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Synthesis of Cd-free water-soluble $ZnSe_{1-x}Te_x$ nanocrystals with high luminescence in the blue region

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Abstract

Cd-free core–shell nanocrystals ($ZnSe_{1-x}Te_x/ZnS$, $0 \leqslant x \leqslant 0.5$) emitting in the pure blue region were prepared using an aqueous colloidal method followed by post-preparative ultraviolet irradiation. The photoluminescence (PL) efficiency and peak wavelength were maximized (40%, 448 nm) through a heat treatment of the nanocrystals during irradiation in a Zn^{2+}-containing thiol solution. Because of the small lattice mismatch between $ZnSe_{1-x}Te_x$ and ZnS, post-preparative irradiation at high temperature resulted in the formation of a thick ZnS shell (ca. 1.6 nm) around the core (ca. 2.2 nm in diameter) without deterioration of PL efficiency. Surface substitution of Te by S and size-selective precipitation of nanocrystals before ultraviolet irradiation resulted in intense PL. Quantum mechanical calculations show that the wave function of the electron of the exciton in the Te-containing core extends well into the ZnS shell. The calculations also reveal that a thick shell can confine the electrons inside the particles and thereby improve the PL efficiency and stability against the pH of the solution. Nanocrystals that had been post-preparatively irradiated showed good stability in solution and in a glass matrix even after months of storage in air.

Keywords: $ZnSe_{1-x}Te_x$; Nanocrystals; Cd free; Irradiation; Photoluminescent efficiency; Quantum mechanical calculation; Glass

1. Introduction

Semiconductor nanocrystals (NCs) have attracted a great deal of research interest over the past two decades [1–17] for their application to light-emitting diodes [2,3], lasers [4,5], and biological labels [6–10]. With the recent advances in colloidal chemistry, luminescent NCs made of different II–VI semiconductor materials can now be synthesized in the liquid phase through an organometallic approach based on a high-temperature thermolysis of precursors [11–14] or an aqueous method using thiol as a stabilizing agent [15–17]. Compared with the organometallic approach, aqueous synthesis is simpler, more reproducible, less toxic, and lower cost. NCs thus prepared have better water solubility and are more compatible with biological applications [16]. Aqueously prepared CdTe NCs have been the most extensively studied, owing to their size-dependent photoluminescence (PL) that is tunable from green to red, and their PL efficiencies have been increased to 65% by optimizing the preparation conditions [18]. However, colors in the blue region (440–485 nm) are practically unobtainable for CdTe NCs. Furthermore, the toxicity of cadmium is another disadvantage.

ZnSe is a II–VI semiconductor material that is less toxic than CdSe, and it has ultraviolet-blue luminescence. High-quality ZnSe NCs has been synthesized with the organometallic method [19,20]. Moreover, ZnSe NCs have been prepared in aqueous solution, and their PL efficiency reached 10% when the stabilizer thioglycerol was used [21,22]. However, emissions from defect centers were dominant. It was found out that the excitonic emission component of these NCs could be significantly increased by creating a passivating shell (ZnS) through post-preparative irradiation [23]. Water-soluble ZnSe NCs reached a PL efficiency of 50% with a PL maximum at ca. 410 nm when they were post-preparatively irradiated using the optimum conditions [24]. Moreover, blue emissions have been achieved by

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modifying the surface of ZnSe NCs with Cd and S in aqueous solution. By creating a type-II structure on an alloyed core, the emissions of ZnSe NCs could be sequentially tuned from 408 to 483 nm with high PL efficiency ($\eta > 40\%$) [25].

Changing the components of the NCs is another way to obtain tunable optical properties. Preparation of high-quality Cd-containing alloyed NCs such as $Zn_xCd_{1-x}S$ and $Zn_xCd_{1-x}Se$ has been thoroughly investigated [26–28]. Alloyed $ZnSe_{1-x}Te_x$ materials are wide band-gap semiconductors, and they have potential applications to blue-green lasers and light emitting diodes. $ZnSe_{1-x}Te_x$ semiconductors are usually grown on a GaAs substrate by molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD). Their structural properties, electrical properties, and lattice vibrations have been well studied [29–31]. However, colloidal $ZnSe_{1-x}Te_x$ NCs synthesized through either an organometallic or aqueous method have not been reported as far as we know.

In this study, we report on the preparation of blue-emitting ZnSe-based NCs with high efficiency, relatively low toxicity, and excellent stability. The composition-tunable $ZnSe_{1-x}Te_x$ NCs were synthesized in an aqueous solution and irradiated with ultraviolet (UV) light to create a ZnS shell. Surface substitution from Te to S was done by introducing a sulfur source into the solution before irradiation. Increasing the Te content (x in $ZnSe_{1-x}Te_x$/ZnS) red-shifted the PL peak wavelength of the irradiated NCs by as much as ca. 100 nm. By using a combination of size-selective precipitation and heat treatment during UV irradiation, the PL efficiency of the NCs was increased to 40% and the emission peak was tuned into the blue range. The quantum mechanical calculation was able to explain the increase in efficiency accompanied by the red shift. Moreover, the irradiated $ZnSe_{1-x}Te_x$ NCs were dispersed into a glass matrix without significant deterioration of their spectral properties.

2. Experiment

2.1. Synthesis of a crude colloidal solution of $ZnSe_{1-x}Te_x$ nanocrystals

All chemicals were of analytical grade or of the highest purity available. Zinc perchlorate hydrate ($Zn(ClO_4)_2{\cdot}6H_2O$) and 3-aminopropyltrimethoxysilane (APS) were purchased from Aldrich. Al_2Se_3 and Al_2Te_3 lumps were acquired from CERAC Inc. Thioglycolic acid (TGA), methanol, and 2-propanol were obtained from WAKO Chemicals. Ultrapure deionized water (18.2 MΩ/cm) was obtained from a Milli-Q synthesis system (Millipore).

Aqueous colloids of $ZnSe_{1-x}Te_x$ NCs capped by TGA were prepared by modifying the method for ZnSe NCs [22]. Zn precursor solutions were prepared by mixing $Zn(ClO_4)_2{\cdot}6H_2O$ and TGA, and the solutions were adjusted to pH 6.5 with 1 M NaOH. After the solution was deaerated by Ar bubbling for 1 h, a mixed gas of H_2Se and H_2Te was passed through it. The H_2Se and H_2Te gases were obtained by reacting a mixture of Al_2Se_3 and Al_2Te_3 (lumps) and H_2SO_4. The typical molar ratio of the Zn^{2+}:Se^{2-}:Te^{2-}:TGA was 2.13:$1-x$:x:3.28, where x was 0, 0.1, 0.2, 0.3, or 0.5. Hereafter, the ratio x represents the molar ratio of Te used in the synthesis instead of the ratio in the prepared NCs. The resulting solution was heated to ca. 100 °C and refluxed for 48–72 h.

2.2. Surface substitution and size-selective precipitation of $ZnSe_{1-x}Te_x$ NCs

The surface substitution of Te by S was carried out before the post-preparative irradiation by mixing 3 ml of crude $ZnSe_{1-x}Te_x$ NCs solution with 1 ml of a solution containing $Zn(ClO_4)_2{\cdot}6H_2O$ and TGA (called Solution ZT, hereafter) for 1 h. The Te precipitates that appeared were removed by passing the solution through 0.22-μm membrane filters. In Solution ZT, the concentration of Zn^{2+} ions was 0.26 M, while the molar ratio of Zn^{2+} and TGA was fixed at 1:2.43. The pH of Solution ZT was adjusted to 11.0 by using 1 M NaOH. This solution was later used for size-selective precipitation and glass fabrication to prevent agglomeration of NCs.

Size-selective precipitations of NCs were also carried out before the post-preparative irradiation according to the reported method [16,17]. 2-Propanol was added drop by drop to the NC solution as it was being stirred, until it became slightly turbid. The precipitate of $ZnSe_{1-x}Te_x$ NCs was isolated by centrifugation and re-dissolved in 1 ml of deionized water. This procedure was repeated several times until no more NCs were precipitated.

2.3. Post-preparative irradiation of size-selectively precipitated $ZnSe_{1-x}Te_x$ NCs

The post-preparative irradiation of the $ZnSe_{1-x}Te_x$ NCs was carried out using the reported method for ZnSe NCs [24]. 1 ml of Solution ZT was added to the solution of $ZnSe_{1-x}Te_x$ NCs. This solution was then irradiated by UV light ($\lambda = 365$ nm, ca. 1 W/cm^2) from a 250-W UV lamp (SP-7, USHIO) for 1–2 h, with continuous stirring. During the irradiation, the solution was heated to 75 °C when needed. The absorbance and PL spectra of the NCs were frequently measured during irradiation.

2.4. Incorporation of nanocrystals in a glass matrix

The prepared $ZnSe_{1-x}Te_x$ NCs were incorporated in a glass matrix using a silane coupling agent (APS), as previously reported for thiol-capped CdTe NCs [32,33]. 10 ml of a mixture of APS and methanol with a molar ratio of 1:50 was placed in a Teflon petri dish (50 mmϕ). Then, 1 ml of deionized water was added to the solution, and the solution was stirred for 1 h to promote hydrolysis. After the solution had been kept under atmospheric conditions for ca. 12 h, an aqueous solution of 0.75 ml of $ZnSe_{1-x}Te_x$ NCs and 0.25 ml of Solution ZT was added and mixed well. Transparent glass was obtained after the solution had been left in the dark for two days.

2.5. Characterization of $ZnSe_{1-x}Te_x$ NCs dispersed in solution and glass matrix

X-ray powder diffraction (XRD) patterns were taken with a Rigaku Rotaflex diffractometer with Cu$K\alpha$ radiation ($\lambda =$