International Journal of Modern Physics B, Vol. 15, Nos. 28, 29 & 30 (2001) 3881–3884

SYNTHESIS AND OPTICAL PROPERTIES OF WATER SOLUBLE ZnSe NANOCRYSTALS

N. Murase
Physics Department and CeNS, University of Munich
Amalienstrasse 54, D-80799, Munich, Germany
and
Department of Optical Materials, Osaka National Research Institute
Ikeda-city, Osaka-563-8577, Japan [*]

M. Y. Gao[†]
Physics Department and CeNS, University of Munich
Amalienstrasse 54, D-80799, Munich, Germany

N. Gaponik
Physics Department and CeNS, University of Munich
Amalienstrasse 54, D-80799, Munich, Germany
and
Physico-Chemical Research Institute, Belarusian State University,
220050 Minsk, Belarus

T. Yazawa
Department of Optical Materials, Osaka National Research Institute
Ikeda-city, Osaka-563-8577, Japan

J. Feldmann
Physics Department and CeNS, University of Munich
Amalienstrasse 54, D-80799, Munich, Germany

ZnSe nanocrystals are prepared in water by a wet chemistry method. By selecting an appropriate pH value and surface-capping agents, a whitish blue fluorescence peaking at 470 nm is observed under UV irradiation. The intensity of this fluorescence increases dramatically under reflux and saturates after ∼40 hrs. The final mean size of the ZnSe nanocrystals measured by transmission electron microscopy is about 2 nm in diameter. The quantum efficiency of the fluorescence from the final solution is estimated to be ∼1%, although the preparation conditions have not yet been completely optimized. These properties are discussed in comparison with those of similarly prepared CdTe and differently prepared ZnSe nanocrystals.

1. Introduction

Methods of attaining bright photoluminescence (PL) from semiconductor nanocrystals have attracted a lot of attention in the past decade. Carefully controlled colloidal preparations have realized high PL efficiency in the case of CdS,[1] CdSe,[2] and CdTe.[3] Measurement of PL from single particles of these nanocrystals becomes possible due to their high PL efficiency.[4,5,6] Moreover, the PL color tunability by size, and robustness of the semiconductor nanocrystals

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[*] Parmanent address

[†] Corresponding author

make them a new type of light-emitting materials. However, the stability, particle size, and optical properties of these nanocrystals depend strongly on the specific method of preparation.

Here we report the preparation and optical properties of water soluble ZnSe nanocrystals. The water solubility is of importance for applications such as biological staining. In addition, the possibility of inclusion of such highly fluorescent nanocrystals in a transparent matrix by a sol-gel method will also provide a new way to fabricate highly fluorescent composite glasses.

ZnSe has a direct bandgap of ~2.7 eV (460 nm) at room temperature. Therefore, it is more suitable for producing nanocrystals with a short wavelength emission than those of CdS, CdSe and CdTe. In this paper, ZnSe nanocrystals are prepared by a method derived from the established colloidal method for CdTe.[5] The properties of ZnSe have been discussed in comparison with those of CdTe and differently prepared ZnSe nanocrystals.[7–12]

2. Experimental

The preparation method is similar to a previously reported one for highly fluorescent CdTe nanocrystals with their PL ranging from green to red.[3] The details are described below.

Ultra-pure water (Millipore, Milli-Q synthesis grade) was used in every case after degassing for more than 30 min with Ar. An aqueous solution of zinc perchlorate (0.013 mol/L, 60 mL) was mixed with thioglycerol ($CH_2(SH)CH(OH)CH_2(OH)$) which was used as a surface-capping molecule. The pH of the solution was set to 11.4. Aqueous solution of NaHSe was prepared by introducing H_2Se that was generated by the reaction between Al_2Se_3 and H_2SO_4 in a NaOH solution. The molar ratio among Zn, Se, and thioglycerol was set to 1:0.47:2.4.[13] The mixture was clear and colorless in the beginning and then changed to yellow upon a reflux. Fluorescence appeared in the course of the reflux and kept increasing in intensity until the colloidal solution had been refluxed for 43 hours. Absorption spectra by a Varian Cary 50 spectrometer, fluorescence and excitation spectra by Varian Cary Eclipse were measured by using a 1-cm cuvette at room temperature during the reflux. A TEM image of the final ZnSe nanocrystals was taken using a Hitachi H-9000 transmission electron microscope.

3. Results and Discussion

Figure 1 shows the absorption spectra of the ZnSe colloid (13 times diluted) as a function of the refluxing time. The inset of the figure is an enlarged version of a specific region. At an early stage of the reflux, the onset of absorption was in the ultra-violet region. The colloidal solution at this stage was transparent and colorless. As the reflux proceeded, the onset of the absorption

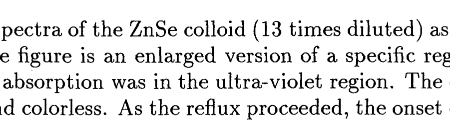

Fig. 1. Absorption spectra of the ZnSe recorded at different refluxing time. The inset is the enlarged version of the specific region to show the onset of the absorption.

as shown in the inset of the figure steadily moved to the visible range. Consequently, the color of the colloid became shallow yellow. During the same period of this absorption change, the fluorescence intensity increased dramatically until a saturation was reached after 43 hours, as shown in Fig. 2. It can be seen that the peak position of the PL emission remains unchanged at 470 nm even though the absorption spectrum is red-shifted during the reflux, whereas one shoulder at around 400 nm appears gradually. The final fluorescence looks whitish blue. The excitation spectrum observed at the PL peak position (470 nm) showed some structure that was not observed in other kinds of similar samples. The origin of this structure is under investigation. Figure 3 is a TEM image of the final colloid. Even though most of the particles are agglomerated during the specimen preparation, the structure of $\sim$2 nm is observed. From this we estimate the particle diameter to be $\sim$2 nm. The quantum efficiency of the fluorescence from the final solution is estimated to be 1.4% by a comparison with R6G (Lambda Physik laser dye).

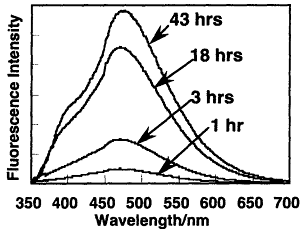

Fig. 2. Fluorescence spectra of the ZnSe measured at different refluxing time. The excitation wavelength is 320 nm.

So far, several methods have been reported for the preparation of ZnSe nanocrystals. ZnSe ranging in diameter from 3 to 10 nm in glass was prepared by a sol-gel method.[7] The fluorescence of the nanocrystals was heavily red-shifted to 600 nm probably due to presence of Se-vacancies. ZnSe nanoparticles of 4 - 6 nm in diameter dispersed in glass have also been prepared using a melt-quenched method.[8] This paper describes a band-edge emission. A simple aqueous synthesis was also tried.[9] The ZnSe nanocrystals about 3 nm in diameter were prepared. Their emission spectra were broad and peaking at around 455 nm. Reverse micelle method was also used to prepare ZnSe of 3 - 4 nm in diameter.[10] In this case, a heavily blue-shifted fluorescence is observed at 355 nm. Another different wet chemistry method was adopted to produce 2 - 3 nm ZnSe.[11] The emission peak was observed at 450 nm. However, in all these cases, the efficiency and properties of the emission were not clarified. An organometallic synthesis route similar to the commonly called TOPO method[2] gave the most successful results.[12] ZnSe nanocrystals ranging from 4 - 6 nm in diameter were successfully synthesized. The band edge emission around 400 nm was observed with high quantum efficiency (20% - 50%).

In the case of CdTe, a bright photoluminescence can be produced by the colloidal method presented here.[3] By prolonging the refluxing time, the bright band edge emission can be tuned from 540 nm to 650 nm.

In view of these results, especially the results from similarly prepared CdTe, a peculiar thing in the present research is that there is no change in the fluorescence peak position when the absorption onset shifts to the red during reflux. The observed fluorescence peaking at 470 nm has not been reported to the best of our knowledge. As this fluorescence is red-shifted with respect to the absorption edge, the PL is related to trap states. The increase of PL intensity during reflux indicates that the fluorescent ZnSe nanocrystals are formed from non-fluorescent small clusters during the reflux and increase in concentration. This is supported by the change

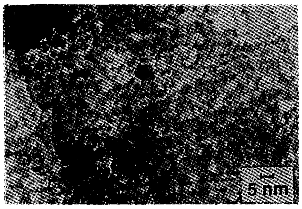

Fig. 3. Transmission electron microscope image of the final ZnSe nanocrystals.

in absorption spectra which indicate that the reflux process leads to both the formation of the ZnSe nanoparticles and their growth in size. However, more experiments such as ESR spectroscopy, temperature dependent PL and transient PL spectroscopy of the nanocrystals are required to further understand the PL properties as has been done in the case of ZnS nanocrystals.[14]

It is worth mentioning here that we also tried to prepare ZnSe nanocrystals by using another thio-compound, mercaptoacetic acid ($CH_2(SH)(COOH)$). By the adoption of pH 10.0 and the molar ratio among Zn, Se, and merocaptoacetic acid of 1:0.47:5.0, the resultant colloidal solution was transparent and clear, however much weaker PL was obtained. A different PL behavior was also observed from the CdTe system when different surface-capping agents were employed. For example, thiolactic acid covered CdTe exhibits both excitonic and surface trap emissions. We believe that the PL from ZnSe can be further improved by choosing an appropriate surface-capping molecule. The appearance of the PL shoulder at 400 nm has already given a hint of band edge emission. Effective surface passivation may also help to further improve the PL efficiency.

Acknowledgements

This work is supported by a BMBF (03N8604 9) project and a bilateral international joint research program by special coordination funds for promoting science and technology (Fiscal year 2000) from Science and Technology Agency of Japan.

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