Preparation of ZnS semiconductor nanocrystals using pulsed laser ablation in aqueous surfactant solutions

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Abstract. Cubic ZnS semiconductor nanocrystals with the size of 2 to 5 nm were prepared by pulsed laser ablation in aqueous surfactant solutions of sodium dodecyl sulfate and cetyltrimethylammonium bromide without any further treatments. The obtained suspensions of the nanocrystals have broad photoluminescence emission from 375 to 600 nm. The abundance and emission intensity of the nanocrystals depend on the concentration of the surfactant in solution.

1. Introduction

Pulsed laser ablation in liquid media (PLAL) is a versatile technique to fabricate various kinds of nanoparticles such as noble metals [1-3], alloys [4], oxides [5-7] and semiconductors [8]. In PLAL, crystallized nanoparticles and nanocrystals (NCs) can easily be formed through high energetic states of ablated species and their aggregation and dispersion can also be controlled by chemicals in liquid media. CdS and ZnSe semiconductor quantum dots have been prepared by PLAL using organic solvents with Cu laser ablation [8]. It is very difficult to prepare semiconductor NCs in aqueous solution by PLAL, because ablated high energetic species can easily be oxidized at the interface of plasma and aqueous solution resulting in the formation of the oxide or hydroxide species.

Herein we report the preparation of ZnS semiconductor NCs using pulsed laser ablation in aqueous solutions of an anionic surfactant, sodium dodecyl sulfate (SDS) and a cationic surfactant, cetyltrimethylammonium bromide (CTAB), and how surfactant molecules stabilize the semiconductor NCs during PLAL process. The optical and structural properties of obtained semiconductor NCs were also investigated.

2. Experimental details

ZnS NCs were produced by pulsed laser ablation of the semiconductor single crystal of cubic ZnS (100) in aqueous solution of SDS (0.001 to 0.1 mol/dm³) or CTAB (0.0001 to 0.01 mol/dm³). The ZnS single crystal (10 x 10 x 1mm thick) was fixed as the ablation target on the bottom of a glass vessel filled with 10 cm³ of the solution. The target was ablated with a third harmonic nano second Nd:YAG pulsed laser (355 nm, Spectra Physics LBA-150-10) operating at 10 Hz with the pulse energy of 100
mJ/pulse for 60 min. The spot diameter of the laser beam on the target surface was adjusted to 1 mm. UV-Vis and photoluminescence (PL) spectra of the obtained colloidal suspensions of ZnS NCs were recorded using a spectrophotometer (Shimadzu UV-1200PC) and a spectrofluorophotometer (Shimadzu RF5300PC). The produced colloids were repeatedly centrifuged, and the obtained sediments were washed with deionized water several times to remove excess surfactant molecules. X-ray diffraction (XRD, Rigaku, RAD-C) measurements with CuKα radiation were performed for the precipitates dried on silicon wafers. The average crystallite sizes of ZnS NCs were estimated from full width at half maximum of the diffraction peaks using the Debye-Sherrer formula. The particle size, distribution, and crystallinity were more directly investigated with a high resolution transmission electron microscope (HR-TEM, JEOL JEM2010) and selected area electron diffraction (SAED) techniques.

3. Results and Discussion

The typical XRD pattern of ZnS NCs fabricated in 0.1 mol/dm³ SDS is shown in Fig. 1. The broad peaks observed at 29.0, 48.0 and 57.0 degree of 2θ, which were identified to be cubic zinc blende (111), (220) and (311) diffraction peaks according to JCPDS No. 80-0020 as shown in Fig. 1. The XRD pattern in Fig. 1 exhibits the remarkable broad feature, which is a quite similar diffraction pattern of ZnS NCs chemically prepared with micellar solution [9]. The observed broad diffraction peaks suggests the products are composed of the NCs. The crystallite size was estimated to be 2.5 nm with the Debye-Scherer formula using these diffraction peaks. The trace diffraction peaks were also observed at 20.75, 21.85 and 53.8 degree of 2θ. These peaks could assigned to be zinc carbonate and zinc carbonate hydroxide and have more narrow peak width compared with broad peaks of ZnS, suggesting that the such by-products could be formed via chemical reaction between carbonate ions casesd by solved CO₂ in air and Zn²⁺ ions which may formed by ablation. The XRD analysis of the sediments collected from the colloidal suspension obtained by the laser ablation of ZnS in deionized water, 0.001 mol/dm³ SDS and 0.0001 mol/dm³ CTAB indicated that ZnS diffraction peaks were not so clearly observed, suggesting that the ZnS mostly decomposed by ablation. Theses results suggesting the surfactants molecules with higher concentration in the solutions could play an important role to stabilize and preserve the nuclei of ZnS from the decomposition during the laser ablation. These tendencies were consistent with the optical absorption measurements of obtained colloidal suspensions, which would be described later.

Figure 1. X-ray diffraction pattern of ZnS semiconductor nanocrystals prepared in 0.1 mol/dm³ SDS aqueous solution. The (111), (220) and (311) diffraction peaks indicates a zinc blende structure.

Figure 2 shows the typical TEM with SAED pattern and HR-TEM images of ZnS NCs prepared in 0.1 mol/dm³ SDS. The NCs with diameters of 1 to 5 nm were observed and hollow electron diffraction rings observed as shown in Fig 2a. The clear lattice images can also be observed in each NCs in HR-TEM image of the NCs as shown in Fig. 2b and the lattice spacing in the NCs was estimated about 0.29 nm, which value is very close to ZnS (111) spacing. The average diameters of ZnS NCs prepared in solutions were statistically estimated from the HR-TEM images, where sizes of 200 NCs were manually measured. The size distributions were well fitted with Gaussian distribution function. The average sizes of ZnS NCs prepared in different solution ranged from 2.7 to 3.1 nm. The average
size and standard deviation of the ZnS NCs prepared in 0.1 mol/dm$^3$ SDS were 2.8 nm and 1.0 nm and the size is in good agreement with that estimated from the XRD peak using Debye-Sherrer formula stated above. No clear dependency of the average size on the surfactant concentrations was observed.

Figure 3 depicts the UV-Vis absorption spectra of colloidal suspensions of ZnS NCs prepared by pulsed laser ablation in SDS and CTAB solutions with different concentrations. Clear absorption increases were observed at the wavelength region less than 325 nm, which are based on the absorption of ZnS NCs [9,10]. Furthermore, the abundance of ZnS nanocrystals in solution with different surfactant concentration can be monitored by the absorbance at around 250-300 nm which followed almost proportional to the abundance of ZnS nanocrystals. The abundance of ZnS nanocrystals increases with the concentrations of surfactants. High abundance of ZnS NCs in the colloidal suspensions was obtained at 0.1 mol/dm$^3$ SDS and 0.01 mol/dm$^3$ CTAB. These results suggest that both anionic and cationic surfactant can stabilize the ZnS NCs at higher concentrations resulting from the attachment of theses molecules on ZnS nuclei.

As stated above, sizes of ZnS NCs were estimated to be in the range of 1 to 5 nm by TEM observations. Thus, the obtained ZnS NCs are expected to be in quantum confinement regime since the excitonic Bohr radius of ZnS is ca. 2.5 nm. The bandgap of ZnS NCs was estimated from their absorbance basically according to the procedure previously reported for direct allowed band-to-band transitions [11]. The band gap of the produced ZnS NCs were calculated to be in the range of 3.90 to 4.02 eV, which was blue-shifted than that of bulk ZnS is 3.6 eV. The estimated bandgap was smaller than that of 4.36 eV for the chemically prepared ZnS NCs with diameters of 2 to 6 nm [9].

Figure 4 shows the normalized PL spectra by the absorbance at 280 nm for colloidal suspensions of ZnS NCs prepared in different surfactant solutions. The suspensions of ZnS NCs were irradiated at 340 nm for the PL excitation, which caused the Raman scattering of water observed at 370 nm [5] as shown in Fig. 4. The broad emission from 375 to 600 nm was observed except for the lean surfactant.
solutions. No emission was observed from the colloidal suspension prepared in deionized water. It is well known that the nanocrystals of ZnS exhibits broad PL emission which can be contributed by sulfur vacancies, cation vacancies and surface states in the NCs [10,12]. The observed normalized emission intensity is dependent on emission efficiency of ZnS NCs. The most intense emission in 0.01 mol/dm$^3$ CTAB was observed. In contrast, the weak emission was observed in 0.1 and 0.01 mol/dm$^3$ SDS, suggesting the low emission efficiency of NCs in these suspensions. The origin of such low efficiency is not clear yet. However the SDS may passivate the surface defects which can contribute the broad ZnS emission. Thus, CTAB molecules with certain concentration can improve the emission efficiency and abundance of ZnS NCs prepared by PLAL.

4. Conclusions
Cubic ZnS NCs with the size of 2-5 mm were prepared by pulsed laser ablation of a ZnS single crystal in aqueous surfactant solutions of SDS and CTAB. Surfactant molecules with high concentration can stabilize the nuclei of ZnS during the ablation and give the high abundance of the NCs. The obtained suspensions of the ZnS NCs have broad photoluminescence emission from 375 to 600 nm. The abundance and emission intensity of the nanocrystals depend on the concentration of the surfactant in solution. Surfactant can play an important role to stabilize the ZnS NCs and improve their emission intensities.

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