Facile Preparation of Rare-earth Semiconductor Nanocrystals and Tuning their Dimensionalities

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EuS and Gd₂S₃ nanocrystals with narrow size distribution are synthesized in high yields by the thermal decomposition of Eu(oleate)₃ or Gd(oleate)₃ in oleylamine using CS₂ as the sulfur source. The dimensionalities of these nanocrystals can be facilely tuned by the addition of 1-dodecanethiol. The morphologies and crystal structures of EuS and Gd₂S₃ nanocrystals are characterized by TEM and XRD. The magnetic properties of the obtained nanocrystals are also investigated. The experimental results illustrate that CS₂ is an effective sulfur source for the preparation of metal sulfides and lanthanide oxysulfides semiconductor nanocrystals.

Introduction

The rare-earth containing semiconductor, which have been studied extensively since the 1960s, have attracted renewed interest due to their remarkable semiconducting and magnetic properties. Among the rare-earth containing semiconductors, EuS and Gd₂S₃ receive special attention. Because the pronounced ferromagnetism of EuS provides spin-polarized electrons which induces promising application in spin-filter devices as the tunnel barrier. Furthermore, enhanced Curie temperature of EuS via hydrostatic pressure, epitaxial strain, or electrons injecting with other rare-earth ions such as Tb and Gd, promotes the possibility of EuS to be applied for semiconductor-based next-generation spintronic devices. Gd₂O₂S is known as a wide-gap material with high chemical stability and high thermal stability. Rare earth ion activated Gd₂O₂S materials show greatly potential applications in various fields, such as field emission displays, long lasting phosphorescence and bioimaging.

The novel size-dependent properties displayed by semiconductor nanocrystals have initiated the current worldwide intense research on nanomaterials. The ones with magnetism. It is reported that magnetic properties such as tunnelling magnetoresistances and magnetic moments can be easily modulated in nanostructured materials. More interestingly, size-dependent magnetism and size-dependent optics of EuS nanomaterials have been suggested in addition to the increasing number of outstanding properties observed in bulk EuS. Now, research interests have been expanded into controllable synthesis of nanomaterials with the desired dimensionality and also in understanding the correlations between the dimensionality and their properties. Enormous efforts have been devoted to synthesizing EuS and Gd₂O₂S nanocrystals. In order to get monodisperse nanocrystals, sulfur source is one of critical points of experimental conditions, especially in the case of Gd₂O₂S. The theory of hard and soft acids and bases (HSAB) predicts a lack of affinity between the hard Lewis acid Gd³⁺ and the soft Lewis base S⁻. In practice, this theoretical bottleneck is expressed as the lack of an effective sulfurization method in preparing Gd₂O₂S nanocrystals. Reaction of europium metal with thiourea in liquid ammonia under a N₂ atmosphere, thermal decomposed single molecule precursors, as well as liquid phase thermolysis of Eu(oleate)₃ and diethylammonium diethylthiocarbamate in the presence of 1-dodecanethiol and phenanthroline have been proved to synthesize EuS nanocrystals. In the case of Gd₂O₂S nanocrystals, thermal decomposed single molecule precursors, combustion reaction of hydroxycarbonate precursor with urea followed by sulfuration in a H₂S/Ar atmosphere at 750 °C are reported. However, due to various limitations in the reported methods, such as rigorous reaction conditions resulting in aggregates or particles, the cost of precursors, aggregations, special instrument requirements, or time-consuming in production, is still of great significance to develop effective synthetic methods to produce these two nanocrystals with facile tuning of the dimensionality.

Here we report a low cost, facile synthesis of EuS and Gd₂O₂S nanocrystals using CS₂ as the sulfur source with the advantages of high-efficiency, and large-scale production. The shape of EuS can be easily tuned from nanocube (3-D) to...
nanodot (0-D) by the addition of 1-dodecanethiol as a surfactant. Similarly, the shape of Gd$_2$O$_2$S can be easily tuned from nanodots (0-D) to nanorod (1-D) by the addition of 1-dodecanethiol as a surfactant. The magnetic properties of the obtained EuS nanocrystals and Gd$_2$O$_2$S nanocrystals were investigated. It was found that the EuS nanocrystals exhibited strong ferromagnetic property, and the Gd$_2$O$_2$S nanocrystals presented paramagnetic property. Additionally, we also illustrates that CS$_2$ can be used as a cheap and efficient sulfur source for the preparation of other monodispersed metal sulfide, such as CdS, PbS, and ZnS nanocrystals.

**Experimental**

**Materials**

All of the reagents used herein were of analytical grade and used as received without any further purification. Oleylamine (mass concentration: 80 ~ 90%), 1-dodecanethiol (DT), sodium oleate, Gd(NO$_3$)$_3$•6H$_2$O were purchased from Aladdin Industrial Corporation. EuCl$_3$•6H$_2$O was received from Sigma-Aldrich.

**Synthesis of EuS nanocubes (NCs) and nanodots (NDs)**

For the synthesis of EuS NCs, Eu(oleate)$_3$ was first prepared according to the literature.$^{25}$ Eu(oleate)$_3$ (332 mg) was dissolved in oleylamine (4 mL) under N$_2$. The solution was heated up to 280 – 310 °C. CS$_2$ (0.3 mL) was drop-wise added within 5 minutes with a controlled speed to avoid explosive boiling. The addition of CS$_2$ quickly led to the color change of the reaction solution from orange to purple, which indicated the formation of EuS. After reacting for half an hour, the mixture was cooled down to room temperature and dispersed to toluene. The purple-black product was collected via centrifugation and washed for 4 times with the mixture of toluene and ethanol (1:1 in volume). After dried in vacuum oven, 58 mg of final product was obtained. The same procedure was applied for the up-scale synthesis of EuS NCs. 3.32 g of Eu(oleate)$_3$ in oleylamine (40 mL) was used and 0.57 g of final product was obtained. This sample was named as EuS-up-scale.

The synthesis of EuS NDs was similar to the above procedure, except that 1 mL of 1-dodecanethiol was added and the reaction time was 2 hours.

**Synthesis of Gd$_2$O$_2$S nanodots (NDs) and nanorods (NRs)**

The synthesis of Gd$_2$O$_2$S NDs is similar to that of EuS NCs. In brief, Gd(oleate)$_3$ was first prepared according to the literature.$^{26}$ 334 mg of Gd(oleate)$_3$ was dissolved in oleylamine (4 mL) under N$_2$. The solution was heated up to 280 – 310 °C, and CS$_2$ (0.3 mL) was drop-wise added within 5 minutes. After reacting for 6 hours, the reaction mixture was dispersed to toluene, and the products were collected via centrifugation and washed for 4 times with the mixture of toluene and ethanol (1:1 in volume). After dried in vacuum oven, 58 mg of orange-brown product was obtained. The synthesis of Gd$_2$O$_2$S NRs was similar to that of Gd$_2$O$_2$S NDs with the addition of 1 mL of 1-dodecanethiol and the reaction time was 10 hours.

**Characterization of Nanocrystals**

Nanocrystals were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). TEM images were obtained by using a JEM-3010 electron microscope. XRD patterns were collected on a Brucker AXS D8 powder diffractometer unit by using Cu Kα radiation ($\lambda$=0.154 nm) operating at 40 kV and 40 mA. The patterns were recorded from 20° to 80° in 2θ with a 2θ scan step size of 0.02°. XPS experiments were carried out in a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation ($hv$ = 1253.6 eV) or Al Kα radiation ($hv$ = 1486.6 eV). The magnetic properties of EuS nanocrystals were measured by using a physical property measurement system (Quantum Design PPMS-9, San Diego, USA).

**Results and Discussion**

**Morphologies and crystal structure of EuS nanocrystals**

The morphology of EuS nanocrystals prepared via thermal decomposition of Eu(oleate)$_3$ by using CS$_2$ as a sulfur source was first investigated by TEM, as shown in Fig.1a. It is clear that 0.5 hour and 1 hour. The solution was heated up to 280 – 310 °C, and CS$_2$ (0.3 mL) was drop-wise added within 5 minutes. After reacting for 6 hours, the reaction mixture was dispersed to toluene, and the products were collected via centrifugation and washed for 4 times with the mixture of toluene and ethanol (1:1 in volume). After dried in vacuum oven, 58 mg of orange-brown product was obtained. The synthesis of Gd$_2$O$_2$S NRs was similar to that of Gd$_2$O$_2$S NDs with the addition of 1 mL of 1-dodecanethiol and the reaction time was 10 hours.
that the obtained EuS nanocrystals are cubic with a size of 10 nm to 20 nm (Fig. 1d). The EuS NCs show clear lattice-fringe profiles in the high resolution TEM image and the lattice spacing is 2.98 Å, which corresponds to the (200) plane (Fig. 1b). These lattice planes are further confirmed by the electron diffraction rings (Fig. 1c). Prolonging the reaction time to 2 hours led to the growth of EuS NCs and the narrow size distribution, as shown in Fig. 1e and 1h. The average size of obtained EuS NCs is 44 nm. However, the crystals present a bit little surface disorder as shown in the high resolution TEM image (Fig. 1f). The crystal structures of obtained EuS NCs were further characterized by XRD. The results are represented in Fig. 2. Diffraction peaks at 25.8, 30.0 42.8, 50.8, 53.1, 62.2, and 70.6° are assigned (111), (200), (220), (222), (400), (420), and (422) of NaCl type EuS, respectively.

In order to tune the dimensionality of EuS nanocrystals, 1-dodecanethiol was used as a surfactant under the same experimental conditions. The TEM images of obtained EuS nanocrystals are given in Fig. 3. It is clear that the obtained EuS are nanodots, which have a narrow size distribution with the average size of 7.5 nm (Fig. 3d). The lattice fringe of EuS NDs can be clearly seen and the lattice spacing is also 2.98 Å corresponding to (200) plane (Fig. 3b). The XRD profiles of EuS NDs are similar to those of EuS NCs, as shown in Fig. 2. The diffraction peaks are broad and weak because of the small size of EuS NDs. Due to the presence of 1-dodecanethiol which possibly suppresses the anisotropic growth of EuS nanocrystals, the shape of these nanocrystals can be facilely tuned from cube to dot.

Furthermore, a ten-times-scale synthesis of EuS NCs was carried out to investigate the possibility of our method for the large-scale synthesis in practice. A production of 0.58 g EuS NCs in one pot was achieved, which is much larger than previous reported methods. The XRD (Fig. 2) and TEM (Fig. S1 in ESI) results well demonstrate the potential application for the large-scale synthesis of EuS NCs.

Additionally, monodispersed CdS, PbS, and ZnS nanodots have also been successfully prepared by using the suggested reaction system (the experimental details and results are given in ESI), which clearly illustrates the generalization of the suggested method for the synthesis of metal sulfide nanocrystals.

**Morphologies and crystal structure of Gd_{2}O_{2}S nanocrystals**

Using the similar experimental procedure, we undertook the thermal decomposition of Gd(oleate)_{3} in oleylamine/CS_{2}. The obtained product was first characterized by XRD, as shown in Fig. 4a. All diffraction peaks are well indexed as the hexagonal Gd_{2}O_{2}S phase with reference to the JCPDS file 26-1422. The broad diffraction peaks and weak intensity are mainly due to small size of nanocrystals. The composition of the product was further investigated by XPS. The Gd 4p (4p, 4d), O 1s and S (2p, 2s) peaks in the survey spectrum which are in good agreement with the literature reports of Gd_{2}O_{2}S. The obtained products consists of gadolinium, oxygen and sulfur elements (Fig. 4b). The C 1s peak is also observed, possibly due to the C contamination of the oleylamine capping at the surface of Gd_{2}O_{2}S nanocrystals. The TEM images illustrate that the obtained Gd_{2}O_{2}S nanocrystals are nanodots with an average size of ~4.5 nm (Fig. 5a and Fig. 5d). The lattice spacing is 2.98 Å as observed in the high resolution TEM image (Fig. 5b), which corresponds to the distance between the plane (101). The dimensionality of Gd_{2}O_{2}S nanocrystals can also be facilely tuned by 1-dodecanethiol as well. In the presence of 1-dodecanethiol, Gd_{2}O_{2}S nanorods (NRs) were obtained as shown in Fig. 5e and 5f. The average diameter of Gd_{2}O_{2}S NRs is 2.4 nm (Fig. 5h) and the length-to-width ratio varies from 2.1 to 6.2.

The above XRD, EDX and TEM results prove that Gd_{2}O_{2}S nanocrystals were prepared directly from the thermal decomposition of Gd(oleate)_{3} in oleylamine/CS_{2}. As mentioned in the introduction section, it is very difficult to synthesize lanthanide oxysulfides (Ln_{2}O_{2}S) through soft-synthesis techniques, since the hard Lewis acid Ln^{3+} doesn’t preferentially bind to the soft Lewis base S^{2-}. In the previously reported synthesis methods, inconvenient single molecule precursors, high temperature or further sulfuration are needed. The key point in the synthesis of Ln_{2}O_{2}S through soft techniques is to find an effective sulfur source. For example, thiourea was used as the sulfur element source to prepare Gd_{2}O_{2}S. However the product was amorphous. Because the mixed alcoholic solvents are not good...
dissolving $\text{H}_2\text{S}$ which was released from the decomposition of thiourea at high temperature. The low concentration of $\text{S}^{2-}$ ions in this solvothermal reaction system, together with the natural low affinity of $\text{S}^{2-}$ with $\text{Gd}^{3+}$, results in the amorphous product. In our suggested method, $\text{Gd}_2\text{O}_2\text{S}$ nanocrystals can be directly obtained in mild experimental conditions, which illustrates that $\text{CS}_2$ is a good sulfur source for the preparation of $\text{Ln}_2\text{O}_2\text{S}$ nanocrystals.

**Magnetic properties of EuS and $\text{Gd}_2\text{O}_2\text{S}$ nanocrystals**

To investigate the magnetic properties these nanocrystals, the temperature dependence of the magnetizations of these EuS nanocrystals was measured from 300 to 5K by using Physical Property Measurement System. Fig. 6a gives the curves of reverse magnetic susceptibility $\chi^{-1}$ versus temperature of EuS NCs and EuS NDs. The Curie temperatures were estimated to be 16.4 K and 16.1 K for EuS NCs and EuS NDs, respectively, through extrapolation from the curves, which agree well with the recognized value 16.6 K of bulk EuS.\(^{19}\) All magnetic data above 30 K can be well fitted (insets in Fig. 6a) to the Curie-Weiss law:

$$\frac{1}{\chi} = (T - T_C)/C$$

where $\chi$ is the magnetic susceptibility, $T$ is the temperature, $T_C$ is the Curie temperature and $C$ is the material-specific Curie constant. As can be clearly seen from Fig. 6a, the EuS NCs has larger Curie constant (or smaller slope) than that of EuS NDs, which can be attributed to the smaller surface/bulk ratio of the EuS NCs.

To further confirm the ferromagnetic property of EuS nanocrystals, we have also carried out temperature dependent M/H measurement. As shown in Fig. 6b for EuS NDs, the magnetic hysteresis loops are obvious below the Curie temperature. In contrast, they disappear above the Curie temperature. When the temperature locates at 5 K, the
coercive field ($H_c$) is about $42 \text{ Oe}$ (inset in Fig. 6b), suggesting the magnetic anisotropy in EuS NDs is very small. This is expected as the orbital moment of Eu$^{3+}$ should be zero theoretically.

Fig. 7a shows the curve of magnetic susceptibility $\chi$ versus temperature of Gd$_2$O$_2$S nanocrystals. The magnetic susceptibility of Gd$_2$O$_2$S nanocrystals decreases rapidly with the temperature increasing, which indicates the obtained Gd$_2$O$_2$S nanocrystals have a paramagnetic property. The inverse susceptibility ($\chi^{-1}$) curves (Fig. 7b) show the Curie-Weiss-like behavior of the nanocrystals, which is similar to Gd$_2$O$_3$ nanocrystals.\(^\text{31}\)

**Formation mechanisms**

With regards to the possible formation mechanisms of EuS and Gd$_2$O$_2$S nanocrystals by using CS$_2$ as sulfur source, we proposed that CS$_2$ may react with oleylamine to form dithiocarbamate [R(NH)$_2$]$_2$[RNHCS] firstly,\(^\text{32}\) which then reacts with Eu(oleate)$_3$ to give rise to Eu-dithiocarbamate complexes in situ (Scheme 1). Under elevated temperature, the complexes were thermally decomposed and Eu$^{3+}$ was reduced to Eu$^{2+}$ by oleylamine, resulting in the formation of EuS nanocubes. 1-dodecanethiol could adsorb on the surface of EuS nuclei through the −S group and act as a capping ligand, thus suppresses the growth of EuS nanocrystals and lead to the formation of the smaller EuS nanodots. Properly due to the larger standard reduction potential of gadolinium (III) (E°$\text{Gd}^{3+}\rightarrow\text{Gd}^{2+}$ = -3.82 V) compared to europium (III) (E°$\text{Eu}^{3+}\rightarrow\text{Eu}^{2+}$ = -0.35 V),\(^\text{33}\) Gd$^{3+}$ is much more difficult to be reduced to Gd$^{2+}$ by oleylamine under the same reaction conditions. At the same time, because of the relatively high concentration and activity of $\text{S}^{2-}$ in the reaction system, the thermal decompositions of Gd(oleate)$_3$ in oleylamine/CS$_2$ lead to the formation of Gd$_2$O$_2$S NDs. The presence of 1-dodecanethiol could mitigate the growth of Gd$_2$O$_2$S crystals, which indicates by the smaller diameters of Gd$_2$O$_2$S NRs produced with longer reaction time (10 h) compared with that of Gd$_2$O$_2$S NDs. Possibly due to the different adsorption strength of 1-dodecanethiol on the different facets of Gd$_2$O$_2$S nuclei, the nuclei slowly grow along a preferential direction, resulting in the formation of nanorods.

**Conclusions**

In conclusion, we have developed a facile synthesis method of EuS and Gd$_2$O$_2$S nanocrystals by using CS$_2$ as the sulfur source through the thermal decomposition of Eu(oleate)$_3$ or Gd(oleate)$_3$ in oleylamine, respectively. The obtained EuS and Gd$_2$O$_2$S nanocrystals with narrow size distribution illustrate CS$_2$ is an effective sulfur source for the preparation of metal sulfide and lanthanide oxysulfides semiconductor nanocrystals. Indeed, monodispersed ZnS, PbS and CdS nanodots have been synthesized in the suggested reaction system, which illustrates the generalization of the suggested reaction system. The dimensionality of EuS and Gd$_2$O$_2$S nanocrystals can be facilely tuned by the addition of 1-dodecanethiol as a surfactant. The magnetic measurements suggest that the obtained EuS nanocrystals exhibit strong ferromagnetic properties below the Curie temperature, while Gd$_2$O$_2$S nanocrystals are paramagnetic.

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**Notes and references**

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