Journal of Luminescence 130 (2010) 2207–2214

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Synthesis and optical characterization of PVP and SHMP-encapsulated Mn^{2+}-doped ZnS nanocrystals

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ARTICLE INFO

Article history:
Received 30 September 2009
Received in revised form
16 February 2010
Accepted 28 June 2010

Keywords:
Semiconductor materials
Chemical synthesis
Photoluminescence
SEM
TEM

ABSTRACT

Zinc sulfide semiconductor nanocrystals doped Mn^{2+} have been synthesized via a solution-based method utilizing optimum dopant concentration (4%) and employing polyvinyl pyrrolidone (PVP) and sodium hexametapolyphosphate (SHMP) as capping agents. UV–vis absorbance spectra for all of the synthesized nanocrystals show an exitonic peak at around 310 nm. The particle size and morphology were characterized by scanning electron microscopy (SEM), FT-IR, X-ray diffraction (XRD), transmission electron microscopy (TEM) and photoluminescence spectrum (PL). Diffraction data confirmed that the crystallite size is around 3–5 nm. Room temperature photoluminescence (PL) spectrum for the bare ZnS sample shows a strong band at ~445 nm. The uncapped and capped(SHMP, PVP) ZnS:Mn^{2+} samples show a strong and broad band in the ~580–585 nm range.

1. Introduction

Over the past two decades, there have been extensive experimental and theoretical studies of optical and electrical properties of semiconductor nanoparticles. Ultra-thin semiconducting nanomaterials have unique properties due to the quantum confinement effect when they are synthesized in the order of a few nanometer thickness. Semiconductor nanoparticles exhibit size-dependent electronic band gap energies [1], melting temperature [2] and solid–solid phase transition temperature [3] and pressures [4]. Among the semiconductor nanoparticles, zinc sulfide is an important II–VI semiconductor, which has been researched extensively because of its broad spectrum of potential applications, such as in catalysis and electronic and optoelectronic nanodevices [5,6]. It is one of the direct band gap materials having a large value band gap energy of 3.6 eV [7] at room temperature.

Doped ZnS nanomaterials show optical, electronic and mechanical properties distinct from those of conventional bulk materials. It can be obtained by many ways, for e.g. chemical precipitation method [9], organometallic method [8], microemulsion with hydrothermal treatment hydrolysis method [10], reverse micelle method [11], sol–gel method [12], spray-based method [13] and synthesis by γ-irradiation of solution [14]. In this work we use the chemical precipitation method to obtain ZnS:Mn^{2+} nanoparticles. It is the most popular technique that is used in industrial applications because of the cheap raw materials, easy handling and large-scale production [15].

Recently, methods have been developed to cap the surfaces of the nanoparticles with organic or inorganic groups, so that the nanoparticles are stable against agglomeration. Suitable surfactants not only prevent agglomeration but also improve some optical properties of the nanoparticles. Some particular passivators have been used, such as polyethylene glycol (PEG) and pyrocatechol violet (PV) [16], acrylic acid (AA) [17], methacrylic acid (MA) [8], polyvinylalcohol (PVA) [18], mercaptoethanol [19], sodium hexametaphosphate (SHMP) [20] and polyvinyl pyrrolidone (PVP) [21]. These are added during the chemical synthesis for capping the surface of the particles. Understanding the effect of capping on nanoparticles is one of the most important topics now-a-days. The influence of surface passivation on luminescence quantum efficiency of ZnS:Mn^{2+} nanoparticles has been discussed by Bol and Meijerink [18]. The fundamental question that we are attempting to address in this paper is how capping causes any noticeable improvement in luminescence quantum efficiency of nanoparticles. Keeping the above point in view, we report a simple soft chemical method for the synthesis and characterization of polyvinyl pyrrolidone (PVP) and sodium hexametaphosphate (SHMP)-encapsulated ZnS doped Mn^{2+} nanoparticles. The polymers may be a good choice as stabilizers as they can interact with the metal ions by complex or ion-pair formation and can be designed for certain physical properties of semiconductor nanoparticles [22].

2. Experimental

2.1. Synthesis of ZnS:Mn^{2+} nanoparticles

ZnS nanocrystals doped with Mn^{2+} ions were prepared by the chemical precipitation method. The reactants were Zn

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doi:10.1016/j.jlumin.2010.06.021

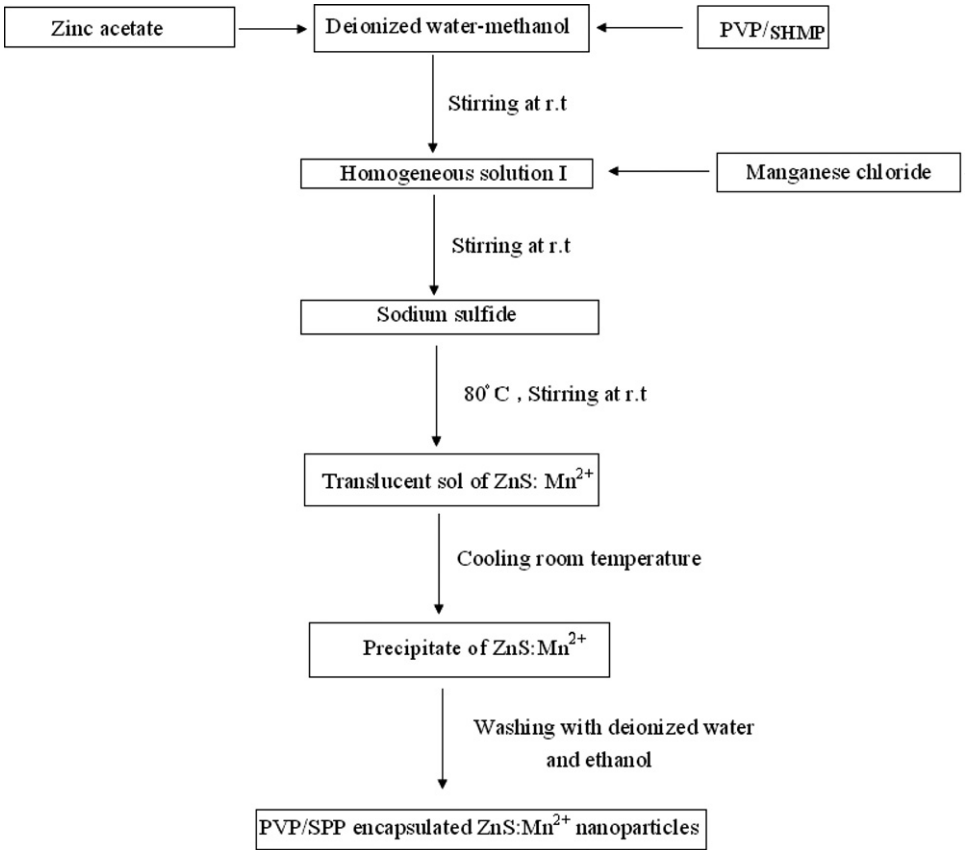

Fig. 1. A schematic of the formation of PVP/SHMP-capped ZnS:Mn^{2+} nanoparticles.

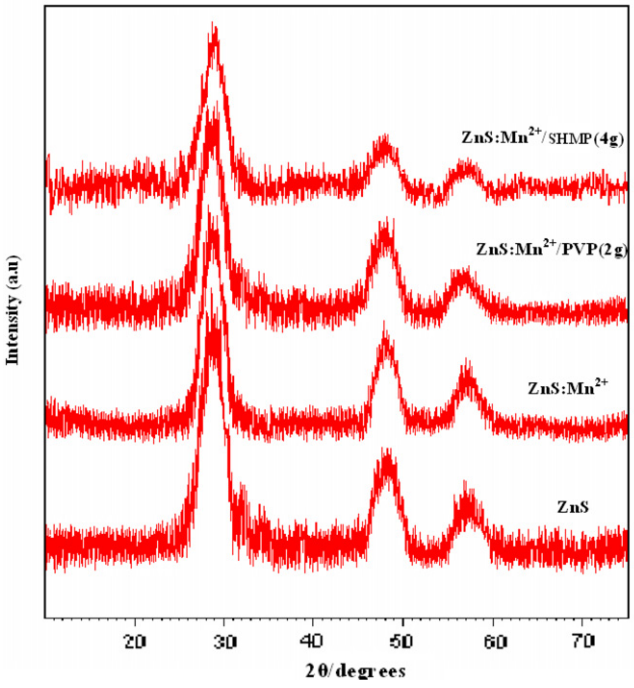

Fig. 2. XRD patterns of uncapped ZnS, ZnS:Mn^{2+} and PVP, SHMP-capped ZnS:Mn^{2+} nanoparticles.

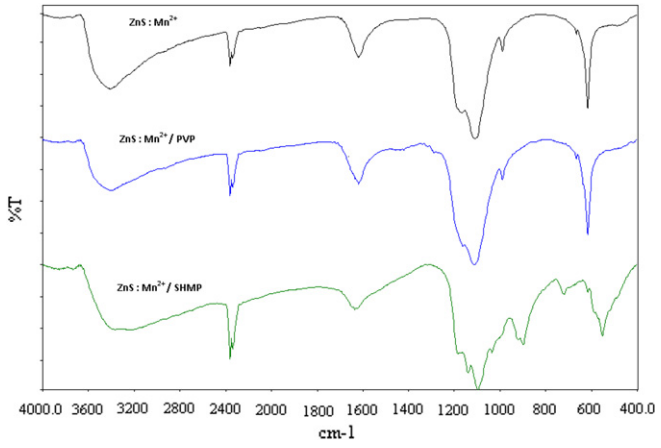

Fig. 3. FT-IR spectra of uncapped and capped (PVP and SHMP) ZnS:Mn^{2+} nanoparticles.

$(CH_3COO)_2 \cdot 2H_2O$, $MnCl_2 \cdot 4H_2O$, polyvinyl pyrrolidone (PVP, mw—40,000)and sodium hexametaphosphate (SHMP, mw—611.78), which are all of analytic purity. Ultrapure deionized water and methanol (same volume ratio) were used as the reaction medium. The mixture solution of Zn $(CH_3COO)_2 \cdot 2H_2O$, $MnCl_2 \cdot 4H_2O$ and deionized-ethanol mixture in stirring was dropped with an amount of Na_2S to form the precipitate. Optimum doping concentration of Mn^{2+} was selected at 4 wt%. The precipitate was washed with water, ethanol and methanol for several times and then dried at 80 °C for 2 h. Next, ZnS:Mn^{2+} nanocrystalline precursors were coated with the polymer polyvinyl pyrrolidone and sodium hexametapolyphosphate. The weight ratio of PVP and SHMP was selected from 1 to 3 g and 2 to 8 g, respectively. Fig. 1 presents a schematic of the formation of PVP and SHMP-encapsulated ZnS:Mn^{2+} nanoparticles. For the synthesis of undoped ZnS nanoparticles, the same precursor