Synthesis of CdS/ZnSe and CdSe/CdS Core Shell Nanoparticles

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Abstract

We report the synthesis of Reverse type I & type II core shell nanoparticles CdS/ZnSe and CdSe/CdS through a one pot synthetic procedure. The Core shell nanoparticles showed optical properties and in comparison to the core, each one showed a red shift. The photoluminescence spectrum shows emission close to the absorption band edge. The TEM results show a variation of shapes; Spherical and rod like shapes with a range of sizes 7.53± 2.46 nm, 5.94±2.31 nm for the spherically shaped and 14.17±3.18 nm, 4.30±1.26 nm for the rod like particles. The XRD shows a cubic phase structure for both core shell nanoparticles.

Keywords: Core-Shell, Nanoparticles, Semiconductors

Introduction

The uniqueness of core shell semiconducting nanoparticles has made it a focus of interest. Core shell nanoparticles are those composed of a quantum dot semiconducting core material and a shell of a distinct semiconducting material (Loukanov et al, 2004). They have properties between those of small individual molecules and those of bulk crystalline semiconductors (Loukanov et al, 2004). They have been found to have better efficiency when compared to the single nanoparticles. They have easy modular properties due to their size and shape. The shape dependent properties are the physical and chemical properties (such as selectivity, catalytic activity), electrical, optical properties, and melting point. Those that are size dependent are blocking temperature magnetic saturation and permanent magnetization. There are various types; type I (Badounas. et al, 2017), reverse type I (Badounas. et al, 2017), type II (Kim. et al 2003) semiconductors. Several methods have been employed in the synthesis of core shell nanoparticles such as wet chemical methods (Mandal. et al 2008), electrochemical methods (Gu. et al, 2009) colloidal methods such as wet chemical methods (Mandal. et al 2008), electrochemical methods (Gu. et al, 2009) colloidal methods (Trallero-Giner. et al,2010). Core shell nanoparticles are applicable in various fields such as biomedical and pharamaceutical fields, catalysis, electronics (Xu. et al , 2016) etc.
The purpose of this work is to synthesise core shell nanoparticles by the selective growth of two different core-shell nanoparticles produced by a two-step synthetic procedure which exclude the purification of core material before the deposition of the shell material. The procedure used in this work is simple and reproducible.

DETAILS EXPERIMENTAL

Materials
All reagents and solvents were analytical grade and used without further purification. Hexadecylamine (HDA), tri-\textit{n}-octylphosphine (TOP), sulfur and selenium were purchased from Sigma-Aldrich. Methanol, Cadmium nitrate, zinc chloride and acetone were purchased from Saarchem, UnivAR, Merck chemicals.

Procedure
In the preparation of both core shell nanoparticles a two step procedure was employed as follows; 0.320mmol of selenium/sulphur powder dissolved in 20ml of deionized water was reacted with 20ml (0.320mmol)sodium borohydride. The reaction was allowed to proceed for 3h and 12h respectively under inert conditions for the complete reduction of selenium and sulphur. 0.64mmol of different metal chlorides dissolved in 20ml of deionized water was added to the sulphide ion solution to give a brownish black solution. The solution was left to stir for 30minutes upon which excess methanol was added. The resultant solution was centrifuged, decanted and dispersed in 6ml TOP.

In the second procedure, the core bulk sample was injected into hot HDA at 230°C and thermolysed for 2h. The shell bulk sample is added to the reaction mixture and allowed to stir for 2h. The reaction was quenched by the addition of excess methanol. It was centrifuged and the resultant particles dissolved in toluene for Characterization.

RESULTS AND DISCUSSION

Characterisation
The crystalline phase was identified by powder X-ray diffraction (XRD), employing a scanning rate of 0.05° min^{-1} in a 2θ range from 20 to 80°, using a Bruker AXS D8 diffractometer equipped with nickel filtered Co Kα radiation (\(\lambda = 1.5418\ \text{Å}\)) at 40 kV, 40 mA and at room temperature. The morphology and particle sizes of the samples were characterized by a JEOL 1010 TEM with an accelerating voltage of 100kV, MegaView III camera, and Soft Imaging Systems iTEM software. A Varian, Cary 50 Cone UV-Visible spectrophotometer was used to carry out the optical measurements and the samples were placed in silica cuvettes (1cm path length), using toluene as reference solvent.

Figure 1 shows the TEM image of the prepared core shell nanoparticles. Fig1a shows a mixture of both spherically shaped and rod like CdS/ZnSe core shell nanoparticles. The Spherically shaped CdS/ZnSe core shell nanoparticles were found to have a size of 5.94±2.31nm while the rod like shape had sizes ranging 14.17±3.18nm and 4.30±1.26nm. Fig 1b shows spherically shaped CdSe/CdS core shell nanoparticles with size 7.53±2.46nm. From the TEM image there is no evidence of defects at the core shell interface. Both ZnSe and CdS shell uniformly covers the entire surface of the GdS and CdSe core material. There has been a report on the growth of CdS on the surface of CdSe in the literature (Li. et al, 2004).

Figures 2 & 3 shows the XRD pattern of core CdS, core shell CdS/ZnSe ,core CdSe and CdSe/CdS core shell nanoparticles. The XRD patterns show broad peaks along (111), (220), (311) reflections which are assigned to the cubic phase structure. Both the core and core shell nanoparticles were found to be cubic zinc blended structure. This suggests that diffraction is predominantly due to the core (Wang. et al,2006).

Figures 4&5 shows the absorption spectra of the nanoparticles. The core absorption spectrum was found to be blue shifted from the bulk values ,core CdS(484nm, 2.5eV) and CdSe(612, 2.03eV) while the core shell nanoparticles are red shifted to the core CdS/ZnSe(609nm) and CdSe/CdS(650nm). This is a strong indication on the formation of core shell nanoparticles.

CONCLUSIONS
A synthetic procedure has been developed for the fabrication of highly luminescent colloidal types I and type II core-shell nanoparticles without the purification of the core material. The X-ray diffraction patterns confirm cubic structure for both core and core-shell semiconductor nanoparticles. The observed red shift in the absorption and photoluminescence spectra of the core-shell nanoparticles compared to the core materials is a strong indication for the formation of core-shell nanoparticles.

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Figure 1: TEM image of (a) CdS/ZnSe Core shell nanoparticles (b) CdSe/CdS Core shell nanoparticles

Figure 2: XRD pattern of (a) CdS core (b) CdS/ZnSe Coreshell nanoparticles

Figure 3: UV-Vis Spectra of (a) CdS core (b) CdS/ZnSe Core shell nanoparticles

Figure 4: UV-Vis Spectra of (a) CdS core (b) CdS/ZnSe Core shell nanoparticles
Figure 3: XRD pattern of (a) CdSe core (b) CdSe/CdS Core shell nanoparticles

Figure 5: UV-Vis Spectra of (a) CdSe core (b) CdSe/CdS Core shell nanoparticles

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