Optical Materials 31 (2009) 1631–1635

Contents lists available at ScienceDirect

Optical Materials

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

Synthesis and photoluminescent properties of doped ZnS nanocrystals capped by poly(vinylpyrrolidone)

Michael W. Porambo, Anderson L. Marsh *

Department of Chemistry, Lebanon Valley College, 101 N. College Ave., Annville, PA 17003, USA

ARTICLE INFO

Article history:
Received 3 July 2008
Received in revised form 17 February 2009
Accepted 18 March 2009
Available online 23 April 2009

PACS:
61.46.+w
61.72.Vv
78.55.−m

Keywords:
Zinc sulfide
Semiconductor nanocrystals
Dopants
Photoluminescence
Poly(vinylpyrrolidone)

ABSTRACT

Zinc sulfide semiconductor nanocrystals doped with selected transition metal ions (Mn^{2+}, Cu^{2+}, and Ni^{2+}) have been synthesized via a solution-based method utilizing low dopant concentrations (0–1%) and employing poly(vinylpyrrolidone) (PVP) as a capping agent. UV/Vis absorbance spectra for all of the synthesized nanocrystals show an exitonic peak at around 310 nm, indicating that the introduction of the dopant does not influence the particle size. Calculated particle sizes for undoped and doped nanocrystals are in the 4.3 nm size range. Photoluminescence spectra recorded for undoped ZnS nanocrystals, using an excitation wavelength of 310 nm, exhibit an emission peak centered at around 460 nm. When a dopant ion is included in the synthesis, peaks in the corresponding photoluminescence spectra are red-shifted. For Mn-doped nanocrystals, an intense peak centered at approximately 590 nm is found and is seen to increase in photoluminescence intensity with an increase in dopant concentration. In contrast, for Cu-doped and Ni-doped nanocrystals, weaker peaks centered at around 520 and 500 nm, respectively, are observed and are noticed to decrease in photoluminescence intensity with an increase in dopant concentration. These results clearly show that careful control of synthetic conditions must be employed in the synthesis of doped semiconductor nanocrystals in order to obtain materials with optimized properties.

1. Introduction

Semiconductor nanocrystals continue to receive much attention due to unique optical and electronic properties that are dependent on a variety of material properties, such as size, shape, and composition [1–5]. These optical and electronic properties arise due to quantum confinement resulting from the nanometer size of the particle. A variety of synthetic methods exist for controlling the size, shape, and composition of these semiconductor nanocrystals, allowing for the tailoring of properties specific to the desired application [6,7]. For nanocrystals prepared by solution-based chemical methods, a capping agent, which adsorbs to the nanocrystal surface, is generally added both to control the size of the nanocrystal and to prevent agglomeration of the synthesized crystals. These adsorbates have been shown to alter the electronic structure of the nanocrystals [4,5]. Additionally, metal ion dopants added during synthesis may modify the luminescent properties of these semiconductor nanocrystals [3]. The resultant properties have allowed the use of these nanocrystals in applications ranging from biological sensors to optical displays. Thus, the synthesis and characterization of semiconductor nanocrystals of various sizes and compositions and with different capping agents remains an active area of current research.

More specifically, the synthesis and characterization of colloidal zinc sulfide semiconductor nanocrystals with selected optoelectronic properties have been carried out [8]. A range of ZnS nanocrystals doped with different transition metal and rare-earth metal ions have been prepared using a variety of synthetic methods. For example, with the Mn^{2+} ion as a dopant, the photoluminescence of the nanocrystal is red-shifted from the blue region of the visible spectrum to the orange region [9–12]. Based on further experimental findings, the authors suggest that the position of the dopant ion, on the surface versus incorporated in the nanocrystal lattice, influences the resulting photophysical properties [12]. In addition to dopants, capping agents with organic functional groups have also been shown to modify luminescence properties [13,14]. Enhanced photoluminescence has been reported for doped ZnS nanocrystals capped with poly(vinylpyrrolidone) (PVP) [13]. The authors suggest that efficient energy transfer occurs between the polymer functional group adsorbed at the surface and the dopant centers in the nanocrystal. This result indicates that PVP may prove to be a suitable capping agent for semiconductor nanocrystals, particularly those targeted for applications such as photocatalysis in aqueous systems. Different synthetic methods for producing PVP-capped, undoped ZnS nanocrystals have recently been reported

* Corresponding author. Tel.: +1 717 867 6149; fax: +1 717 867 6075.
E-mail address: marsh@lvc.edu (A.L. Marsh).

0925-3467/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.optmat.2009.03.013

[15–19]. However, studies on the effect of dopant concentration for PVP-capped ZnS nanocrystals have been limited [20,21]. In order to better understand synthetic conditions needed to prepare these PVP-capped nanocrystals with selected optoelectronic properties, experiments systematically varying the dopant concentration present during synthesis must be performed.

In this work, we report on the synthesis and optoelectronic characterization (UV/Vis absorption and photoluminescence spectroscopy) for PVP-capped zinc sulfide semiconductor nanocrystals prepared using 0–1% concentration of selected transition metal ions dopants (Mn^{2+}, Cu^{2+}, and Ni^{2+}). Analysis of particle sizes using peak positions in UV/Vis absorption spectra indicate that all synthesized nanocrystals are approximately 4.3 nm in size. Undoped ZnS nanocrystals exhibit an emission peak centered at around 460 nm in the photoluminescence spectrum, while doped ZnS peaks are red-shifted to higher wavelengths. The photoluminescence peak centered at around 460 nm decreases in intensity with increasing concentration of the dopant. Only Mn-doped nanocrystals display a strong peak corresponding to the dopant ion. These results signify that PVP-capped zinc sulfide semiconductor nanocrystals may be synthesized with various dopant compositions that modify their optoelectronic properties without changing particle sizes of the synthesized nanocrystals.

2. Experimental

Zinc acetate dihydrate, copper (II) acetate monohydrate, manganese (II) acetate tetrahydrate, nickel (II) acetate tetrahydrate, sodium sulfide nonahydrate, and 55,000 MW poly(vinylpyrrolidone) (PVP) were purchased from Aldrich Chemical and used without further purification. Solutions of 1.0 M $Zn(C_2H_3O_2)_2$, 0.85 M Na_2S, and 0.010 M $Cu(C_2H_3O_2)_2$, $Mn(C_2H_3O_2)_2$, and $Ni(C_2H_3O_2)_2$ were prepared in deionized water. The synthetic methods used in this work have been based on previously reported procedures [11–13,20–27].

Undoped ZnS nanocrystals were synthesized following a simple double replacement reaction in aqueous solution:

$$Zn(C_2H_3O_2)_2 + Na_2S + PVP \rightarrow PVP{-}ZnS + NaC_2H_3O_2$$

To 5.0 mL of a 1.0 M $Zn(C_2H_3O_2)_2$ solution, 0.55 g PVP was added and dissolved while stirring continuously. Next, 5.0 mL of 0.85 M Na_2S was added, and a white precipitate immediately formed. Samples of the precipitate were centrifuged at ~3500 RPM for 10 min, followed by decanting of the liquid and washing of the remaining solid. This procedure was repeated two more times, with no washing after the final centrifugation. The nanocrystals were then analyzed by UV–Vis absorption and photoluminescence emission spectroscopies.

Doped nanocrystals were synthesized in a similar manner. The procedure as detailed in the above paragraph was followed with a modification for the addition of the dopant ion. After 0.55 g PVP was dissolved in 5.0 mL of the $Zn(C_2H_3O_2)_2$ solution, a known volume of one of the doping reagents ($Cu(C_2H_3O_2)_2$, $Mn(C_2H_3O_2)_2$, or $Ni(C_2H_3O_2)_2$) was added to produce a known concentration (0–1%) of dopant. Dopant percentages reported in this work are based on Zn:dopant cation ratios present during synthesis, and not on analysis of the final precipitated products. All subsequent steps of the synthesis and purification were carried out as described.

UV/Vis absorbance spectra were recorded using an HP 8452A diode array spectrophotometer. Photoluminescence emission spectra were obtained over the 330–800 nm wavelength range with a Shimadzu RF-5301 PC spectrofluorometer operating with an excitation wavelength set at 310 nm. Care was taken to ensure that all samples were of the same concentration when recording photoluminescence spectra.

3. Results and discussion

The UV/Vis absorbance spectrum for freshly-prepared undoped ZnS nanocrystals capped by PVP is shown in Fig. 1. As observed in the figure, the sample exhibits an exitonic peak at around 310 nm. This absorption spectrum has been used to calculate an approximate size for these nanocrystals using the Brus equation [28]. Based on the peak position in the absorbance spectrum, the particle size of these nanocrystals has been calculated to be 4.3 nm. This value is close to that reported previously for PVP-capped ZnS nanocrystals [13], and slightly higher than that reported for ZnS nanocrystals synthesized with the same Zn:S concentration ratio but capped with sodium polyphosphate [22]. No reason has been found in the literature as to the slightly larger particle size resulting from the use of PVP as a capping agent, but we speculate that it is most likely due to the differences in coordination between the metal ions and PVP versus sodium polyphosphate. The larger polymer chain may coordinate a higher concentration of metal ions, which leads to the formation of slightly larger nanocrystals. Despite this larger particle size, using PVP as a capping agent for ZnS nanocrystals does lead to the formation of stable nanocrystals. Aging experiments (data not shown) conducted over a period of days clearly indicate no change in the exitonic peak position, suggesting that the PVP prevents the nanocrystals from aggregating in solution.

The photoluminescent properties of these undoped ZnS semiconductor nanocrystals capped with PVP have also been studied. The photoluminescence spectrum of undoped nanocrystals is displayed in Fig. 2. With the sample excited by 310 nm light, the spectrum contained a broad photoluminescence emission peak centered at around 460 nm. This wavelength is within the range of wavelengths reported in the literature for ZnS nanocrystals [9,12,14,15,17,19,20,24,26,27] Sulfur vacancies in the lattice have been suggested to be responsible for this photoluminescence emission [9,12]. The small peak at around 620 nm is believed to be the second order Rayleigh scattering peak from the excitation light, while the origin of the peak at around 375 nm is currently unknown. Both of these peaks appear in the photoluminescence emission spectra for doped nanocrystals as well. No emission bands resulting from the PVP capping agent are believed to be present, because of the selection of 310 nm as the excitation wave-

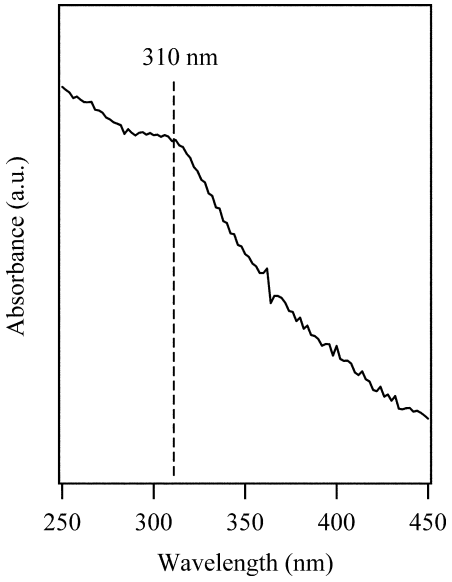

Fig. 1. UV/Vis absorbance spectrum for undoped PVP-capped ZnS nanocrystals.