

Effect of ZnS shell on optical properties of Ni-doped ZnSe nanocrystals

Ehsan Soheyli^{1,*}, Gholamreza Nabiyouni¹, Reza Sahraei²

¹Department of Physics, Faculty of Science, Arak University, Arak, 3815688394, Iran

²Department of Chemistry, University of Ilam, Ilam, 65315-516, Iran

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✉: E. Soheyli
ehs.soheyli@gmail.com

ABSTRACT

The present paper aims to suggest a simple/fast route for direct preparation of the Ni-doped ZnSe/ZnS core/shell NCs in aqueous solution. Using XRD measurement, the zinc blend structure and sub-5 nm average size of the NCs was proved. The FT-IR spectrum also showed the passivation of the NCs surface by means of the deprotonated thiol terminals of the NAC molecules. The intensity of the dopant-related emission at about 476 nm in Ni:ZnSe doped NCs was found to experience more than four times enhancement by utilization of the extra ZnS shell. It was also observed that the increasing of the shell overcoating time from 1 to 3 h, has effective role on better passivation of the surface of the NCs and increasing of the emission intensity.

Keywords: Colloidal synthesis; Ni-doped ZnSe NCs; Core/shell structures; Photoluminescence emission.

1. Introduction

Colloidal nanocrystals (NCs) are nanometer-sized semiconductor particles synthesized and suspended in the both of organic and aqueous solution phases [1]. Ever growing interest

in these materials derives from the convenient fabrication of solids directly from the solution-phase, as well as their rationally-engineered, wide-ranging spectral tunability afforded by the quantum confinement effect [2]. Meanwhile, one of the most important breakthroughs was the development of direct aqueous-based synthesis approaches which fostered their scope in both terms of chemical synthesise and technological point of views [3]. In other hand, introduction of the dopant element opens a new window for making a desired characteristic and optimizing the optical properties in the NCs [4]. Using Ni²⁺ ions and by overcoating the additional shell on core NCs, here, we report a facile way for preparation of Ni-doped ZnSe/ZnS core/shell NCs.

2. Experimental

Materials and methods

Zn(OAc)₂·2H₂O, Ni(OAc)₂·4H₂O, Se, NaBH₄, N-acetyl-L-cysteine (NAC), NaOH and acetone were purchased from Merck company. The deionized water was also used in all experiments. The Ni-doped ZnSe NCs were prepared as follows; first, the suitable amounts of Zn and Ni precursors were dissolved in aqueous solution of the NAC with molar ratios of Zn:Ni:NAC equal to 1:0.02:3. After titration by 1 M NaOH (pH=9.5) and N₂ bubbling in 3-necked flask, the solution temperature was increased to 100 °C. Next, the freshly prepared NaHSe solution (by reaction of Se and NaBH₄) was swiftly injected and the temperature was cooled down to 80 °C. The flask was refluxed for 1 h yielding to Ni:ZnSe NCs. After that, 3 ml of the NCs solution was exited for optical measurements. Then, the reaction temperature was further decreased to 75 °C and the pre-prepared solution of Zn, NAC (Zn:NAC molar ratio of 1:2) and 11 ml deionized water was added to stirring solution and the refluxing process was continued for 1, 2 and 3 h for formation of core/shell NCs. After cooling to room temperature, the required amounts of solution were used for PL and PLE spectroscopies. The powder of the NCs was obtained by adding of acetone to as-prepared

solution. XRD, FT-IR, PLE and PL analysis were carried out for characterization of the prepared samples.

3. Results and discussion

As is observed in Fig. 1, the XRD pattern ($\lambda_{Co}=1.79 \text{ \AA}$) of the NCs powder, show a zinc blend cubic structure of ZnSe with three broad peak at 32, 53.6 and 63.5 degrees which are attributed to (111), (220) and (311), respectively [5]. The obvious broadening of the peaks indicates the small size of the core/shell NCs. Using the well-known Scherrer equation, the size of the NCs were estimated to be near 3.5 nm.

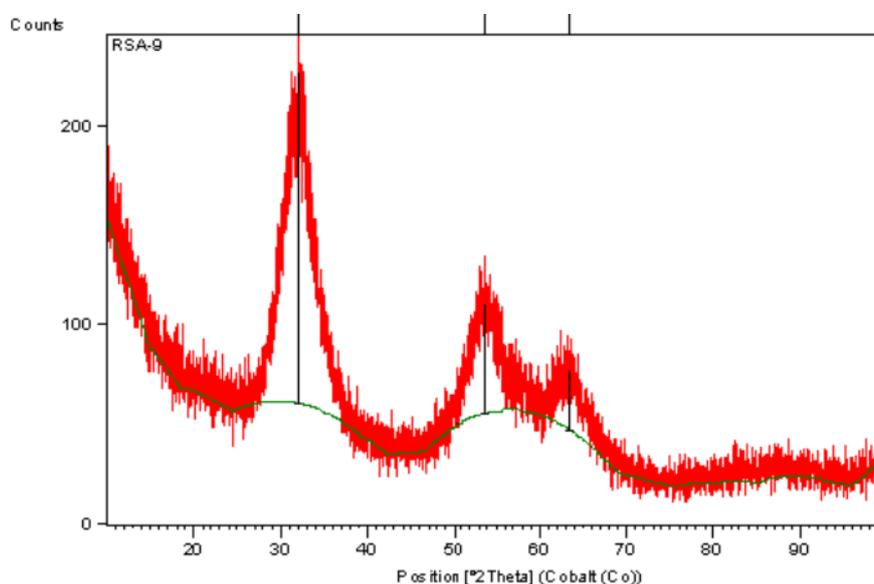


Fig. 1: The XRD pattern of the Ni:ZnSe/ZnS NCs

The FT-IR transmittance spectra show the complete disappearance of the thiol-related peak which is located about 2500 cm^{-1} in pure NAC (Fig. 2). This demonstrates the possible passivation of the NCs with deprotonated thiol group of NAC molecules and their interaction with Zn^{2+} ions in the surface of the NCs. Whereas the carboxylate group were found to be still presented in NAC-capped Ni:ZnSe/ZnS NCs which exhibit their possible interaction with surrounding medium [6].

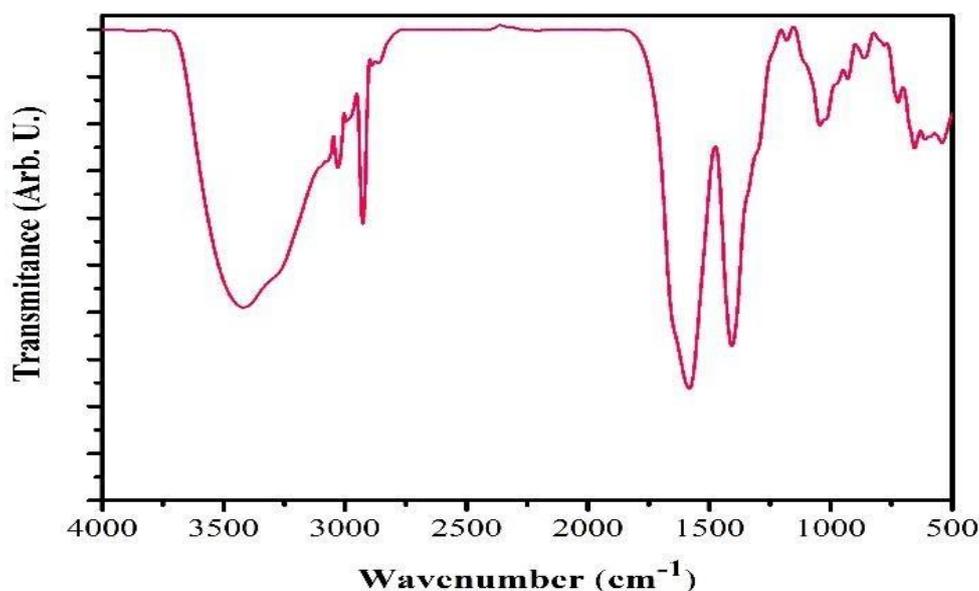


Fig. 2: FT-IR spectrum of the Ni:ZnSe/ZnS NCs.

As an important factor for application of NCs in light emitting systems, the excitation and emission PL spectra of the core and core/shell- doped NCs were recorded and showed in Fig. 3. There are several conclusions, implied from these spectra. The large Stokes shift between absorption and emission peaks (100 nm) indicates that the PL emission can be related to impurity states. Indeed, it can be attributed to recombination of the charge carriers between conduction band and Ni^{2+} energy levels. Interestingly, this dopant-related peak experiences a very substantial enhancement by addition of Zn-NAC solution. It demonstrates the effective surface passivation of the NCs and formation of doped- core/shell structure. When we do use the additional inorganic shell with higher band gap energy, it can prohibit the charge carriers from surface of the NCs where the surface defects can act as trap states for them, leading to non-radiative recombination and decreasing of the emission intensity [7]. However, increasing of the shell growth (by increasing of the shell overcoating time duration) from 1 to 3 h, the emission intensity goes higher. It can be related to increasing of the shell thickness and better surface passivation. In fact, it can truly force on the Ni^{2+} dopant ions to be located at the inside lattice of the core structure. There are another behavior by injection of shell

precursor. As the refluxing time is increased, it is expected to make a red-shift in spectra, but blue-shift in both of the PL and PLE spectra is observed. Such behavior can be related to partial hydrolyzing of the S-H group in NAC molecules and subsequent insertion of the S^{2-} ions to lattice of the ZnSe NCs and formation of the ZnSe(S) alloys.

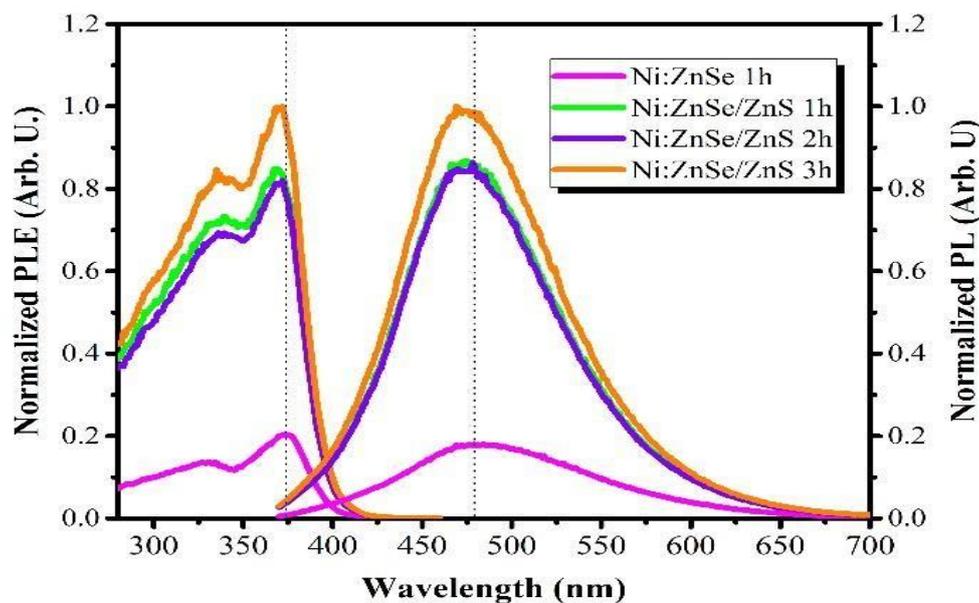


Fig. 3: Effect of shell overcoating on PLE and PL spectra of the as-prepared NCs.

4. Conclusions

A facile and one-pot method was suggested for preparation of the aqueous-based Ni:ZnSe/ZnS NCs with intense cyan emission and cubic zinc blend crystal structure. The coordinating interaction between cations and deprotonated thiol terminals of the NAC molecules was proved by elimination of the S-H related peak in FT-IR spectra. These phenomena in high temperature may lead to diffusion of the S^{2-} species to lattice structure of the ZnSe NCs and formation of the ZnSe(S) alloys which was indicated by blue-shift of the PLE and PL spectra after growth of the ZnS shell. The obtained optical results have also demonstrated that the Ni^{2+} ions show their own PL emission peak at around 476 nm which was further intensified by using of higher band gap ZnS shell. In addition, increasing of the refluxing time for shell overcoating was accompanied to further enhancement of the emission

intensity which is attributed to better surface passivation of the doped NCs.

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