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Structural Studies of ZnS Nanoparticles by High Resolution Transmission Electron Microscopy

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Abstract. Zinc sulfide (ZnS), a representative of wide band gap semiconductor nanocrystals, has an excitonic Bohr radius (a_{BZnS}) of 2.5 nm. It makes ZnS nanoparticles (ZnS NP) having such size very interesting as small biomolecular probes for fluorescence and laser scanning microscopy. To date, ZnS NP of diameters larger than a_{BZnS} has been subject of extensive experimental and theoretical studies. However many questions remain open concerning the synthesis of undoped and uncapped ZnS NP of diameters less than 2.5 nm. To further probe into the physical properties of undoped and uncapped ZnS NP, in this work we report on studies of uncapped ZnS nanoparticles synthesized by a wet chemical process at room temperature. Three colloidal suspensions (named A, B and C, respectively) were obtained from 9:1, 1:1 and 1:9 volume mixtures of 1mM $ZnSO_4$ and 0.85mM Na_2S aqueous solutions. Qualitative differences in UV-Vis absorption spectra are discussed in the context of Z-contrast scanning transmission electron microscopy (Z-contrast), low and high resolution transmission electron microscopy (TEM) results. Distribution of particle size is dependent on different volumes of source solutions. For the intermediate mixture, it has been found that about 78% of ZnS nanoparticles have a diameter smaller than the excitonic Bohr Radius of 2.5 nm. HRTEM studies have revealed that nanoparticles grow preferentially with hexagonal structure.

Introduction

In the last decade many efforts have been dedicated to synthesis and study the physicochemical characterization of nanometer-scale semiconductors. Nanoparticle synthesis has opened alternative ways in the design of materials with new properties. Interest in semiconductor nanoparticles is justified by the fact that fundamental physical and chemical properties of them can be very different from those of the bulk materials. Their reduced dimensions enable one to reduce the size of electronic circuitry. They are expected to have higher quantum efficiencies due to increased oscillator strengths as a result of quantum confinement. A threshold for the occurrence of quantum effects is given by the value for the Bohr radius of exciton (a_B) in the bulk material [1]. The band gap of particle can be tuned by changing the size of nanocrystals below a_B. Thus, one observes an increase in the band gap of semiconductor with a decrease in particle size. Moreover, as the particles