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A Study of Optical Properties of Green Synthesized ZnO/CdS Core/Shell Nanopins for Photosensor Application

P. RADHIKA¹ and KMR ACHARY²

¹Department of Physics, CMR Technical Campus, Hyderabad (India)

²Department of Physics, Malla Reddy College of Engineering & Technology, Hyderabad (India)

¹Corresponding Author E-mail: radhika.peddi@yahoo.com

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Abstract

ZnO nanoparticles and ZnO/CdS Core/Shell heterostructures have been prepared in the two-step hydrothermal method by using Starch as a capping agent. The tunability of the optoelectronic properties of ZnO/CdS can enhance the exciton life time. These type of Core/Shell nanostructures are coming under Type-II band alignment. The thickness of the shell CdS is varied, keeping the core ZnO nanopins are in the same sizes. The absorption and luminescence properties of ZnO/CdS Core/Shell are well studied. The longer exciton life time of these Type-II Core/Shell nanostructure could be beneficial for the potential application in Photosensor.

Key words: Heterostructures, Shell Thickness, Absorption, Luminescence Properties.

Introduction

Core/Shell nanostructures constitute a special class of nanocomposite materials and have novel properties for potential application. These are highly functional materials with tailored properties, which are quite different than either of the core or the shell material. Therefore, these core/shell heterostructures can lead to a new revolution in the field of science and technology in association with optics, physics, electronics, biomedical and material sciences. The wide band gap and electron-hole separation properties of ZnO/CdS heterostructures have made them one of the best candidate for photovoltaic device application. The optoelectronic properties of these core/shell nanoparticles are important for the scientific and industrial application. On the other hand, green synthesis method is simple, cost effective two step method for the growth of core/shell nanoparticles¹⁻³.

The high electron mobility, flexible morphologies, low cost and nontoxicity of ZnO nanoparticle makes it as a good choice for the fabrication of photonic device application. However, fast internal recombination of photogenerated electron and hole pair always resulting in low photo degradation efficiency. Zinc oxide (ZnO) is a wide band gap semiconductor material with energy gap 3.37 eV. Cadmium sulfide is also wide band gap semiconductor material and the energy band gap is 2.42 eV. The green chemical synthesis method is an attractive option for the synthesis of both ZnO and CdS nanoparticles. Therefore, this green chemical method is employed for the synthesis of ZnO/CdS core/shell nanoparticles in this work. The physical and the optical properties of ZnO/CdS core/shell heterostructures can be modified by this cost effective method. A simple two steps one pot synthesis method is applied for the growth of these nanoparticles⁴⁻⁷.

The use of core/shell ZnO/CdS nanostructure provides an opportunity for designing Type II core/shell material via engineered spatial distribution of electron and hole wave functions. In case of Type I core/shell nanoparticles the electron and hole experience a confinement potential that tends to localize both of the carriers in either core or shell material, which will reduce their interactions with trap states and improve the quantum yield of these heterostructures. In case of Type II core/shell material, the electron and hole are spatially separated between the core and shell material. The reduced electron-hole overlap in ZnO/CdS make them prominent candidate for photovoltaic application. The conduction band of ZnO is located between the valence band and the conduction band of CdS, therefore it will hinder the recombination of photogenerated electron and hole. The thickness of the shell nanoparticle CdS is varied in this work and the optical properties of newly formed core/shell material is proposed for device fabrication⁸⁻¹⁰.

Experimental

A simple green synthesis method was applied for the preparation of ZnO/CdS core/shell nanoparticles. This method is considered as extremely viable method for the production of core/shell heterostructures with high purity and without necessity of any posterior treatments. The optical properties of core/shell nanoparticles can be altered by using this method. This one-pot synthesis method aims the production of core ZnO nanostructure by solo chemical method with reaction temperature of 70⁰ C. The Zinc nitrate hexa hydrate [Zn(NO₃)₂.6H₂O] and sodium hydroxide (NaOH) was adopted as synthesis precursors. The production unit for this chemical synthesis method was consisted of three neck glass flask and of a magnetic stirrer with temperature control. The reaction was carried out in a nitrogen environment to prevent oxidation. In the Glass chamber, NaOH was dissolved in Starch solution (3% concentration of Starch in double distilled water solution) to a concentration of 0.1M and the resulting solutions were stirred at 70⁰ C for 1 hour. Then, a solution of 0.5 M Zn(NO₃)₂.6H₂O was added dropwise under constant stirring. For collection of core ZnO, half portion of the material was filtered and washed several times with deionized water and ethanol. The washed samples were dried at 65⁰ C in the oven for 1 hour. The shell CdS nanoparticles were prepared by simultaneous addition of Cadmium Acetate solutions and Sodium Sulfide (Na₂S) solutions. The synthesis was carried out at room temperature. The pH of the solution was kept at 9 by adding ammonia solution. The molarity of the solution was maintained at 0.1 M. ZnO/CdS core/shell nanostructures were prepared by altering core to shell ratio as 1:1 (B), 1:2 (C) and 1:3 (D) for thicker shell coating of CdS. The three samples of the core/shell were considered for structural and optical properties along with the core ZnO(A) for photosensor device application.

Results and Discussions

The X-ray diffraction pattern of ZnO and three samples of ZnO/CdS core/shell nanostructures are presented in the Fig-1. All diffraction peaks of Sample A ZnO was found at 31.9⁰, 36.5⁰, 48.2⁰, 56.7⁰, 63.2⁰, 68.1⁰ can be well attributed to the crystal planes (100), (101), (102), (110), (103) and (112) of ZnO. These planes

indicated that the prepared core ZnO can be indexed to the hexagonal wurtzite structure of ZnO particle without any impurity in the sample (JCPDS:79-0205).

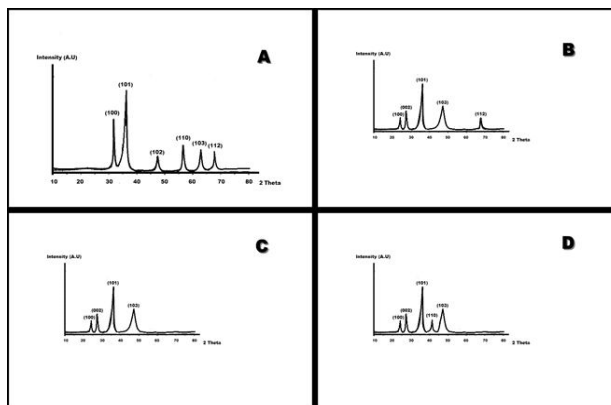


Fig 1. (A) ZnO, (B) ZnO/CdS 1:1, (C) ZnO/CdS 1:2, (D) ZnO/CdS 1:3

In the sample B ZnO/CdS core/shell 1:1, the peaks at 24.7° , 26.8° , 47.5° were identified as the (100), (002), (103) planes of hexagonal CdS nanoparticles (JCPDS:41-1049). The (101) and (112) planes of hexagonal ZnO were observed at 36.8° and 67.8° . In the sample C ZnO/CdS core/shell 1:2, the thickness of the shell material was increased and the most of the peaks were found for hexagonal CdS at 24.6° , 26.7° , 47.7° attributed to (100), (002), (103) planes. One single peak of hexagonal ZnO was seen at 36.5° for the plane (101). In the last sample D of ZnO/CdS core/shell 1:3, more peaks were found for hexagonal CdS at 24.9° (100), 26.6° (002), 28.3° (110) and 47.8° (103). There was one peak at 36.3° for the plane (101) of hexagonal ZnO. The result revealed that all core/shell samples were composed of hexagonal ZnO and hexagonal CdS structure. The core ZnO was also found in hexagonal phase. Therefore, no crystal phase transformation was found after CdS shell formation, confirming the growth of high purity product. The disappearance of peaks of ZnO in the core/shell samples suggested that with increase of CdS shell thickness, the ZnO/CdS core/shell nanoparticles were showing the shell dominating behavior^{11,12}.

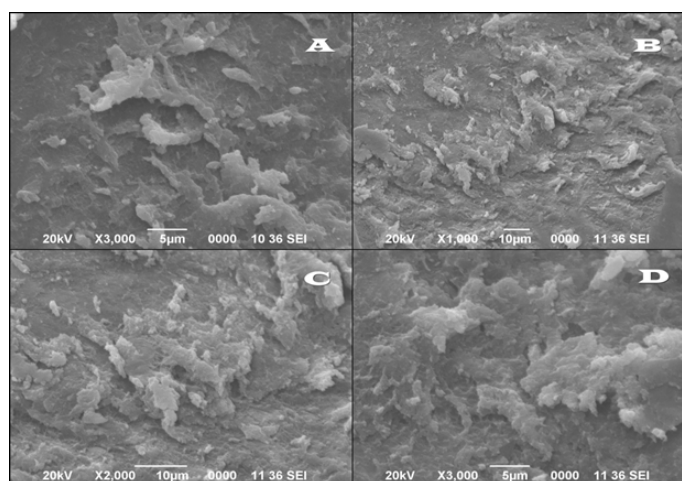


Fig 2. (A) ZnO, (B) ZnO/CdS 1:1, (C) ZnO/CdS 1:2, (D) ZnO/CdS 1:3

The particle sizes were calculated from Fig. 1 by using Scherrer's formula. The formula is given as

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Here D is the average Grain Sizes of the particles, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) and θ is the diffraction angle. The particle sizes were calculated for sample (A) ZnO, (B) ZnO/CdS 1:1, (C) ZnO/CdS 1:2, and (D) ZnO/CdS 1:3 as 16 nm, 23 nm, 26 nm and 29 nm respectively.

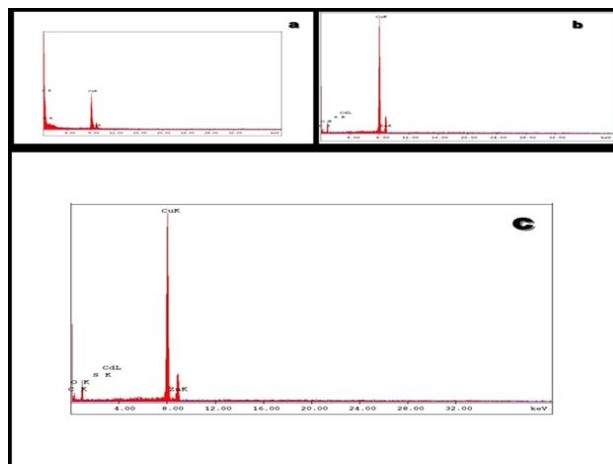


Fig 3: (a) Core ZnO, (b) Shell CdS, (c) ZnO/CdS Core/Shell

The morphology of ZnO and core/shell ZnO/CdS nanostructures were shown in the typical SEM images of Fig 2. The as-prepared ZnO nanoparticles showed highly aggregated wire like structure. In the Fig-2, samples B, C and D were found as dense bundles of nanowires. The Energy Dispersive X-ray (EDX) spectra were recorded for core (a), shell (b) and (c) core/shell material. The EDX images in the Fig 3(a) and Fig 3(b) clearly showing the composition of Zn, O and Cd, S atoms. In the Fig 3 (c), the peaks of Cadmium(Cd), Sulphur (S) and the presence of Zinc(Zn), Oxygen(O) were separately found. Therefore, similar results were obtained for the presence of elements from XRD and the EDX spectra¹³⁻¹⁶.

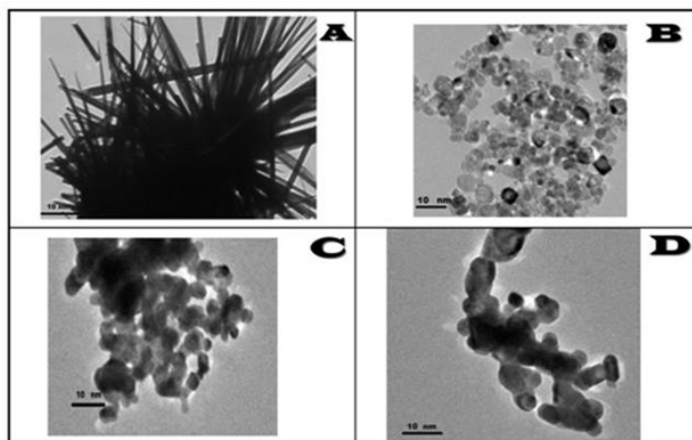


Fig 4: (A) ZnO, (B) ZnO/CdS 1:1, (C) ZnO/CdS 1:2, (D) ZnO/CdS 1:3

The growth of ZnO/CdS core/shell nanostructure was confirmed by HRTEM analysis in the Fig 4. In the Fig 4 (A), the images of the ZnO nanopins were found with an average diameter of 5 nm and a length of 21 to 27 nm with smooth surface. The formation of ZnO/CdS core/shell was confirmed by the apparent contrast in the core ZnO and the shell CdS. The sizes of the core ZnO nanoparticles were measured as 15 nm in all the three core/shell samples. Polycrystalline images of ZnO/CdS core/shell nanostructures were recorded in Fig 4(B), Fig 4(C) and Fig 4(D). An increase in the weight percentage of CdS was made with respect to the concentration of core ZnO. Therefore the shell thickness was increased from sample B to D. The shell thickness of CdS was 3 nm in the sample B (ZnO/CdS core/shell 1:1), it was increased to 5 nm in the sample C (ZnO/CdS core/shell 1:2) and finally the shell thickness was 8 nm for the sample D (ZnO/CdS 1:3).

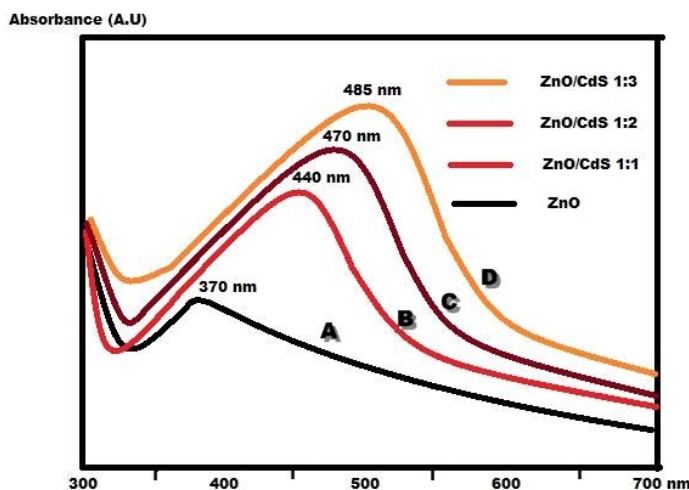


Fig 5: (A) ZnO, (B) ZnO/CdS 1:1, (C) ZnO/CdS 1:2, (D) ZnO/CdS 1:3

The surface related defects in the core and the interface of core/shell material can play a major role in defining the optical properties of these materials. The UV-Visible absorption spectra of ZnO and ZnO/CdS core/shell nanoparticles have been depicted in the Fig 5. In the UV-Vis spectra, the absorption peaks were observed at 370 nm for ZnO and 440 nm, 470 nm, 485 nm for ZnO/CdS core/shell B, C and D sample respectively. The red shift in the absorption spectra of sample B, sample C and sample D from ZnO nanoparticles clearly indicated the formation of core/shell nanostructures. The surface coating of ZnO nanopins with CdS nanostructure can promote the novel optical properties of these heterostructure for photovoltaic device application. The coating of CdS nano shells on ZnO core nanoparticles had increased the exciton lifetime and the lifetime of exciton was further extended with the higher thickness of the shell material. In Type II core/shell band alignment, the carrier excitation electrons and holes were spatially separated in the core and the shell material¹⁷⁻¹⁹. The absorption spectra of the ZnO/CdS core/shell indicated that the exciton lifetime was extremely sensitive to the CdS shell. The separation of electron and hole wave function becomes more prominent with thicker CdS shell as shown in the Fig 5(D).

The photoluminescence spectra of core ZnO and ZnO/CdS core/shell nanostructures were recorded and shown in the Fig 6. The intensity of PL spectra was lowered by increasing the shell thickness. The photoluminescence peak of core ZnO was appeared at 660 nm. Among the three core/shell samples, the PL peak was red shifted with increasing the thickness of CdS shell material. The electron-hole recombination was significantly reduced with thicker CdS shell and ZnO/CdS core/shell nanostructures were supporting the excitonic separation behavior of Type II heterostructure²⁰⁻²⁶.

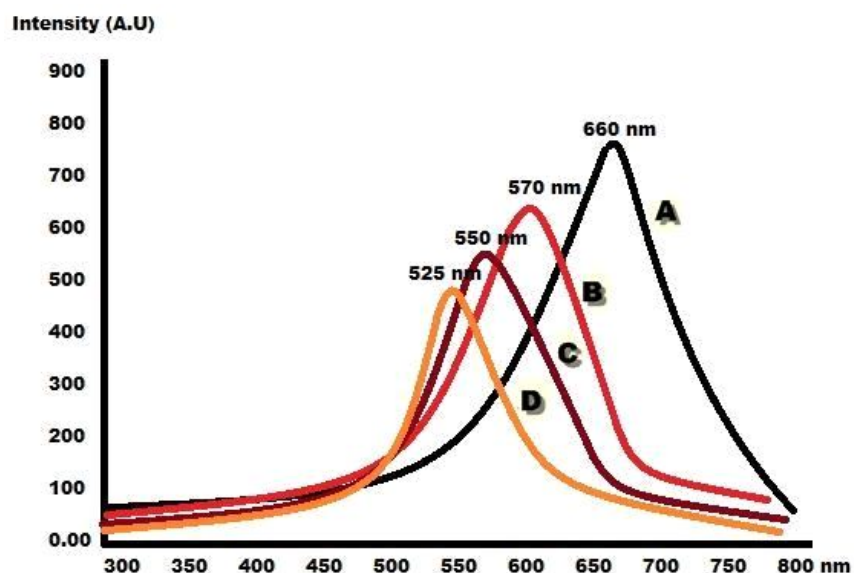


Fig 6: (A) ZnO, (B) ZnO/CdS 1:1, (C) ZnO/CdS 1:2, (D) ZnO/CdS 1:3

Conclusions

The Green synthesis chemical method was employed for the synthesis of ZnO and ZnO/CdS core/shell nano structures. The cost effective one pot two step synthesis method was well explained for the growth of core/shell nanoparticles. The core znO nanoparticles were prepared for 0.1M molarity using Starch as capping agent. Three samples of ZnO/CdS core/shell were prepared at the same molarity by changing the molar ratio of core and shell material as 1:1, 1:2 and 1:3 respectively. The structural characterization of the prepared samples was carried out by using XRD, SEM, EDX and HRTEM analysis. The grain sizes were calculated from XRD by using Scherrer formula. The morphology of the prepared samples was studied by SEM and EDX spectra. The formation of ZnO/CdS core/shell nanostructure was confirmed by using High resolution transmission electron microscopy (HRTEM). The shell thicknesses were calculated for all the three core/shell samples and the optical properties of these samples were recorded by using UV-Vis and PL spectra. The type II characteristic of ZnO/CdS core/shell nanostructure was depicted in absorbance spectra. The spatial electron hole wave function separation between the core and the shell material, greatly by the type II band structure offset. It will enhance the exciton lifetime and therefore the ZnO/CdS core/shell nanostructure with thicker CdS shell can be used for the fabrication of photodetector. These type II ZnO/CdS core/shell nanostructure are promising materials for High-Performance UV detector. These new type of UV-detector fabricated with ZnO/CdS core/shell nanoparticles will achieve high detection efficiency and fast response to UV-light irradiation in near future.

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