Size-controlled synthesis of quantum-sized EuS nanoparticles and tuning of their Faraday rotation peak

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Size-controlled EuS nanoparticles were synthesized by the reaction of europium metal with thiourea as a sulfur source in liq. NH_3, whose surface was confirmed to be modified with thiourea by FT-IR measurement, and the opto-magnetic properties (Faraday effect) of the EuS nanoparticles were investigated by using PMMA films containing the nanoparticles, showing that their Faraday rotation peaks were adjustable by control of their particle size.

Europium sulfide (EuS) has degenerate 4f orbitals located between the conduction band (5d orbitals of Eu^{2+}) and the valence band (3p orbitals of S^{2-}).[1,2] The 4f–5d electron transition and spin configuration of EuS lead to unique magneto-optical properties, i.e., Faraday effect.[3,4] Note, that the energy gap between the 4f orbitals and the conduction band can be manipulated by controlling the size of the EuS particle (quantum size effect). The manipulation of the energy gap is directly linked to a novel wavelength-tunable Faraday device (isolator) for fiber-optical telecommunication systems. The size control of EuS nanoparticles, however, is extremely difficult, as long as the conventional reactions are employed such as the reaction between Eu^{2+} and H_2S[5] and the photochemical reaction of the Eu^{3+} complex.[6,7] In order to control the particle size, two criteria should be taken into account for the synthesis of EuS nanoparticles; (1) selection of an appropriate sulfur source for quantitative introduction of sulfur to the reaction system, leading to an accurate control of the synthetic conditions, and (2) introduction of surface modification reagents to prevent particle aggregation.[8] To satisfy these two criteria, we have selected thiourea as an ideal sulfur source, which is expected to perform not only as a quantitative sulfur source, but also as a surface modification reagent.

In this communication, we report a novel method for the size-controlled synthesis of EuS nanoparticles (7–14 nm) by reaction of Eu metal with thiourea in ammonia, and we discuss the quantum size effect on their energy gaps and Faraday effect.

EuS nanoparticles were prepared by reaction of europium metal (0.2 g) with thiourea (0.1 g, 0.2 g, 1.0 g, thiourea/Eu mole ratio was 1, 2, 10, respectively) in liquid ammonia under a N_2 atmosphere. Eu metal was dissolved in liquid ammonia at 195 K, giving a blue liquid containing Eu^{2+} and solvated electrons. When thiourea was introduced into the liquid, the liquid turned yellow, indicating that the reaction of Eu^{2+} with thiourea proceeded. After reaction, the liquid ammonia was removed by evaporation at room temperature, and the resulting powder was washed several times by centrifugation with methanol. Prepared purplish powder was identified by X-ray diffraction (XRD) measurements. The diffraction peaks of the powders were observed at $2\theta = 26.0°$, $30.1°$, $43.1°$, $50.9°$, $53.4°$, $62.5°$, $70.9°$ and $78.7°$, and they were assigned to the (111), (200), (220), (311), (222), (400), (420) and (422) planes of NaCl-type EuS (Fig. 1). Some other peaks were also observed at $2\theta = 16.1°$, $28.0°$, $29.2°$ and $40.9°$, assigned to the (100), (110), (101) and (201) planes of hexagonal $Eu(OH)_3$. Because $Eu(OH)_3$ is stable and not dissolved in general solvents, it was difficult to isolate pure EuS nanoparticles. These peaks were so weak compared with those of EuS, indicating a very small amount of byproduct. The average sizes of EuS were calculated by the Sherrer equation from the peaks corresponding to the (111), (200) and (220) planes. It is noteworthy that the peaks broadened as the amount of thiourea increased, indicating that the average size of EuS nanoparticles depended on the amount of sulfur source, i.e. thiourea. Excessive introduction of thiourea (thiourea/Eu mole ratio = 2 or 10) gave smaller EuS nanoparticles (average size = 8 or 7 nm), although the stoichiometric reaction gave the larger size (average size = 14 nm). This size control should be due to the effect of thiourea as a surface-modification reagent, suppressing the particle growth. From the above results, we have found that EuS
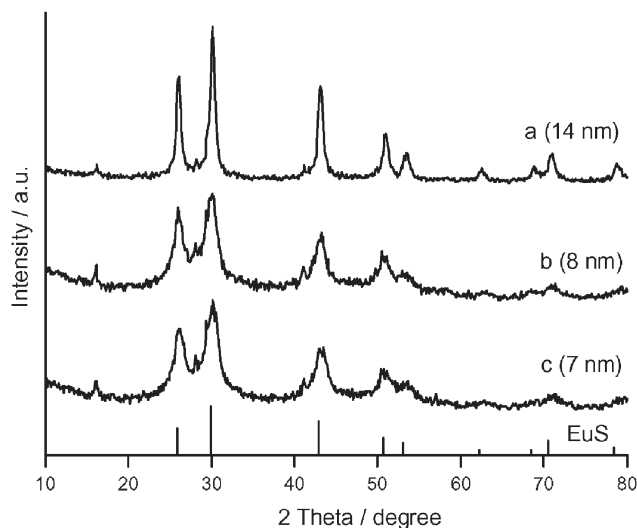

Fig. 1 XRD spectra of EuS nanoparticles prepared by reaction of Eu metal and thiourea, (a: Thiourea/Eu ratio = 1, b: 2, c: 10).

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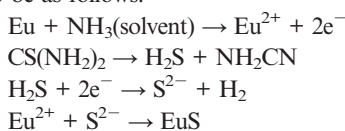E-mail: ywada@mls.eng.osaka-u.ac.jp; Fax: +81 (0)6 6879 7875; Tel: +81 (0)6 6879 7926
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nanoparticles of controlled size can be prepared by changing the amount of thiourea.

The transmission electron microscopy (TEM) images of EuS nanoparticles are shown in Fig. 2.† From the TEM image observed at low magnification (Fig. 2 (a)), the EuS nanoparticles (size: 14 nm) were found to be aggregated. This aggregated situation was also observed in other samples. Some EuS nanoparticles were barely observed with enough clear fringe to determine the particle size in the high-resolution TEM (HRTEM) images (Fig. 2 (b)–(d)). The particle sizes determined by the HRTEM images (Fig. 2 (b); 13 nm, (c); 9 nm, and (d); 7 nm) agreed with those calculated by the Sherrer equation based on XRD data. However, there was not enough EuS nanoparticles available for determination of their size distributions.

P. C. Rieke and S. B. Bentjen have proposed a reaction mechanism for the preparation of CdS film from $Cd(NO_3)_3$ and thiourea.[7] Based on their mechanism, we would suppose the reaction mechanism of the present synthesis of EuS nanoparticles to be as follows:

$$Eu + NH_3(solvent) \rightarrow Eu^{2+} + 2e^-$$
$$CS(NH_2)_2 \rightarrow H_2S + NH_2CN$$
$$H_2S + 2e^- \rightarrow S^{2-} + H_2$$
$$Eu^{2+} + S^{2-} \rightarrow EuS$$

When europium metal is dissolved in liquid ammonia, divalent europium ions (Eu^{2+}) are formed with the solvated electrons.[4] Thiourea molecules produce sulfur anions (S^{2-}) in the liquid ammonia solution by combining with solvated electrons. Thus, EuS nanoparticles are gradually formed by the crystal growth of Eu^{2+} and S^{2-} in the liquid ammonia. Thiourea molecules also perform as a surface stabilizer suppressing the EuS crystal growth. In order to prove the presence of thiourea on the surface, we measured the FT-IR spectra of the EuS nanoparticles (Fig. 3).†

The absorption bands attributed to H–N–H deformation vibration and S=C stretching vibration were observed at 1590 and 1000 cm^{-1}, respectively. The wavenumbers of these peaks were shifted to low values compared to free thiourea molecules (1620 and 1090 cm^{-1}). These results indicate that the surface of the EuS nanoparticles is capped by thiourea molecules, resulting in stabilization of the nanoparticles.[9,10]

The UV-Vis absorption spectra of EuS nanoparticles are shown in Fig. 4.† Broad absorption bands were observed at the region of 400–759 nm, which was assigned to the electronic transition between $4f^7$ and $4f^6(^7F_J)5d(t_{2g})$. The absorption peak wavelength

Fig. 3 IR spectra of the EuS nanoparticles, whose sizes were 14 nm (black solid line), 8 nm (pale gray line), and 7 nm (dark gray line), and that of a thiourea (dashed line). The spectra are shown in (a) the hole region, (b) the region corresponding to the H–N–H deformation vibration of thiourea, (c) the region corresponding to the S=C stretching vibration of thiourea.
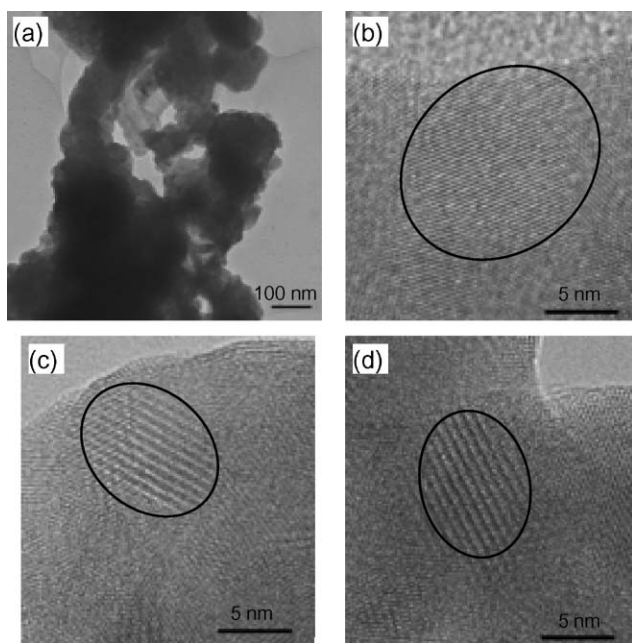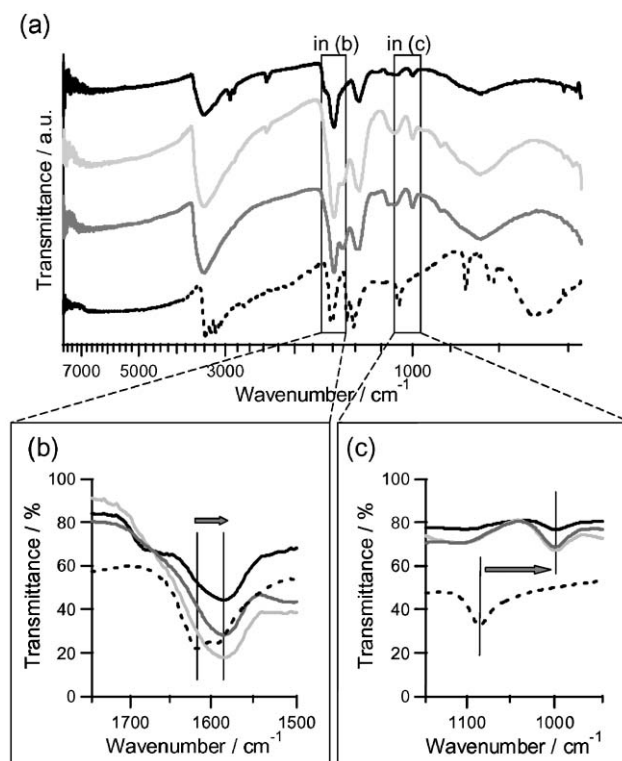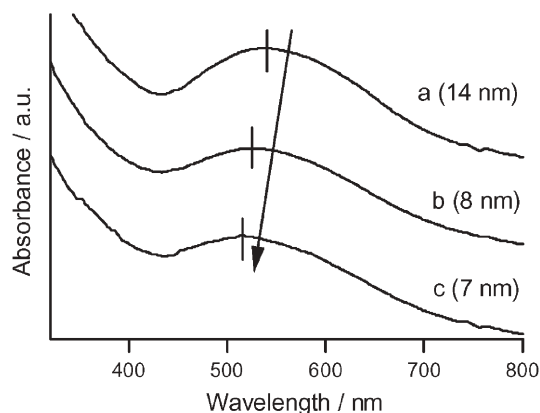

Fig. 2 (a) The TEM image of the EuS nanoparticles prepared by the reaction of europium metal and thiourea (a: Thiourea/Eu ratio = 1). (b)–(d) The high-resolution TEM image of the EuS nanoparticles prepared by reaction of Eu metal and thiourea, (b: Thiourea/Eu ratio = 1, c: 2, d: 10).
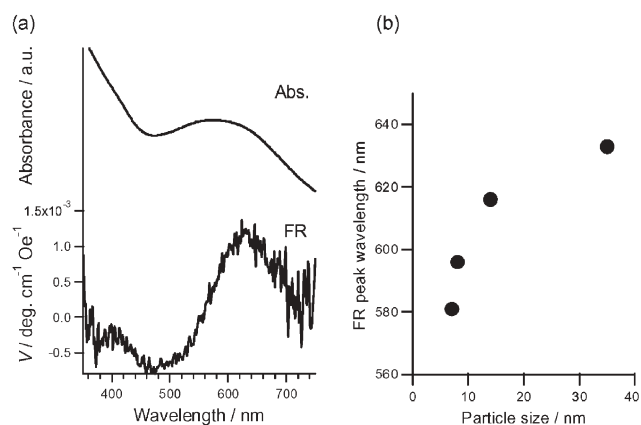

Fig. 4 Absorption spectra of EuS nanoparticles.

Fig. 5 (a) Absorption spectrum (up) and Faraday rotation spectrum (down) of EuS nanoparticles (size: 14 nm). (b) The particle-size dependence of the peak top wavelength on Faraday rotation.

of a (14 nm), b (8 nm), and c (7 nm) were found to be 515, 520, and 540 nm, respectively. The blue shift of the absorption bands accompanied by the decrease of the particle size should be due to the quantum size effect. This is the first observation of the quantum size effect on the energy gap of EuS induced by the size control. With these photophysical findings, we carried out Faraday effect measurements of the EuS nanoparticles.† Polymeric thin films containing dispersed EuS nanoparticles were prepared for the Faraday measurements according to the procedure described in the literature.[4] The UV-Vis absorption (Abs.) spectrum and the Faraday rotation (FR) spectrum of the EuS sample (size = 14 nm) are shown in Fig. 5(a). The peak of the Faraday rotation spectrum of the EuS sample appeared at a little higher wavelength than that of the absorption peak. The Verdet constants (V) of the EuS samples calculated from the Faraday rotation angles[4] were calculated to be 1.4×10^{-3} deg. cm^{-1} Oe^{-1} (a), 6.3×10^{-4} (b), and 1.6×10^{-3} (c) respectively. V values of EuS nanoparticles already reported in the literature[4] were 8.9×10^{-3} deg. cm^{-1} Oe^{-1} (the EuS size = 23 nm), 2.3×10^{-3} (the EuS size = 28 nm), and 4.2×10^{-3} (the EuS size = 31 nm). These values were of the same order as those of the EuS nanoparticles prepared in the present work. The particle-size dependence of the Faraday rotation peak wavelength is also shown in Fig. 5(b). In order to compare the wavelength values of the FR peak of the EuS nanoparticles prepared in this work with that of large EuS particles, the FR peak wavelength of the EuS nanoparticles (35 nm in diameter) was added in Fig. 5(b). The particles were prepared by reaction of europium metal and H$_2$S according to the literature.[5] The size was determined by the Sherrer equation as well as the case of EuS nanoparticles prepared in this work. The EuS sample of smaller particle size showed a blue shift in the Faraday rotation because of the increased energy gap. This physical relation between the particle size and the peak wavelength of the Faraday rotation should be understood from the quantum size effect. We have successfully manipulated the peak wavelength of the Faraday rotation by using size-controlled EuS nanoparticles.

In conclusion, the particle size of EuS has been successfully controlled by using thiourea, resulting in the control of the Faraday spectra. To the best of our knowledge, this is the first report on manipulation of the Faraday spectra for EuS nanoparticles having a quantum size region.‡ The size control of EuS by using thiourea should open the gates for the creation of new opto-magnetic devices such as wavelength-adjustable optical-isolators.

Notes and references

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