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A study of Structural and Optical Properties of ZnO/CdS Core/Shell Nanoparticles for Sensor Applications

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Abstract:

The type – II core/shell nanostructures have attracted interest because of their wide range of applications in the area of optics, electronics and sensor applications. The core/shell of ZnO/CdS Nanoparticles are synthesized at room temperature by a simple one pot green chemical synthesis method using starch as a capping agent. The structural and optical properties of the as-prepared ZnO/CdS nanostructures are examined through comprehensive characterization methods. The X-Ray diffraction pattern identified the hexagonal phase of the ZnO/CdS core/shell nanostructures. The UV-Vis absorption spectra for the ZnO/CdS core/shell reveal the red shift of the prepared core/shell material. The particle sizes are estimated by HRTEM and the morphology of the prepared sample are observed by the SEM analysis. The Photoluminescence spectra of the prepared nanoparticles are also recorded. The optical properties of ZnO/CdS nanoparticles have great importance for photovoltaic device application.

Keywords: *Core/Shell, Type II Nanomaterials, XRD, EDS, HRTEM, UV-Vis, PL*

I. Introduction

The quantum size dependent optical properties of nanostructures have been the focus of significant scientific research over the past decade due to the quantum size effect[1, 2]. The nanostructure material results in a very high surface to volume ratio. A significant fraction of nanostructures typically exhibit surface related trap states acting as non radiative de-excitation channels for photo generated charge carriers and thereby reducing the quantum yield[3]. A new strategy can be taken to improve the surface passivation of nanoparticle with an overgrowth of shell nanomaterial for the formation of hybrid core/shell heterostructures[1-5]. In this way the absorption, luminescence, fluorescence efficiency and the stability against photo oxidation of various types of semi conductor nanostructures can be improved. The size related properties of core/shell nanostructures can be utilized quantum mechanically by

using the concept of size quantization[4,5]. In the nanometer regime, the optoelectronic properties of the nanoparticle depend on the shape and can be controlled by the number of dimensions as well as the confinement of the nanoparticle[1-5]. The different kinds of synthesis strategies towards the growth of core/shell nanostructures with strong quantum size effect will be adopted in this work. The semiconductor core/shell nanostructures of ZnO/CdS are of great interest for fundamental studies and their technical application for different kinds of device fabrication. The unique opto electronic properties of ZnO and CdS nanostructures were previously reported by different workers. Therefore, the core/shell of these two nano materials will be synthesized for examining the new properties of these materials.

This work will focus on different chemical growth procedures for the preparation of ZnO/CdS core/ shell nanostructures. These core/shell nanostructures have wide applications in the LED fabrication, photovoltaic device and other sensor applications.

II. Experimental setup and chemical synthesis of ZnO/CdS Core/ Shell Nanostructures:

Firstly, 0.01M of ZnO nanostructures was prepared in 3% starch solution. Now, 0.01M each of Na_2S and $(CH_3COO)_2Cd$ were separately prepared in 3% starch solution. The three necks round bottle flask was used for the synthesis of ZnO/ CdS Core shell nanostructures. The prepared ZnO solution was taken in the three neck round bottle flask and it was stirred on the magnetic stirrer for 30 minutes at the temperature of about 60^0C and at 380 RPM.The temperature of the solution was now lowered to the room temperature and the already prepared sodium sulphide and cadmium acetate solutions were added to it drop wise from the two other necks of 3 neck round bottle flask simultaneously maintaining at about 380 RPM of the magnetic stirrer. The solution was stirred for 3 hours at the room temperature at about 380 RPM. The color of the final solution was whitish yellow. It was filtered and the solution obtained after filtration was kept for analysis and the filtered product was washed with methanol, dried, grinded and kept for analysis.

fig. (1)

III. XRD **analysis:**

The XRD powder diffraction was carried out by using Cu Kα radiation and the respective planes for each of the prepared samples are shown in the fig.(2). The particle grain sizes were calculated by using Debye Scherrer formula, $D = k\lambda/\beta\cos\theta$, Here, D is the grain size, k is the constant or shape factor (0.94), λ = 1.5 angstrom for Cu Kα source, β is the full width of half maximum, Θ is the scattering angle. The grain sizes were calculated as (i) ZnO = 6.25nm (ii) ZnO/CdS Core/shell = 9.12nm.

The ZnO hexagonal planes were identified from the XRD patterns as shown in the fig.(2). In the core/shell form with ZnO and CdS planes were identified as shown in the fig. (2). The core dominated properties were observed in the XRD spectra.

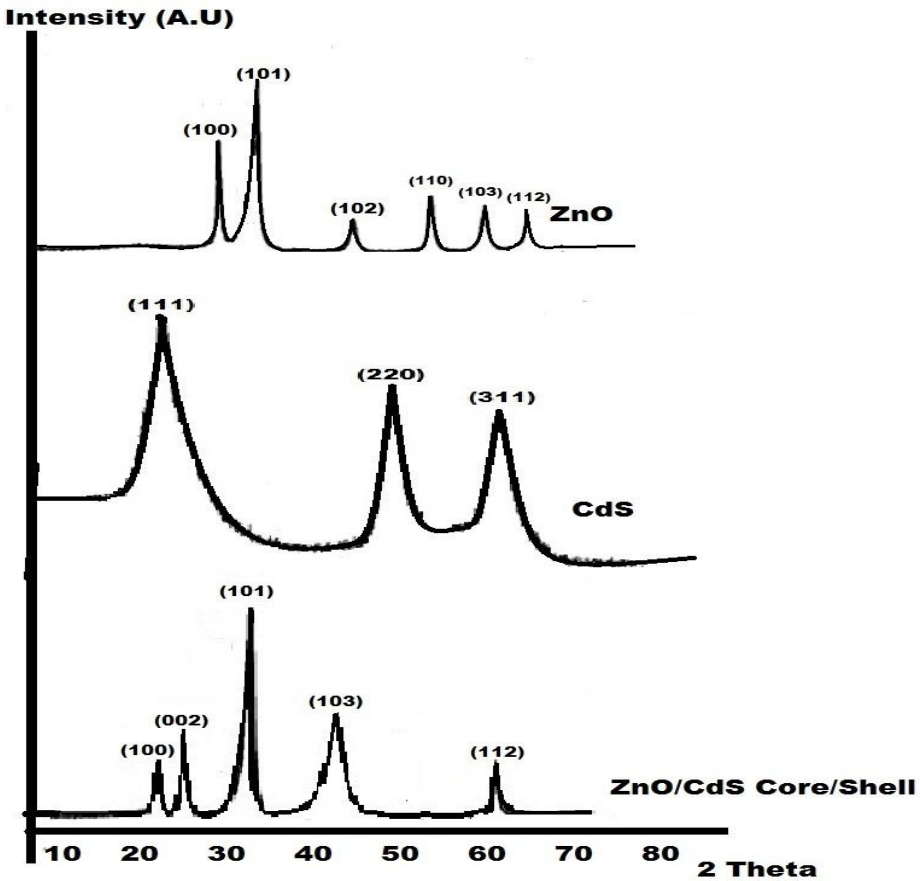

fig. (2)

IV. EDS Spectra:

The EDS spectra of the prepared nanostructures are shown in the fig.(3) and these spectra revealed the presence of the particular element as in the figure.

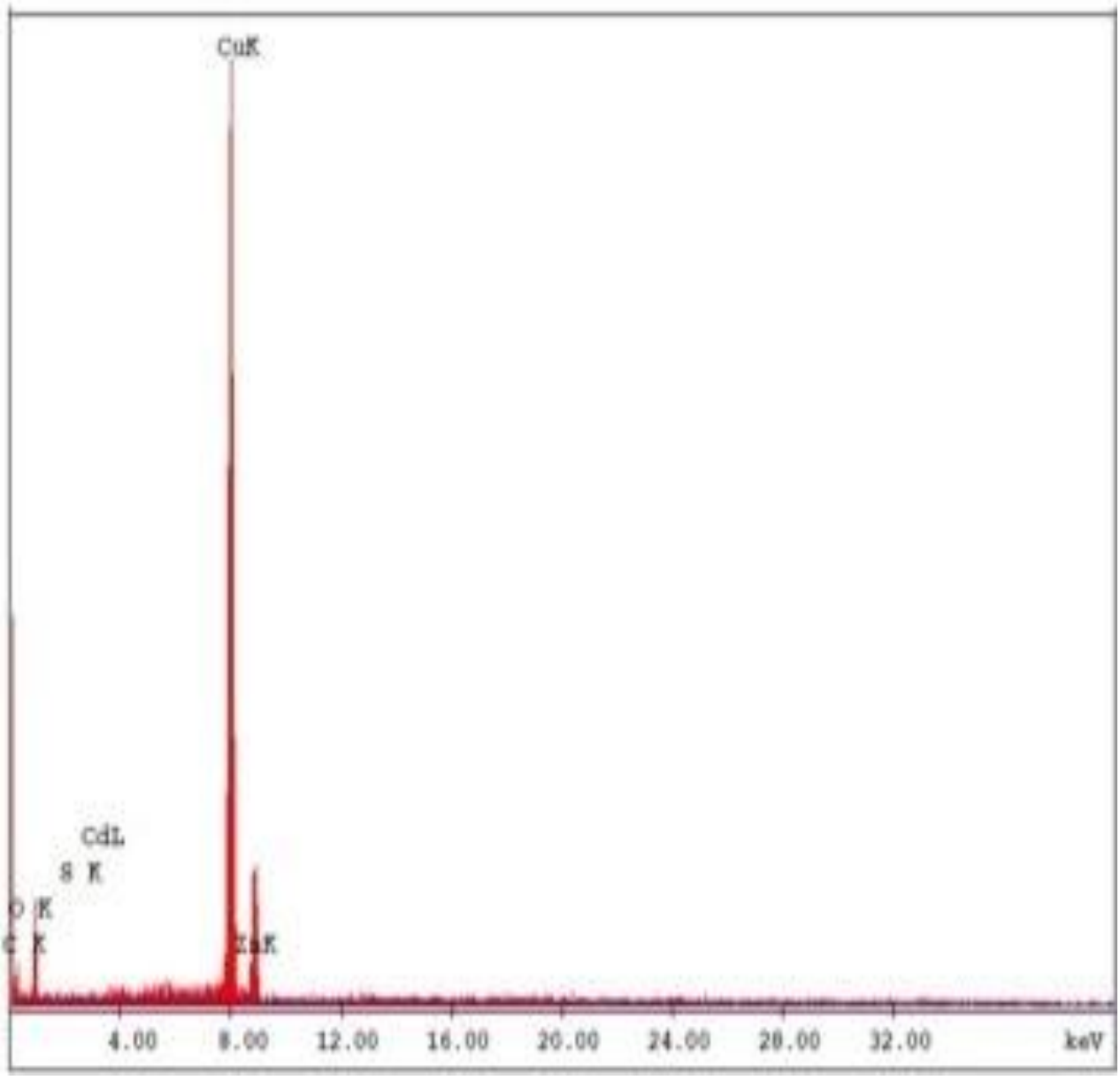

Fig. (3) ZnO/CdS Core/ Shell

V. **HRTEM Images:**

Fig.(4) ZnO

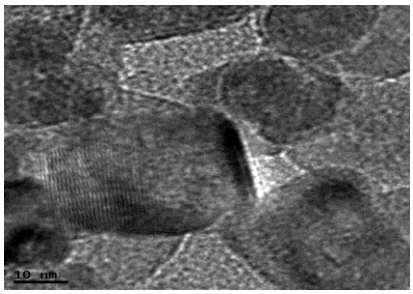

Fig.(5) CdS

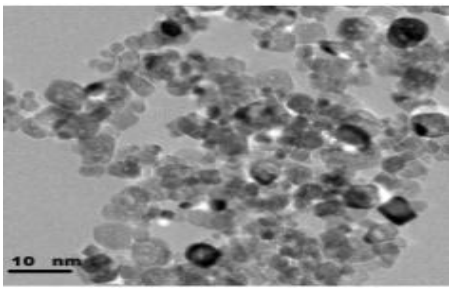

Fig.(6) ZnO/CdS Core/Shell

The sizes of the nanoparticles were examined by using HRTEM analysis. In the core/shell form of the nanostructures the dark spot is covered with a light dark layer and confirmed the formation of core/shell nanostructures. The size of the core nanostructures were calculated as 5.27nm whereas the Core/shell form of ZnO/CdS double quantum dots were measured as 7.15nm. Therefore, the shell thickness of the shell material were calculated as 1.88nm.

VI. SEM Analysis:

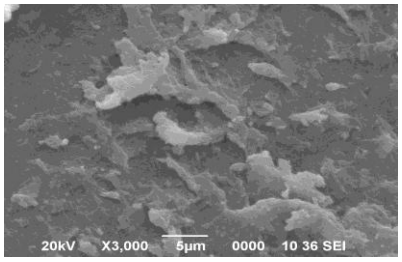

Fig.(7) ZnO

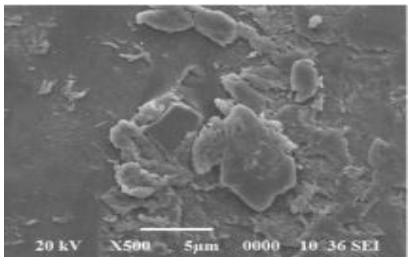

Fig.(8) CdS

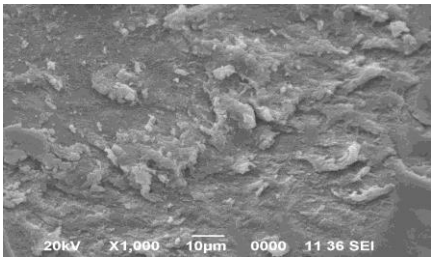

Fig.(9) ZnO/CdS Core/Shell

The morphology of the prepared nanostructures were observed by using SEM analysis and the images were as shown in the fig.(7),(8),(9). The ZnO nanostructures were appeared as nano-hair whereas the CdS shell were found as nano-plates. The ZnO/CdS core/shell nanostructures were in the form of spherical structures as shown in the fig.(9).

VII. Absorption Spectra:

The absorption spectra of the prepared nanostructures were recorded and shown in the fig.(10). The absorption peak of ZnO nanostructures were centered at 345nm whereas the separately prepared CdS nanostructures are centered at 390nm. The blue shift of the absorption spectra clearly indicated the formation of nanostructures and strong quantum size effect.

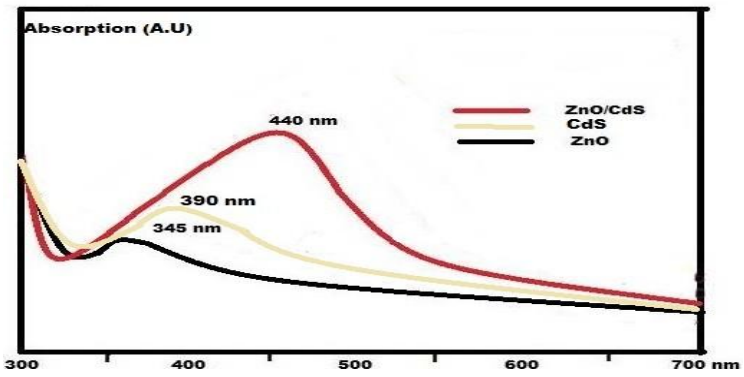

Fig. (10)

The energy band gap of these nanostructures were calculated by using Tauc – method. The absorption spectra of ZnO/CdS core/shell nanostructures is centered at 440nm and it is red shifted than the ZnO core material. Therefore, the formation of type-ll core/shell nanostructures is confirmed from the absorption spectra. The electron –hole wave functions will be delocalised into the core and shell material and reducing the recombination of electron and hole inside the material.

VIII. Luminescence Spectra:

The photoluminescence spectra of the core, shell and core/shell materials are represented in the fig.(11). It is clearly observed that the intensity of PL spectra of the core/shell material is lowered down than the PL spectra of the ZnO core material due to the charge separation. The luminescence spectra is also supporting the result of absorption spectra and the recombination of electrons and holes are reduced.

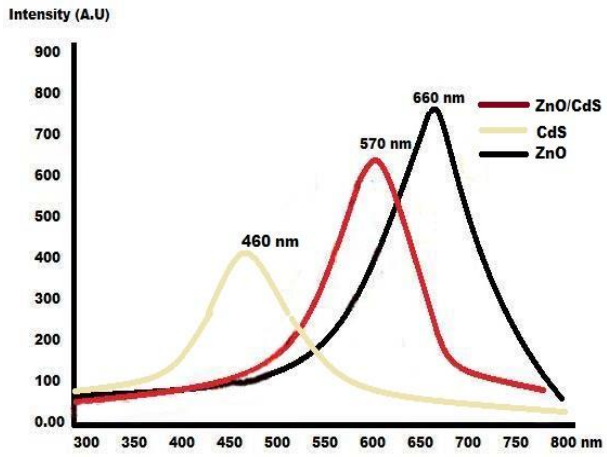

Fig.(11)

IX. Conclusion:

The surface modified ZnO/CdS core/shell-type heterostructures have been successfully synthesized by employing cost-effective chemical method. The X-ray diffraction studies disclose the presence of hexagonal ZnO and cubic CdS crystal structure. HRTEM images demonstrated that ZnO nanoparticles are covered by CdS nano shell layer. The absorption edges of UV-visible spectra are red-shifted and the value of energy band gap decreased. Thus, the absorption ability of the wide band gap core material (ZnO) is stretched to visible region by coating a narrow band gap shell material (CdS) in core/shell heterostructures. It is clear from the UV-Vis spectra that the absorption intensity of the prepared core – shell nanostructures is higher than the absorption of either ZnO or CdS bare nanostructures . The red shift in the absorption spectra clearly indicates the formation of type II core – shell nanostructures. The electron and hole wave functions of these core- shell nanostructures are delocalised into core and the shell material and therefore reduced the recombination possibilities of electron and hole wave functions. This kind of surface modified core/shell heterostructures improves the structural and optical quality of the films and harnesses the energy in the visible spectra for improving the performance of optoelectronic devices. The prepared type II core-shell nanostructures are prominent candidate for a device like photo sensor application.

A device can be fabricated by using these ZnO/CdS core/shell nanostructures by using quartz substrate for thin film fabrication. The aluminium electrode can be deposited as shown in the fig.(12).

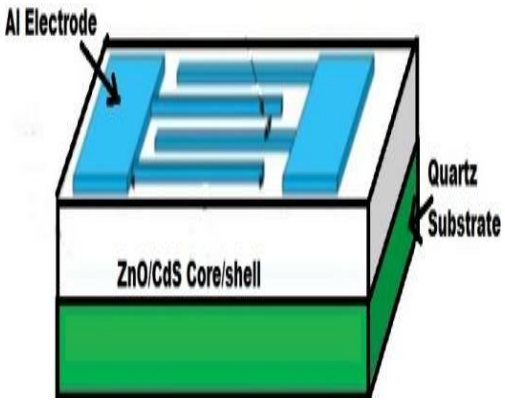

Fig.(12)

The device can be used as photo sensor and due to the more electron and hole separation in the newly synthesized ZnO/CdS Core/shell material it will work as a highly sensitive sensor for future generation. The flexible substrate can be used so that the device will be user handly and durable device as a sensor.

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