Size Selective Synthesis of Surface-modified EuS Nanocrystals Using Pyridine and Their Physical Properties

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The particle size of EuS nanocrystals was gradually increased by addition of pyridine to the reaction mixture of europium metal and hydrogen sulfide in liquid ammonia. The size effect of EuS nanocrystals was found in the absorption spectra for the first time. The size effect on the magnetic properties of the nanocrystals was also observed.

Photophysical and optomagnetic properties of europium chalcogenides are important in applying them as luminescent materials and optical isolator.[1–3] These properties are strongly dependent on their sizes and the environments surrounding them. For example, an enhancement of photoluminescence was found for EuS nanoclusters in zeolite Y.[4] A large Faraday effect was observed in EuS microcrystals-embedded TiO_2 thin films.[2] The size and the environment were considered to change the specific physical properties of the low-dimension EuS crystals. However, there had been no report on the clear relation between particle sizes and physical properties of nanoscaled EuS crystals.

We reported the preparation of the first EuS and EuO nanocrystals by using liquid ammonia as a reaction medium.[5,6] The liquid ammonia reaction is advantageous in preparing EuS nanocrystals (20 nm); however, their crystal sizes had not been controllable yet.

We have found pyridine, which was soluble in liquid ammonia, as a suitable surface modification-reagent of the nanocrystals and succeeded in controlling the particle sizes of the EuS nanocrystals. The size-controlled EuS nanocrystals prepared by addition of pyridine were characterized by XRD, TEM, UV–vis spectra and magnetic measurements.

A liquid ammonia solution including europium metal and H_2S was prepared in the same way as the previous report.[5] To this liquid ammonia solution (50 mL), distilled pyridine (0.5 mL, 2.5 mL, 10 mL) was added. Liquid ammonia was removed by evaporation at room temperature in 1.5 h after the reaction was completed. The resulting products were purple powders.

Each powder was rinsed with methanol for 5 times and dried in vacuum. The resulting compounds were identified by the X-ray diffraction patterns. The diffraction peaks observed at $2\theta = 25.9°$, $30.0°$, $43.0°$, $50.8°$, $53.4°$, $62.3°$, $68.7°$, $70.9°$, $79.0°$ were assigned to the (111), (200), (220), (311), (222), (400), (331), (420), (422) planes of NaCl-type EuS. The intensity ratios of the diffraction patterns agreed with those of bulk EuS. The average sizes of the prepared EuS samples calculated by the Scherer equation from the XRD spectra are shown in Table 1. By addition of 0.5 mL of pyridine, we obtained EuS nanocrystals with average size of 21 nm, almost the same as that prepared without pyridine addition.[5] EuS nanocrystals with average sizes of 30 nm and 36 nm were obtained by the addition of pyridine 2.5 mL and 10 mL, respectively. An increase of the amount of pyridine enlarged the particle sizes of EuS nanocrystals. A TEM image of the surface-modified EuS nanocrystals (EuS-0.5-p) is shown in Figure 1. The observed particle sizes determined in the TEM images agreed well with those calculated from the Scherer equation. The clear lattice fringes indicated high crystalinity of the EuS nanocrystals. We observed the change of the absorption spectra of the dispersion solutions of the nanocrystals in pyridine and found that EuS-0.5-p was more stably dispersed than EuS-0. We prepared pyridine dispersion solutions of surface-modified EuS-0.5-p and bare EuS-0 (10^{-4} wt%), and stood them for 8 h. As the result, the absorption of bare EuS-0 decreased rapidly because of sedimentation of the nanocrystals (Figure 2). In contrast, surface-modified EuS-0.5-p showed high dispersion ability even after 8 h. The result suggests that pyridine molecules prevent aggregation of EuS nanocrystals because of their surface-modification by the pyridine added in the synthesis.

Table 1. Amount of pyridine added in the reaction, average particle sizes and absorption peaks of the EuS nanocrystals

Samples	Pyridine /mL	Particle sizes/nm	Absorption peaks/nm
EuS-0	0	20	400, 665
EuS-0.5-p	0.5	21	295, 560
EuS-2.5-p	2.5	30	385, 600
EuS-10-p	10.0	36	365, 630

The absorption spectra of the EuS nanocrystals in KBr are shown in Figure 3. The absorption of the surface-modified EuS nanocrystals ((b) EuS-0.5-p, 21 nm) shifted to shorter wavelength than that of similar size of pristine EuS nanocrystals ((a) EuS-0, 20 nm). Note that absorptions of europium chalco-

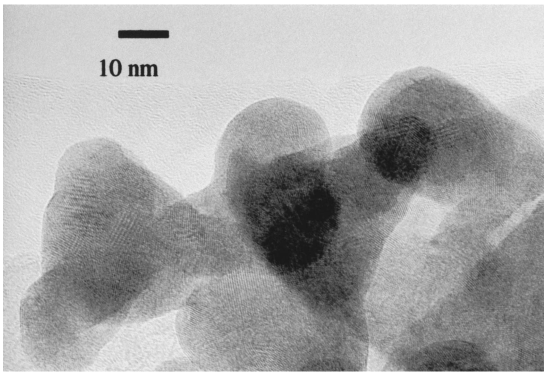

Figure 1. A TEM image of EuS-0.5-p (21 nm).

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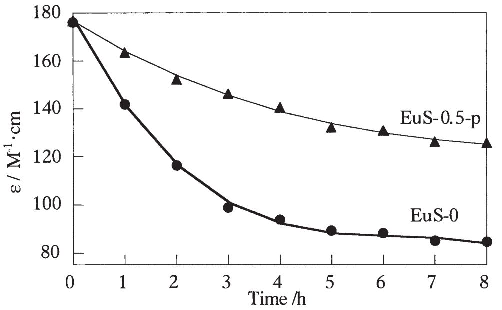

Figure 2. Time dependence absorption values indicating dispersibility of EuS-0 (20 nm) and EuS-0.5-p (21 nm).

genides at low energy region and high energy region originate from $4f^7 \rightarrow 4f^6(^7F_J)5d(t_{2g})$ and $4f^7 \rightarrow 4f^6(^7F_J)5d(t_{eg})$ electron transitions of Eu(II), respectively.[7,8] The energy level of conduction band constructed by 5d orbitals should be affected by the surface-modification of the EuS nanocrystals.

On the other hand, the absorption bands of surface-modified EuS nanocrystals shifted to longer wavelength with increase of the particle sizes (Figure 3 and Table 1). The red shifts in EuS nanocrystals are attributed to the decrease of the energy gap as increase of their particle sizes (the size effect).[9,10] The size effect was also found in the magnetic properties of the EuS nanocrystals. The magnetic moment of 21 nm, 30 nm and 36 nm-EuS observed at 5.0 K was found to be 2.65 μB, 3.02 μB and 4.17 μB, respectively (Figure 4). We previously reported that the magnetic moment of the 20 nm-EuS nanocrystals was smaller that those of bulk compounds, being consistent with the decrease observed here.[5]

According to the rocksalt (FCC) structure of EuS, each Eu(II) ion has 12 nearest neighbor ions (*i*: ferromagnetic interaction) and 6 next-nearest neighbor ions (*j*: antiferromagnetic interaction).[11] In the EuS nanocrystals, the value of i/j decreases with increasing surface area. From this consideration, smaller crystal size leads to decrease of i/j and smaller magnetic moment.

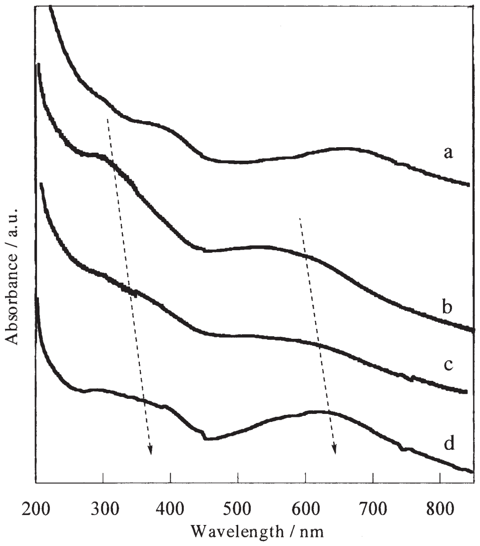

Figure 3. Absorption spectra of a) EuS-0 (20 nm), b) EuS-0.5-p (21 nm), c) EuS-2.5-p (30 nm) and d) EuS-10-p (36 nm).

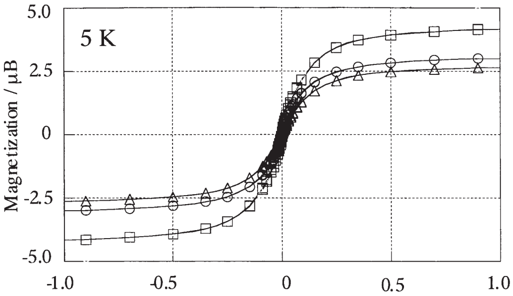

Figure 4. Magnetic filed (*H*) dependence of magnetization (*M*) of the EuS-0.5-p (21 nm) (triangle), EuS-2.5-p (30 nm) (circle) and EuS-10-p (36 nm) (square).

From the results, we concluded that the optical and magnetic properties of EuS nanocrystals depend on both particle size and surface condition of the nanocrystals.

In conclusion, we successfully controlled the particle size and observed the size dependent-physical properties of EuS nanocrystals. These size effects are attributed to the change of the energy level of 5d orbitals of Eu(II) depending on surface conditions of the EuS nanocrystals. Size-controlled and surface-modified EuS nanocrystals are promising materials in application for optoelectric devices.

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