

RESEARCH PAPER

Synthesis and Characterization of Transition Metal Doped ZnSe/ZnS Nanocrystals by a Rapid Photochemical Method

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ABSTRACT

In the present work, a one pot, rapid and room temperature photochemical Synthesis of transition metal (TM; Cu, Mn, Cr)-doped ZnSe/ZnS core/shell nanocrystals (NCs) was reported. FT-IR spectrum confirmed the capping of ZnSe by thioglycolic acid. XRD and TEM analysis demonstrated zinc blende phase NCs with an average size of around 3 and 5 nm for TM:ZnSe and TM:ZnSe/ZnS NCs, respectively. PL spectra of ZnSe NCs showed a broad emission with two peaks located at 380 and 490 nm related to excitonic and trap states emission, respectively. For ZnSe:Cu NCs, excitonic emission disappeared completely and PL intensity of trap states emission increased. For ZnSe:Mn and ZnSe:Cr NCs, the excitonic emission decreased gradually with the increase in the impurity concentration whereas trap state emission increased. Moreover a peak about 580 nm was appeared from 4T₁-6A₁ transition of the Mn impurity. ZnS Shell increased photoluminescence and stability of all of TM-doped ZnSe NCs.

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INTRODUCTION

Over the past decade, driven by interest in unique optical and electronic properties of nanocrystals (NCs), the investigation of preparing NCs is becoming an important area of interdisciplinary research [1-4]. Among several Semiconductor NCs, II-VI semiconductor NCs have also gained substantial consideration because of their great potential application in light emitting-diodes, sensors, solar cells and fundamental researches [5-7]. In recent years experimental results show that cadmium compounds are toxic and dangerous to the biological system [8]. Among the II-IV semiconductor NCs, zinc compounds such as ZnS and ZnSe have less toxicity than cadmium compounds and can be an alternative for biological applications [9]. Doping of transition metals (TMs) into ZnSe NCs can improve their luminous properties for a broader range of applications in

optoelectronics [10,11]. There are some reports on the synthesis of TM-doped ZnSe NCs using different methods by different groups [11-21]. In most of these methods, reaction time is long and reaction temperature is too high [21-23]. Photochemical method is a novel, rapid, mild and environmental friendly method for synthesis NCs [23-26].

In the present work, a one pot, rapid, green and room temperature photochemical Synthesis of transition metal (TM; Mn, Cu, Cr)-doped ZnSe/ZnS core/shell NCs was reported.

MATERIALS AND METHODS

Materials

Zinc acetate dehydrate, Selenium powder, Sodium borohydride, Thioglycolic acid, Copper sulfate, Manganese nitrate (Mn(NO₃)₂) and Chromium(III) nitrate were purchased from Merck chemical Company.

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Synthesis of ZnSe NCs

The synthesis of ZnSe and ZnSe:TM NCs were performed using a photochemical method in aqueous medium and room temperature. The aqueous growth of ZnSe NCs results from the reaction of Zinc acetate and NaHSe in the presence of TGA as capping agent.

In a typical reaction, 0.1314g zinc acetate was dissolved in 75mL of deionized (DI) water, and then 0.1mL TGA was added as a capping agent. The molar ratio of $[Zn^{2+}]:[TGA]:[Se^{2-}]$ was 2:8:1 respectively. NaHSe was prepared using a reaction between 0.024g Se powder and 0.04g $NaBH_4$ under Argon gas flow in a way that the final concentrations were 0.5 and 0.15M, respectively. After 5 min, mixture solution transferred to a syringe through a filter.

Synthesis of TM:ZnSe@ZnS core-shell NCs

Synthesis of TM-doped ZnSe NCs, were done by adding proper amount of copper acetate, manganese nitrate and Chromium(III) nitrate before adding TGA to Zinc acetate solution. Mole ratio of dopant ions to Zn^{2+} were 1% for Cu, 1% for Cr and 0.08% for Mn impurities. The prepared solution was exposed to UV illumination only for 10 min at room temperature.

Synthesis of TM:ZnSe@ZnS core-shell NCs

After the synthesis of ZnSe, 10 cc of ZnSe NCs was added to a 20 cc solution of zinc acetate and $Na_2S_2O_3$. The concentration of $Zn(Ac)_2$ and $Na_2S_2O_3$ was 1.6 and 8mM, respectively. The prepared

solution was exposed to UV illumination only for 10 min at room temperature. $Na_2S_2O_3$ is a UV sensitive material, which dissociates and creates some S species and free electrons needed for the reaction, and leads to the ZnS formation around ZnSe cores [25].

Characterization

Infrared absorption data were obtained by using an AVATAR-370-FTIR THERMONICOLET Fourier-transform-infrared (FTIR) spectrometer. UV-visible (UV-Vis) and photoluminescence (PL) spectra were performed using an Avantes spectrometer (Ava Spec-2048 TEC). X-ray diffraction (XRD) was carried out by an advanced d8Bruker system. Transmission electron microscopy (TEM) image was taken using Philips EM 208 with an accelerating voltage 100 kV. SEM images have been obtained using LEO 1450 VP system.

RESULTS AND DISCUSSION

To confirm the capping of particles by TGA and formation of NCs, FTIR spectroscopy was done. Fig. 1 displays the FT-IR spectra of TGA and TGA-capped ZnSe NCs. The band at 3427 cm^{-1} corresponds to the O-H stretching. For ZnSe NCs disappearance of S-H bond (2500 cm^{-1}) in free TGA showed that H atom has been replaced by Zn at S-H bond [12]. Moreover, The peak at 1720 cm^{-1} which corresponds to COOH shifts to 1580 cm^{-1} which is attributed to asymmetric COO^- and symmetric COO^- bond at 1385 cm^{-1} was appeared [27,28]. This accumulates negative charges on

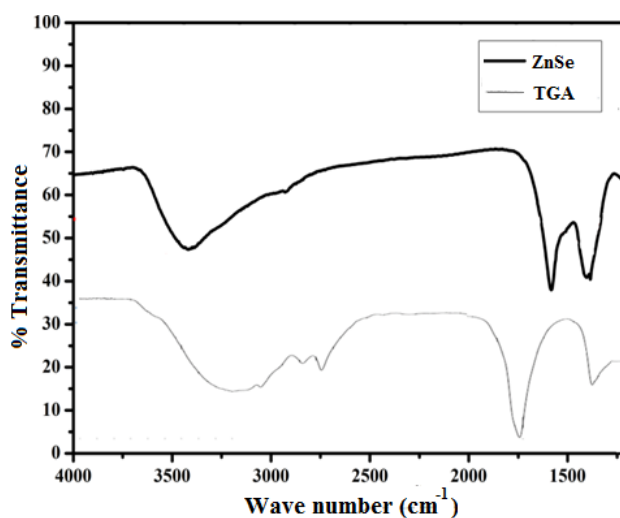


Fig. 1. FT-IR spectra of TGA and TGA-capped ZnSe NCs.

the outer surface of NCs and prohibits from their agglomeration. These results clearly confirm that TGA covers the surface of ZnSe NCs successfully. The crystallinity and structure of the obtained NCs were demonstrated by the x-ray diffraction pattern (Fig. 2). There is no obvious diffraction peak shift after doping. For TM:ZnSe/ZnS NCs, as expected, diffraction peaks clearly shifted to the higher angles, which confirmed TM:ZnSe/ZnS formation. The XRD pattern of both undoped and TM-doped ZnSe samples had characteristic diffraction peaks at (2θ) 28.6°, 47.5°, and 56.4° which could be indexed to typical (111), (220) and (311) crystal planes of cubic zinc blend ZnSe, respectively. The crystallite size of the TM:ZnSe and TM:ZnSe/ZnS NCs was calculated to be 2.5 and 5 nm, respectively, using Debye-Sherer's formula with the full width of half

maximum (FWHM) of the first main XRD peak [17]. For ZnSe@ZnS NCs, as expected, diffraction peaks clearly shifted to the higher angles, which confirmed TM:ZnSe@ZnS formation.

The morphology of the NCs was observed by SEM and TEM images. Fig. 3(a) shows the scanning electron micrographs of synthesized Cu doped ZnSe NCs. It demonstrates that the products are spherical and there is a well size distribution in NCs.

Fig. 3(b) is a typical TEM image of the synthesized TM:ZnSe/ZnS core/shell NCs. The image showed that particles were round in shape and most of the NCs have a diameter of about 5 nm which is bigger than that for ZnSe NCs and a shell around ZnSe cores can be observed from Fig. 1 (b) clearly.

Fig. 4 shows PL spectra of the ZnSe, TM:ZnSe

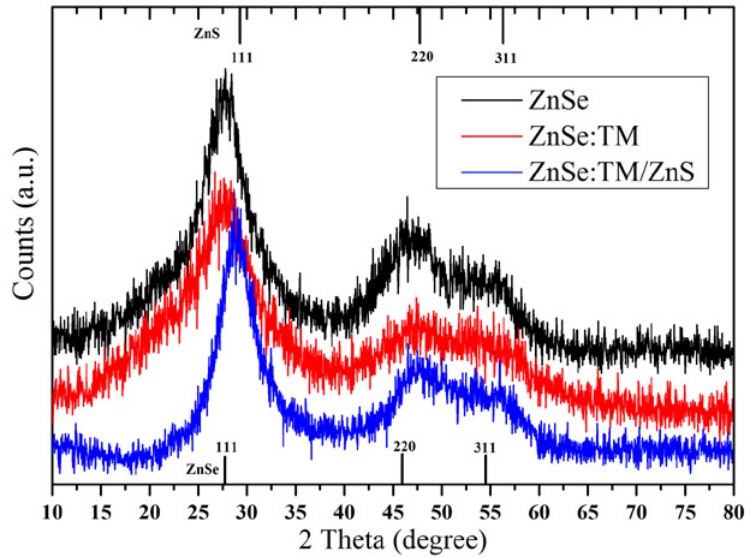


Fig. 2. XRD pattern of ZnSe, ZnSe:TM and ZnSe:TM/ZnS core-shell NCs.

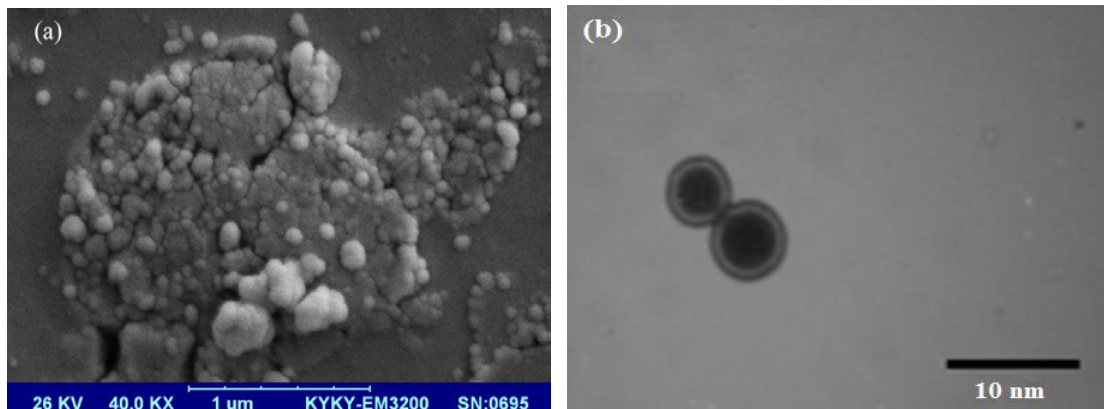


Fig.3. (a) SEM and (b) TEM images of as-synthesized ZnSe:TM and ZnSe:TM/ZnS NCs.

and TM:ZnSe/ZnS NCs for 10 min illumination time using an excitation of 254nm. From Fig. 4(a) it is seen that the PL spectra of ZnSe NCs is dominated by a near band edge emission (excitonic emission) with a peak located at about 370 nm, accompanied with a broad band emission with a peak located at about 490 nm which is due to deep trap emissions [24].

The PL spectra of ZnSe:Mn and ZnSe:Mn/ZnS NCs

can be seen in Fig. 4(a), and show three emission peaks, located at 370nm, 490nm and 590 nm. The emission peak at 370 nm is from the ZnSe excitonic emission that significantly decreased compared to that of undoped ZnSe NCs. The peak at 490 nm which is related to ZnSe trap states increased compared to that of undoped ZnSe NCs. The 590nm emission is assigned to ${}^4T_1-{}^6A_1$ electronic transition of the Mn^{2+} impurity [29].

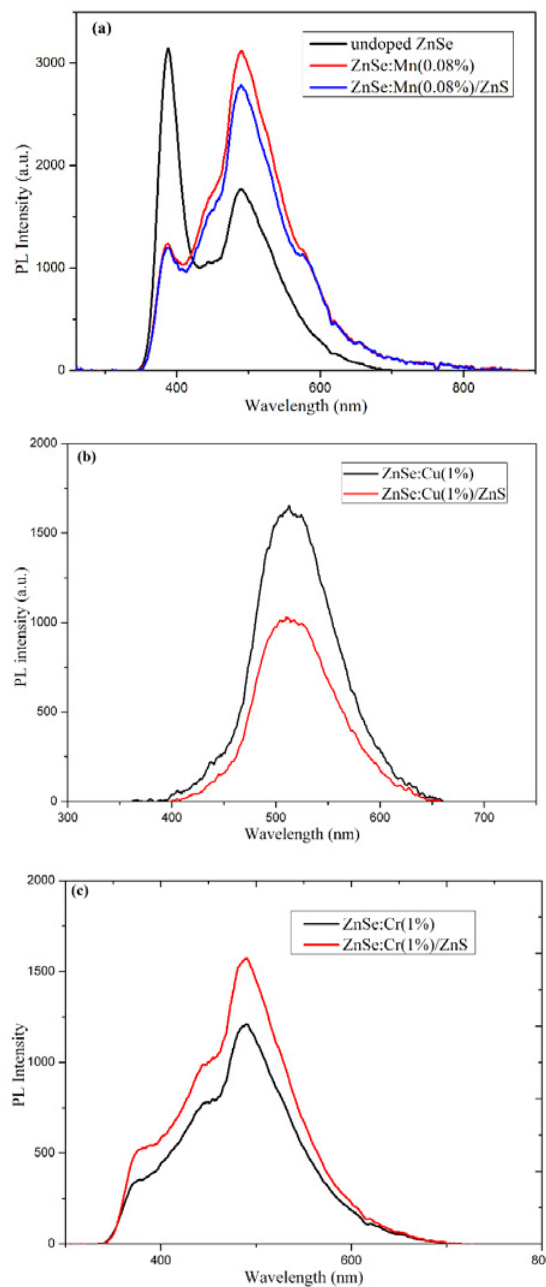


Fig. 4. PL spectra of TM:ZnSe and TM:ZnSe/ZnS NCs for TM=Mn (a), Cu (b) and Cr (c) impurities.

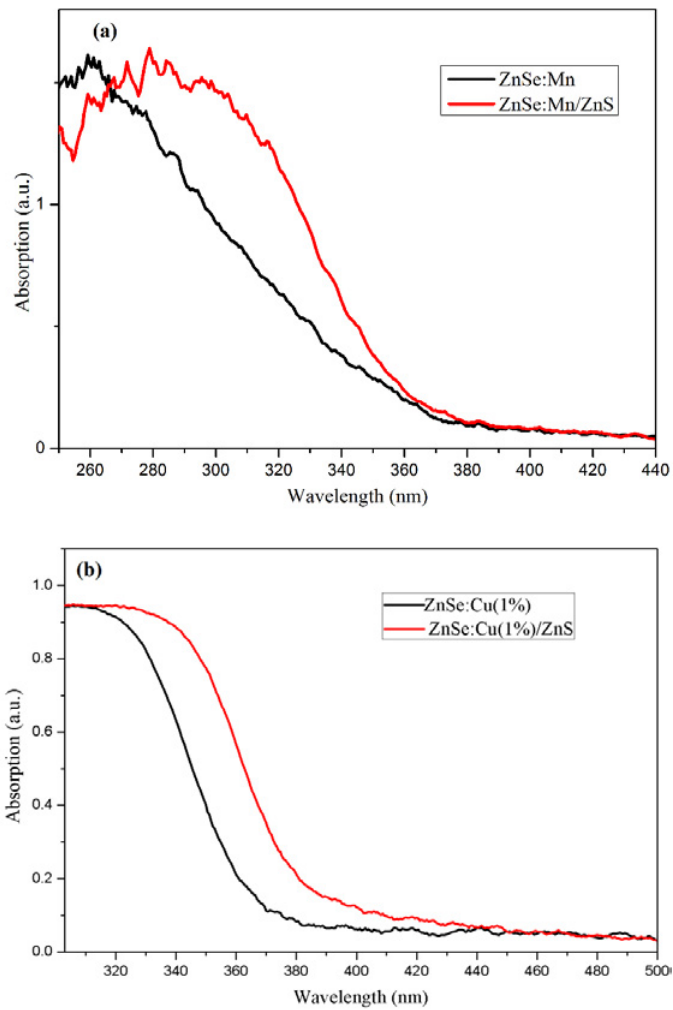


Fig. 6. UV-Vis spectra of TM:ZnSe and TM:ZnSe/ZnS NCs for TM=Mn (a), Cu (b) and Cr (c) impurities.

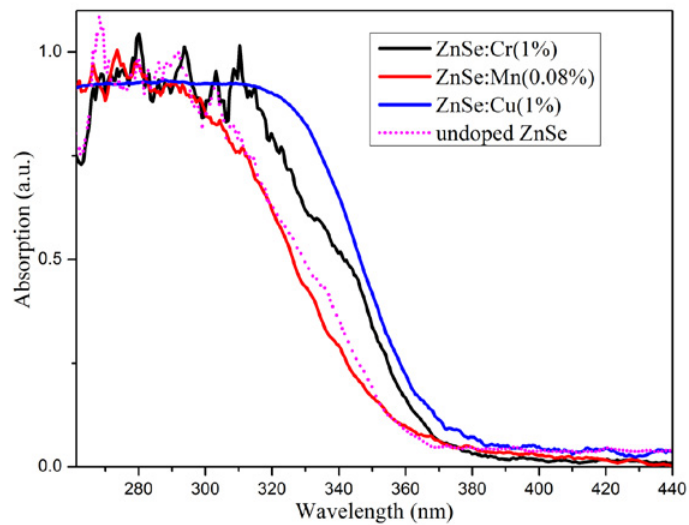


Fig. 5. UV-Vis spectra of undoped and TM-doped ZnSe NCs for TM=Mn, Cu and Cr impurities.

The PL intensity of the excitonic emission of ZnSe NCs was quenched with doping of Cu impurity and trap states emission increased as shown in the Fig. 4(b). Similar results have also been reported for ZnSe:Cu NCs [30]. In the case of Cr impurity, intensity of the excitonic peak decreased and trap states emission significantly increased (Fig. 4 (c)). These obtained results confirm doping of TM impurities into ZnSe host NCs.

Fig. 5 demonstrates absorption spectra of undoped ZnSe and ZnSe:TM NCs with TM=Mn, Cu and Cr impurities. The band edge of the Pure and TM-doped ZnSe NCs was located at about 3.58eV for undoped NCs and 3.71, 3.52 and 3.49 eV for Mn, Cu and Cr impurities, respectively which was higher than that for ZnSe in bulk case (2.7 eV). Apparently, For Cu and Cr impurities absorption edge exhibits clear red-shift whereas in the case of Mn impurity absorption edge shows blue-shift compared to that of undoped ZnSe NCs due to size effect [29,30]. Similar shifts in absorption band have also been reported for Cu and Mn doping[29,30].

As shown in Fig. 6 (a, b and c), ZnSe:TM/ZnS core/shell NCs absorption edge has a clear red shift compared to ZnSe:TM NCs, which due to the size effect induced by the shell growth. This results could demonstrate the overcoating reaction of the ZnS shell on the ZnSe:TM cores.

CONCLUSION

ZnSe, ZnSe:Cu, ZnSe:Cr and ZnSe:Mn NCs were synthesized by a rapid photochemical method using TGA as capping agent and catalyst of reactions. XRD patterns indicates cubic zinc blend TM-doped ZnSe NCs with an average size around 2.5 nm. TEM image demonstrated round shape NCs with an average size around 3 nm.

The PL spectra of ZnSe NCs showed two peaks located about 400 and 500 nm related to excitonic and trap states emissions, respectively. For ZnSe:Cu NCs the excitonic emission was quenched and PL intensity of trap states emission increased. For ZnSe:Mn and ZnSe:Cr NCs, the excitonic emission decreased gradually with the increase in the impurity (Cu) concentration whereas trap state emission increased. Moreover in the case of ZnSe:Mn NCs a peak about 580 nm was appeared from ${}^4T_1-{}^6A_1$ transition of the Mn^{2+} impurity, demonstrating the Mn incorporation inside the ZnSe NCs structure. ZnS shell was grown around ZnSe cores using a reaction based on the photo

sensitivity of $Na_2S_2O_3$. For TM:ZnSe@ZnS core-shell NCs, XRD diffraction peaks shifted to the higher angles and a shell can be seen around ZnSe cores from TEM image. After ZnS growth, PL intensity was increased considerably.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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