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Synthesis and optical study of green light emitting polymer coated CdSe/ZnSe core/shell nanocrystals

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ABSTRACT

CdSe/ZnSe Core/Shell NCs dispersed in PVA are synthesized by chemical method at room temperature. This is characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV/Vis spectra and photoluminescence spectroscopy (PL). TEM image shows the spherical nature of CdSe/ZnSe core/shell NCs. The red shift of absorption and emission peak of CdSe/ZnSe core/shell NCs as compared to CdSe core confirmed the formation of core/shell. The superposition of quantum confinement energy model is used for calculation of thickness of ZnSe shell.

1. Introduction

Colloidal semiconductor nanocrystals have attracted great fundamental and technical interest because of their unique optical and electronic properties, such as photoblenching stability, continuous absorption band, narrow photoemission, strong fluorescence, broad photoexcitation [1–5]. Semiconductor heterostructures are typically classified as type-I or type-II nanomaterials. In the type-I structure, the electron and hole can localize the area of core because both the conduction and the valence band edges of the core are located within the energy gap of the shell. In type-II structure, both conduction and valence bands of core are either lower or higher than those in the shell. The applications of these nanocrystals require high luminescence efficiency. This parameter can be improved by the deposition of a passivating “shell” consisting of a larger gap semiconductor on the surface of a “bare” nanocrystal [6–9]. The preparation of such “core/shell” systems requires careful selection of both core and shell materials with the goal to optimize the passivation and to minimize structural defects induced by the mismatch of their lattice parameters [10–12]. Core–shell type-I composite NCs exhibit novel properties making them attractive from both an experimental and a practical point of view. An overcoating nanocrystal with higher band gap inorganic materials has been shown to improve the photoluminescence quantum yields by passivating surface nonradiative recombination sites. Particles passivated with inorganic shell structures are more robust than organically passivated dots and have a greater tolerance to processing conditions necessary for incorporation into solid state structures [13].

To improve quantum efficiency, the CdSe nanocrystal core is often covered by another semiconductor shell with a high energy bandgap such as ZnS, ZnSe and CdS [14,15]. Introducing these shells onto the surface of CdSe cores nonradiative recombination between electrons and holes, caused by dangling bonds forming on the surface of bare CdSe nanocrystals and acting as trap sites, can be prevented, and thus the quantum efficiency of CdSe nanocrystals can be greatly improved [16–19]. Examples of colloidal CdSe core/shell quantum dot structures reported so far include CdSe/ZnSe [20], CdS/ZnSe [21] and CdSe/ZnS [22]. Among all, ZnSe is a nontoxic, chemically stable wide band gap (2.7 eV for the bulk material) semiconductor. The ZnSe shell should provide the best passivation of CdSe core. ZnSe-overcoated CdSe nanocrystals have advantage that the ZnSe has larger band gap (2.72 eV) than that of CdSe (1.74 eV) resulting in formation of quantum-well structure and also CdSe (6.3%) core has lower lattice parameter mismatch than that of the preferred ZnSe (10.6%) shell.

The combination of CdSe and ZnSe into a core/shell structure is highly desirable to prevent the evolution of interfacial misfit dislocations that also act as traps for electrons and holes. Such core–shell particles exhibit efficient luminescence with stability superior to single phase nanopaticles and organic dyes [23,24]. Reiss et al. [20] and many other authors [21,22] have also reported that the luminescence properties are much more stable and less

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sensitive to surface ligand exchange as compared to "bare" core nanocrystals. This effect is a fundamental prerequisite for the use of nanocrystals in applications such as biological labeling and light-emitting devices, which rely on their emission properties [25–30].

The objective of the present study is to synthesize CdSe/ZnSe core/shell nanocrystals with different shell thicknesses by controlling the concentration of shell precursors. CdSe/ZnSe nanocrystals are characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM), UV/Vis and photoluminescence (PL) spectroscopy. Photo-emission characteristics of CdSe/ZnSe nanocrystals having different shell thicknesses are investigated using photoluminescence (PL). Unfortunately, the synthesis of core/shell materials is based on the high temperature decomposition of pyrophoric organometallic reagents. In the last 2 years, safer reagents have been proposed for the preparation of core materials, while the shell growth still requires organometallic precursors. In this paper, we have synthesized CdSe/ZnSe core/shell NCs at room temperature with a capping agent polyvinyl alcohol (PVA) matrix. The CdSe/ZnSe core/shell is showing enhancement in quantum yield as compared to CdSe nanoparticles. The ZnSe shell thicknesses are calculated by using superposition of quantum confinement energy (SQCE) model [31] is of order ~0.1–0.4 nm. CdSe/ZnSe core/shell NCs show strong green light emitting behavior which is helpful in using these nanocrystals in biological labeling and light-emitting device applications.

2. Materials and methods

2.1. Materials

Cadmium acetate dihydrate extra pure, zinc acetate, ammonia and glacial acetic acid used in the experiment has purchased from Merck Pvt. Ltd. Selenium is purchased from Loba Chemie Pvt. Ltd. PVA of molecular weight 140,000 is purchased from Himedia Pvt. Ltd. All the chemicals are used as purchased without further purification. Sodium selenosulphate (Na_2SeSO_3) has been chosen as the selenium source.

2.2. Synthesis of the CdSe NPs

Sodium selenosulphate (Na_2SeSO_3) aqueous solution (0.50 M) is prepared by adding 1.0 M of sodium sulphite in 50 ml of distilled water, by adding 0.05 mol of selenium powder. The solution has been stirred for 7 h at 70 °C. The solution is kept overnight. Upon filtration, Na_2SeSO_3 solution is sealed and stored in the dark at 60 °C to prevent decomposition. 0.1 M of metal source, i.e. cadmium acetate has been dissolved in 20 ml of deionized water. Ammonia or sodium hydroxide solution (2.0 M) is used to turn metal ions into complex ions and to reduce the free metal ion concentration. In a 50 ml flask, 20 ml PVA solution is placed and 4.0 ml metal salt solution (0.10 M) is added with constant stirring. Ammonia solution is then slowly added dropwise until a clear solution is obtained. After the pH value is adjusted to 10, 4 ml of cadmium salt is added to the mixture and 6 ml of selenosulfate solution is added. The mixture is stirred for 3 h at room temperature to obtain a solution.

2.3. Synthesis of the PVA-capped CdSe/ZnSe

4.0 ml zinc acetate solution (0.10 M) is added to the freshly prepared CdSe nanoparticle. The solution is stirred for 3 h to obtain CdSe/ZnSe core/shell. The CdSe/ZnSe solution is added to 20 ml of PVA solution to obtain PVA:n-CdSe/ZnSe core/shell quantum dot doped in PVA. The solution is casted on a glass substrate. Upon solvent evaporation, a PVA:n-CdSe/ZnSe nanocomposite film has been obtained. The film is washed with deionized water to remove other soluble salts. The reaction mechanism for CdSe/ZnSe is shown in Fig. 1.

2.4. Characterization

XRD study has been done using a Phillips PW-1710 X-ray diffractometer using Cu Kα radiation in the 2θ range from 10° to 60°. Transmission electron microscopy (TEM) has been done using Hitachi H7500 electron microscope, operating at 110 kV. The sample is deposited on carbon coated copper grid. The absorption spectra of the sample have been measured by a UV/VIS/NIR computer controlled spectrophotometer PerkinElmer LAMBDA 750 in the transmission range 400–700 nm at room temperature (300 K). Photoluminescence (PL) spectrum of the sample is recorded in the visible region on a computer-controlled luminescence spectrophotometer LS-55 (PerkinElmer Instruments) with accuracy = ±1.0 nm. The Xe discharge lamp is used as an excitation source. The values of the room temperature photoluminescence quantum yields (QYs) are then determined by comparison of the fluorescence intensity of nanocrystal samples with that of a solution of Rhodamine 6G (95%) in absolute ethanol.

3. Results and discussion

3.1. Reaction mechanism

The overall chemical reaction for the formation of CdSe/ZnSe is represented as follows:

$$Cd^{2+} + SeSO_3^{2-} + 2OH^- \rightarrow CdSe + SO_4^{2-} + H_2O \tag{1}$$

Na_2SeSO_3 can be prepared by adding elemental selenium in an aqueous hot solution of sodium sulphite as follows by ionic equation:

$$SO_3^{2-} + Se \rightarrow SeSO_3^{2-} \tag{2}$$

When sodium selenosulfate is added to the PVA–metal ion solution, it gradually releases selenide ions upon hydrolytic decomposition in alkaline media:

$$SeSO_3^{2-} + 2OH^- \rightarrow HSe^- + SO_4^{2-} \tag{3}$$

$$HSe^- + OH^- \rightarrow H_2O + Se^{2-} \tag{4}$$

The released selenide ion reacts with metal ions to form seed particles (nucleation):

$$nCd^{2+} + nSe^{2-} \rightleftharpoons (CdSe)_n \tag{5}$$

Sodiumselenosulfate is relatively stable under weakly basic conditions (pH ~10), and gradually release Se^{2-} upon hydrolytic decomposition. In all reaction processes, complex ions played an important role in the formation of nanocrystalline selenides. Under synthetic conditions, complex ions can slowly release free metal ions, which can steadily combine with Se^{2-} to form nanocrystalline selenides. The surface passivation is done with the addition of zinc source to CdSe solution. The zinc ions take excess of selenium ion from the reaction mixture of CdSe nanoparticles resulting CdSe/ZnSe core/shell.

$$mZn^{2+} + \{mSe^{2-} + (CdSe)_n\} \rightleftharpoons (CdSe@ZnSe)_{m+n} \tag{6}$$

3.2. Microstructural characterization

Fig. 2 shows the XRD spectra of CdSe and CdSe/ZnSe core/shell NCs. XRD pattern of PVA is amorphous in nature [32]. When CdSe