

Luminescent nanoparticles of Mn doped ZnS passivated with sodium hexametaphosphate

H.C. Warad^a, S.C. Ghosh^a, B. Hemtanon^a, C. Thanachayanont^b, J. Dutta^{a,*}

^aMicroelectronics, School of Advanced Technologies, Asian Institute of Technology, P.O. Box 4, Klong Luang, Pathumthani 12120, Thailand

^bNational Metal and Materials Technology Center, 114 Thailand Science Park, Phaholyothin Road, Klong 1, Klong Luang, Pathumthani 12120, Thailand

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Abstract

We report the synthesis of luminescent nanoparticles of manganese doped zinc sulfide (ZnS:Mn²⁺) with an emission peak at around 590 nm. Nanoparticles of ZnS:Mn²⁺ are prepared by a co-precipitation reaction from homogenous solutions of zinc and manganese salts. Based on Ostwald ripening and surface passivation, we discuss a mechanism for the formation of ZnS:Mn²⁺ nanoparticles. The reaction proceeds with the nucleation of ZnS crystals, which are immediately passivated by the anions in the solution. This in turn attracts cations including zinc and manganese which contribute to the growth of the crystal. These nanoparticles are sterically stabilized using polyphosphates of sodium namely sodium tripolyphosphate (STTP) and sodium hexametaphosphate (SHMP). The nanoparticles consist of particles of 60–80 nm in diameter, each containing primary crystallites that was estimated from the X-ray diffraction patterns to be at around 2.2 nm.

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1. Introduction

Semiconductor nanocrystals are described as a state of matter that is intermediate between individual molecule and bulk [1]. Transition from bulk to nanoparticles lead to the display of quantum mechanical properties and an increased dominance of surface atoms which increases the chemical reactivity of a material. Notable examples include tunable bandgap [2] and catalytic behavior [3], respectively. The small size and high optical activity of certain semiconductors make them interesting for applications in disciplines ranging from optoelectronics [4], catalysis [5] to fluorescence microscopy [6].

Particles in nanometric sizes show unique physical properties, for example with the decrease of particle size, extremely high surface area to volume ratio is obtained leading to an increase in surface specific active sites for

chemical reactions and photon absorption to enhance the reaction and absorption efficiency. The enhanced surface area increases surface states, which changes the activity of electrons and holes, affecting the chemical reaction dynamics. For instance, the size quantization can increase the bandgap of photocatalysts to enhance the redox potential of conduction band electrons and valence band holes [7]. Also, nanoparticles can induce the possibility of indirect electron transitions at the boundary of the crystals and realize the essential enhancement of light absorption.

The conventional approach for synthesis of nanoparticles involves chemical or physical attrition from bulk into objects of desired sizes and shapes (e.g. mechanical milling, ion implantation, etc.), and is referred as the ‘top-down’ approach. Inverse to the ‘top-down’ approach is a process universal in nature, involving the assembly of materials from molecular levels to form micro or macro-sized shapes and structures, often referred as ‘bottom-up’ approach or ‘self-assembly’ [8].

Wet chemical synthesis involving colloids is the most energy efficient ‘bottom up’ technique for the synthesis of nanoparticles. The chemical synthesis has the advantages of producing size-controlled, un-agglomerated nanoparticles.

* Corresponding author. Tel.: +66 2 524 5680; fax: +66 2 524 5697.
E-mail address: joy@ait.ac.th (J. Dutta).

During synthesis of nanoparticles from a chemical reaction to form a colloidal system, upon addition of the reagents initially formed product molecules are called seeds. The number of seeds remains constant and over time; as more product molecules are formed the seeds grow in size in a thermodynamically controlled manner to form nano-crystallites [9]. Most of the physical or chemical properties exhibited by these nanoparticles are due to these crystallites. Further growth in size is due to these crystallites agglomerating to form primary particles. If this growth of particles is not controlled, then due to Ostwald ripening and van Der Waals interactions between particles, they agglomerate and settle down [10]. This agglomeration can be arrested by either stabilizing electrostatically or by inducing steric hindrances at appropriate stages in the precipitation reaction, to achieve size selective synthesis.

Electrostatic stabilization involves the creation of an electrical double layer arising from ions adsorbed on the surface and associated counter ions that surround the particle in the dispersing media. Thus, if the electric potential associated with the double layer is sufficiently high, columbic repulsion between the particles will prevent their agglomeration. Steric hindrance can be achieved by the adsorption of large molecules such as polymers on the surface of the particles. Two distinct effects describe this type of stabilization. First, the fact that the adsorbed molecules are restricted in motion causes a decrease in the configurational entropic contribution to the free energy. Second, the local increase in concentration of polymer chains between approaching particles results in an osmotic repulsion, since the solvent re-establishes equilibrium by diluting the polymer molecules, consequently separates the particles [8].

ZnS nanoparticles are often used as phosphors for display devices [11]. ZnS doped with manganese (orange red emission at around 590 nm) [12], copper (green emission at around 510 nm) [13] and silver (blue emission at around 440 nm) [14] have a potential application in field emission devices (FED) [15]. Semiconductor nanoparticles show effective photocatalysis property, e.g. in the artificial fixation of CO₂ [16]. It is believed that catalysis occurs on the surface of the particles. Cadmium sulfide (CdS) [17], zinc sulfide (ZnS) [17] and cadmium-rich cadmium selenide (CdSe) [16] of certain sizes act as efficient photocatalytic semiconductor nanoparticles. But CdS and CdSe are toxic and are also unstable undergoing photoanodic corrosion in aqueous media [18]. In this regard, the use of undoped ZnS nanocrystals could achieve similar results, and has the inherent advantage of being non-toxic also.

Organometallic method of synthesis of nanoparticles has been described by Bhargava et al. [19,20]. Yu et al. synthesized nanoparticles of ZnS:Mn²⁺ in methanol by using sodium polyphosphate as the capping agent [21]. Precipitations from homogeneous solutions have also been reported where it was found that particle size is a function of the nature of the associated anions [22,23]. Here, we describe the synthesis of ZnS:Mn²⁺ nanoparticles using an

organometallic to inorganic synthesis employing a coprecipitation reaction, and stabilized by steric hindrances by using polyphosphates of sodium namely sodium hexameta-phosphate and sodium tripolyphosphate as capping agents.

2. Experimental

All synthesis was carried out in water for its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at room temperature and under ambient conditions.

Ten grams of sodium polyphosphate namely SHMP (Fluka Chemika) and STTP (Fluka Chemika) were separately dissolved in 70 cm³ of De-ionized (DI) water and stirred. To each of this an aqueous solution of 0.25 M Zn(CH₃COO)₂ (Univar) and 1 mM Mn(CH₃COO)₂ (Fluka Chemika) was mixed together and stirred constantly and heated till boiling. After cooling to room temperature, 0.25 M sodium sulfide (Panreac) was added drop wise in an ice bath with constant stirring, resulting in formation of white precipitate of ZnS nanoparticles almost immediately. The supernatant was then centrifuged at 4000 rpm for 20 min to separate undesired agglomerates. In a few of the experiments, after washing the particles with de-ionized water the sample was freeze-dried to obtain fine powder of ZnS:Mn²⁺ nanoparticles.

The sample characterizations were carried out using UV–Visible Spectroscopy (ELICO SL-164), Scanning Electron Microscope (JEOL, JSM-6301F), Fourier Transform Infrared Spectroscopy (Perkin–Elmer), Fluorescence Spectroscopy (Hitachi, F-4500 FL Spectrophotometer) and X-ray Diffraction (JEOL, JDX- 3530).

3. Results and discussions

Zinc acetate dissociates into zinc ions (Zn²⁺) and acetate (Ac⁻) ions in aqueous solution. Similarly, manganese acetate and sodium sulfide dissociate into their respective cations and anions. Sodium being more reactive than zinc and manganese, readily forms sodium acetate. Particles of ZnS nucleate due to the reaction between Zn²⁺ and S²⁻, which subsequently grow by consuming more ions from the solution. The growth mechanism can be explained on the basis of Ostwald ripening [10]. Upon nucleation, the surface energy of the particles is very high and consequently the surface is passivated by adsorption of anions in the solution (Ac⁻ and S²⁻). The accumulation of anions in turn attracts cations (Zn²⁺, Mn²⁺ and Na⁺) towards the surface of the particle. Zn²⁺ and Mn²⁺ react with S²⁻ and get incorporated into the crystal lattice of the nucleus (Fig. 1a). Eventually enough Na⁺ accumulates (sodium is not known to form alloys with zinc [24]) to repulse Zn²⁺ ions from approaching the particle surface and the particle growth stops. These accumulated Na⁺ ions form the stern

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