Rapid Communication

Optical properties of manganese-doped zinc sulfide nanoparticles classified by size using poor solvent

So Komada, Tomoya Kobayashi, Yasuyuki Arao, Katsumi Tsuchiya, Yasushige Mori *

Department of Chemical Engineering and Materials Science, Doshisha University, 1–3 Tatara Miyakodani, Kyotanabe 610-0321, Japan

A B S T R A C T

To elucidate the dependence of the optical properties of semiconductor nanoparticles (NPs) on their size, it is of requisite importance to control or narrow the size distribution of NPs. In this paper, we demonstrated how to attain such controlled states by classifying manganese-doped zinc sulfide (ZnS:Mn) NPs. The classification method proposed was the gradual stage-wise flocculation of NPs relying on interparticle interaction forces between NPs, which were controlled by the addition of a poor solvent, 2-propanol. The mean diameter of ZnS:Mn NPs was evaluated from X-ray diffraction pattern and UV–vis absorption spectrum with the tight-binding approximation. As the number of classification cycles increased, smaller-sized particles were collected. The first-collected sample, which comprised a group of the largest-sized NPs, showed the highest photoluminescence intensity.

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1. Introduction

Semiconductor nanoparticles (NPs) have attracted persisting attention owing to their unique physical properties, including nonlinear optical behavior and unusual photocatalytic activity. These functional characteristics can be attained by size quantization, i.e. the confinement of charge carriers (electrons and holes) within the NPs [1–3]. Bhargava et al. [4] reported that photoluminescence (PL) intensity or PL quantum yield increased when the particle size became smaller, indicating that the particle diameter played an important role in controlling the optical characteristics of NPs [4–6]. It is thus crucial to obtain well-regulated, monodispersed NPs for the desired properties. The special preparation method, such as a reversed-micelle method [7–10] or a hot-soap method [11–14], is one of the techniques to attain the monodispersity of NPs. Despite such special techniques to prepare crystalline NPs, it is often the case that some additional classification procedure is needed to a certain extent for obtaining monodispersed NPs, as in other general precipitation methods used in the NPs preparation.

Gel electrophoresis is an effective method of analysis generally used for classifying NPs [15–19]. The reproducibility and accuracy of classification in this method to apply for NPs of sizes less than 10 nm are generally excellent. The amount of classified sample, however, is too small a level to apply for industrial production.

As another class of classification method utilizing crystallization, Murray et al. [11] and Vossmeyer et al. [20] reported that narrower-sized samples of CdSe NPs capped with tri-n-octylphosphin oxide or 1-thioglycerol could be obtained as the flocculation of NPs by adding another solvent. These researchers called this procedure "size-selective precipitation" because NPs of larger sizes, which were estimated from the relevant absorbance spectrum, could be selected when the procedure was repeated.

Mastronardi et al. [21] applied the same procedure to classifying Si NPs by size, and reported that the PL quantum yield of the NPs decreased with decreasing size and some classified samples almost doubled their quantum yields compared to the original sample prior to the classification. This procedure has been often used for the sample purification, being called mostly the size-selective precipitation, while the NPs are not precipitated but flocculated, during the purification. In this regard, we propose that the procedure should be called "classification with poor solvent" because its principle lies in the flocculation process, similar to the poor-solvent method for the crystallization process where an excess amount of poor solvent was added in the feed solution to have solid materials precipitated.

It is attempted in this study to separate manganese-doped zinc sulfide (ZnS:Mn) NPs in the solution by their size using the poor-solvent method where the poor solvent was added step by step instead of adding an excess amount of poor solvent for crystallization. ZnS:Mn NPs are one of typical low-toxic semiconductor NPs for the industrial use, and in this study had sharp size distribution below a range of few nanometers. One of the research trends