A Review on the Structural and optical Properties of ZnO/CdS Core/Shell Double Quantum Dots

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Abstract

The various types of synthesis procedures for the preparation of ZnO/CdS core/shell double quantum dots are extensively studied in this work and the mechanism behind the formation of core/shell nanostructures are investigated. The comparative studies for variation of structural and optical properties of ZnO/CdS core/shell nanostructures in different synthesis methods are carried on. The reasons behind the variation of structural and optical properties with respect to the synthesis procedures are investigated.

Keywords: *Core/Shell, Quantum Dots, Nanostructures*

1. Introduction

ZnO/CdS core/shell double quantum dots are extensively studied due to their application in electronics, optics, chemical engineering, biology and photo catalyst. These double quantum dots exhibit interesting optical properties such as tunable band gap, wide range of absorption spectra, quantum transportation and good luminescence properties. In this core/shell assembly, the core ZnO is a semiconductor with a wide band gap of 3.34 eV while the shell material CdS has a band gap of 2.4 eV and it is well known as visible light photo catalyst. The formation of CdS shell on the core ZnO nanoparticles with controlled core diameter or shell thickness will be a key step towards the realization of new properties of ZnO/CdS double quantum dots [1–5]. This ZnO/CdS core/shell nanoparticles form the type – II band alignment and facilitate charge separation and also useful for photo voltaic devices [1, 5, 9, 13, 17]. Moreover, by controlling the core diameter or the shell thickness of core/shell double quantum dots, the optical and electrical properties of these heterostructures can be optimized [13].

In this review work different chemical growth mechanisms are explained for the preparation of ZnO/CdS double quantum dots as reported by the earlier workers. In most of the cases two step chemical routes were employed for the growth of ZnO/CdS core/shell nanostructures. The surface coating of core ZnO nanoparticles with a CdS shell is always preferable for their remarkably different optical properties due to quantum confinement effect. Thus the optical properties of ZnO/CdS nanocomposites are improved compared to pure ZnO or CdS nanoparticles [1-17]. Different types of synthesis procedures are explained for the production of high quality ZnO/CdS core/shell nanostructures.

2. Synthesis of ZnO/CdS core/shell nanostructures

Manu Sharma et al. prepared the ZnO/CdS nanocomposites by two step method. The ZnO nanostructures were prepared by using zinc acetate dehydrate, trisodium citrate and sodium hydroxide. Zinc acetate dehydrate solution was stirred at room temperature for 10 minutes and then ammonia solution were added to it drop wise and stirred vigorously. The temperature was now raised to 85^0 C and kept stirring for 12 hours. The final product were washed and dried at 60^0C for obtaining the ZnO nanostructures in powder form. The CdS nanoparticles were deposited on the ZnO nanostructures using the different cadmium salts. ZnO powder was dispersed in water and then suitable cadmium salts and thioacetamide were added to it and then the mixtures were stirred for the formation of core/shell nanostructures. The yellow color ppt obtained were filtered out, washed and dried at 70^0C. The pure CdS nanomaterials were also prepared separately at room temperature [1].

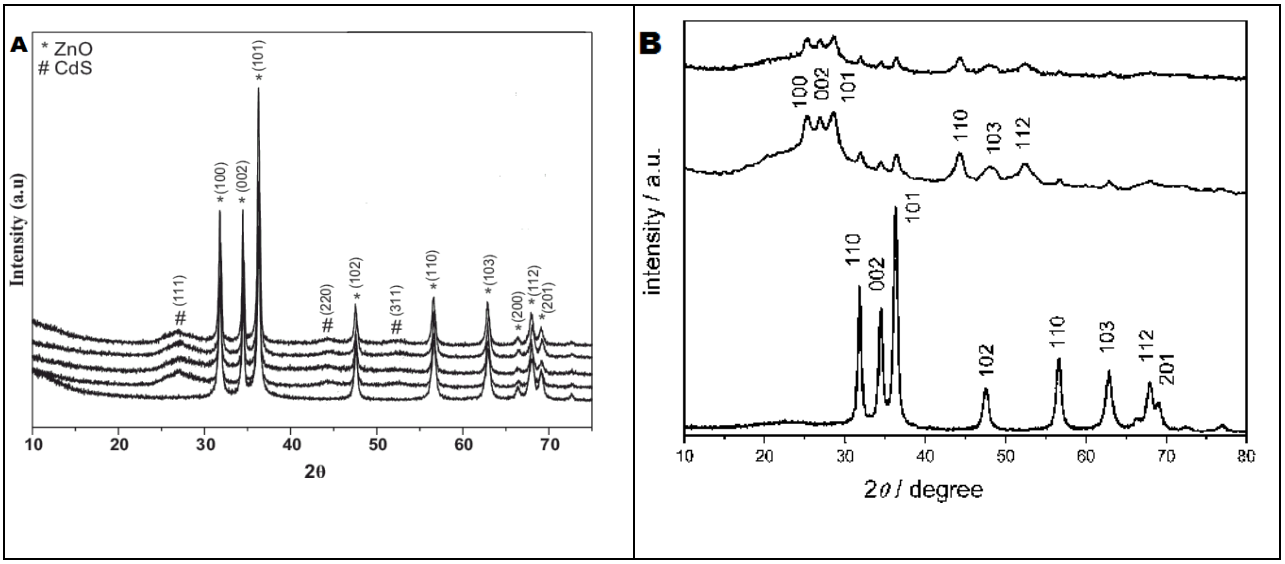
Jung Geng et al. synthesized ZnO/CdS core/shell nanocomposites by using ultra sound assisted solution phase conversion method. ZnO nanospheres could be obtained by dissolving zinc nitrate hexahydrate in water followed by addition of suitable amount of PEC – 200 and TEA in it with a constant stirring. The mixture solution was then exposed to high intensity ultra sound irradiation for 30 minutes at ambient air. The white ppt produced were washed with distilled water, ethanol and dried. In order to prepare ZnO/CdS core/shell nanostructures, ZnO nanoparticles and $CdCl_2$ were dissolved in EtOH followed by addition of thiourea. The mixture obtained was then exposed to high intensity ultrasound irradiation for half an hour [5].

Avinash Rakade et al. prepared ZnO and ZnO/CdS core/shell nanostructures by two step chemical synthesis method namely, electro deposition and chemical bath deposition. ZnO nano rods were prepared on FTO glass substrate by electro deposition method. The equimolar aqueous solution of zinc nitrate hexahydrate and hexa methylenetetramine (HMT) were applied by a constant potential of -0.75 V for 4 hours at 80^0C in order to obtain dense nano rods on the surface of the substrate. The CdS thin films were prepared separately on FTO glass substrate by CBD method in which $CdSO_4$, thiourea and NH_4OH were mixed by maintaining the pH at 11. Then ZnO films were placed inside it at 70^0C to obtain the CdS shell on the ZnO core [9].

Youngjo Tak et al. fabricated ZnO/CdS core/shell nanostructures by two step chemical synthesis method. ZnO nano arrays were prepared on Si, transparent oxide (TCO) and Ti metal in ammonia solution method in which a sputtered ZnO film was used as a buffer layer. The SILAR techniques were employed to obtain the CdS shell on the ZnO core. The ZnO nano arrays were immersed in aqueous solution of Cd $(NO_3)_2$ and Na_2S successively for 20 s. The immersion process was varied from 10 cycles to 120 cycles for coating the CdS shell of different thickness. After the CdS coating the final samples were dried with N_2 gas [13].

Garine Guerguerian et al. fabricated the ZnO/CdS core/shell nanostructures by two step method. The electrochemical deposition method was employed to obtain the ZnO nanostructures. The ZnO nanorods were grown on the transparent electrode substrate having fluorine doped tin oxide (SnO_2: F) as a conductive thin film on one side. A conventional 3 electrode electrochemical cell was used for the electro deposition method with the substrate as cathode, zinc sheet as counter electrode and a saturated calomel electrode as reference electrode. The electro deposition was carried out at -1.0V constant potential. The electro deposition was maintained at 1 hour. The FTO/ZnO samples were rinsed with distilled water after the electro deposition process in order to remove the unreacted products. The samples finally obtained were dried in air. The SILAR techniques were employed to obtain the CdS shell on the ZnO core [17].

3. Comparative studies of Structural properties



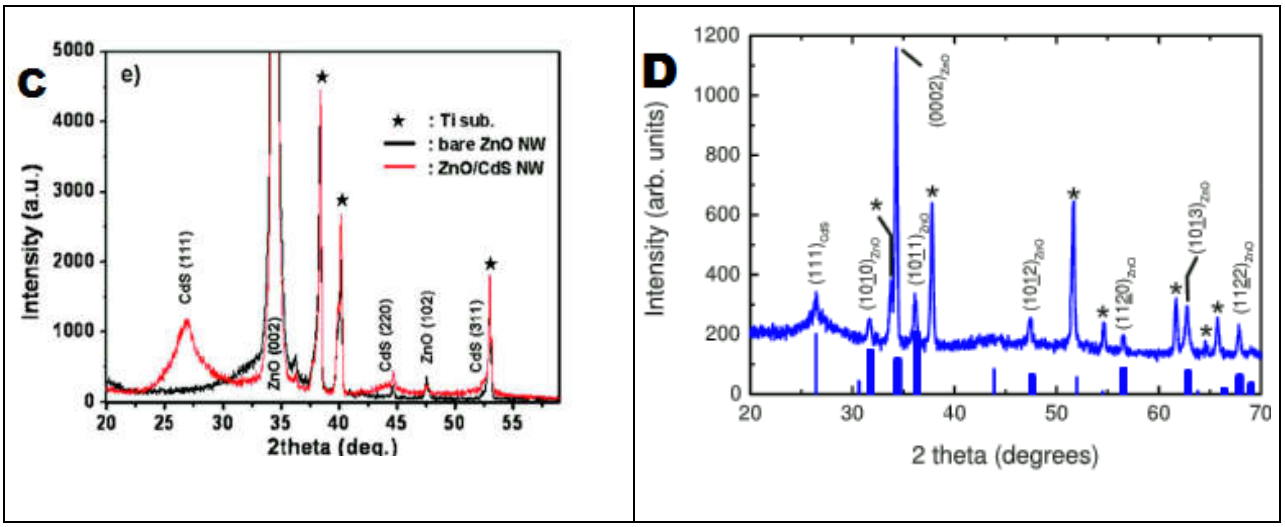
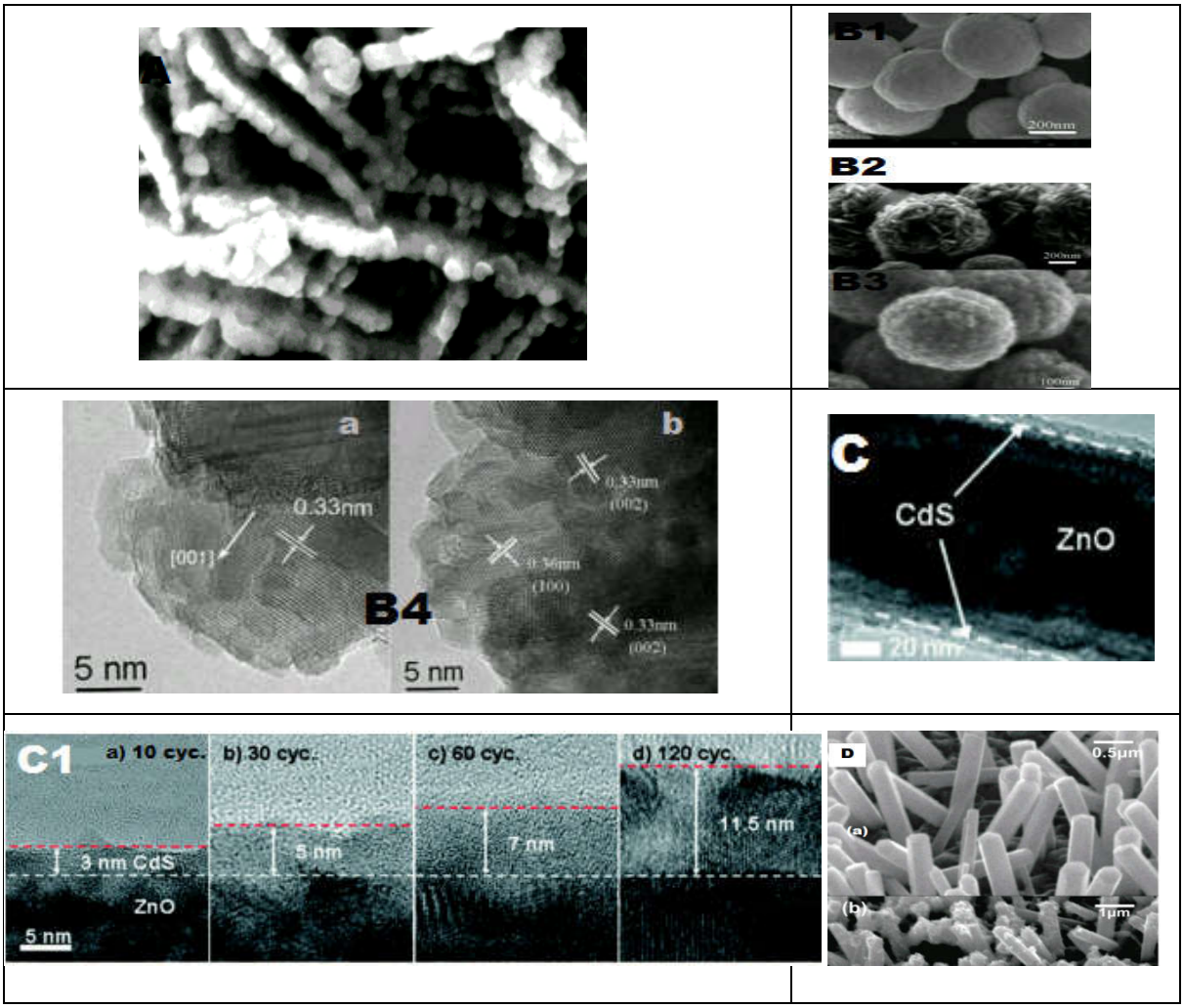
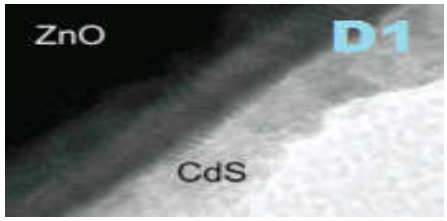


Figure1. XRD patterns of ZnO/CdS core/shell nanostructures (A) Courtesy to M. Sharma (B) Courtesy to J. Geng (C) Courtesy to Y. Tak (D) Courtesy to G. Guerguerian





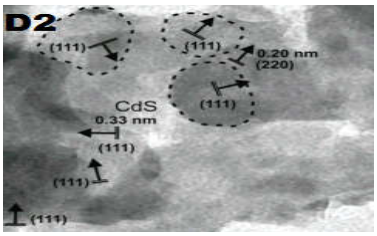


Figure 2. (A) FESEM image of ZnO – CdS nanocomposites (Courtesy to M. Sharma); (B1) SEM images of ZnO nanospheres, (B2) SEM images of ZnO/CdS core/shell nanostructures using thiorea as sulfur source, (B3) SEM images of ZnO/CdS core/shell nanostructures using TAA as sulfur source, (B4) HRTEM images of ZnO/CdS core/shell nanostructures (Courtesy to J. Geng); (C) TEM image of ZnO/CdS core/shell nanowire, (C1) HRTEM images of ZnO/CdS nanostructures with increasing SILAR cycles (Courtesy to Y. Tak); (D) (a) SEM image of bare ZnO nanorods (b) SEM image of ZnO nanorods coated with CdS nanocrystalline layer, (D1) HRTEM images of ZnO/CdS core/shell nanorod, (D2) HRTEM images of ZnO/CdS single quantum dots (Courtesy to G. Guerguerian)

The structural properties of ZnO/CdS core/shell nanocomposites were studied by Manu Sharma et al. by varying the reaction time and different concentrations of precursors. The XRD peak of ZnO was found at (100), (002), (101), (102), (110), (103) and (112) which corresponds to wurtzite structure (JCPDS file no. 80 – 0075) and peaks of CdS were found at (111), (220), (311), (200) and (201) which reflects the cubic structure of CdS (JCPDS file no. 80 – 0019). They have observed that the XRD peak intensity of ZnO was decreased with the formation of ZnO/CdS nanocomposites and the new peaks corresponding to CdS was observed confirming the formation of CdS layer over the ZnO nanoparticles. The diffraction peaks due to CdS were found to be broadened implying the small size of the CdS crystallites. The calculation of the particle size of ZnO by Debye- Scherrer formula, $D = \frac{0.94\lambda}{\beta cos\theta}$ was found to be 28 nm and that of CdS 2 nm [1]. When the reaction time was varied from 30 minutes to 6 hours, they did not found major change in the crystallite size of CdS in the nanocomposites. They found that the increase in concentration of the reagents favoured the crystallinity of the nanocomposites. They have suggested the optimum conditions for the preparation of ZnO/CdS nanocomposites at room temperature. They have studied the FESEM image of ZnO/CdS nanocomposites by varying the reaction time of cadmium sulfate and thioacetamide with bare ZnO. They found that there was no clear sign for deposition of CdS on ZnO nanoparticles in the lower reaction time (30 min) but with the increase of reaction time the quality of CdS coating on ZnO core were clearly visible [1-4]. The average size of CdS on the ZnO core was found to be 63 ± 7.0 nm.

Jun Geng et al. studied the XRD characterization of ZnO and ZnO/CdS core/shell structures by using thiourea and TAA as a sulfur source. They observed the peaks of ZnO at (110), (002), (101), (102), (110), (103) and (112) which corresponds to hexagonal wurtzite phase of ZnO (JCPDS file no. 36 – 1451). In ZnO/CdS nanocomposites the CdS peaks were found at (100), (002), (101), (110), (103) and (112) which signified the hexagonal phase of CdS (JCPDS file no. 41 – 1049) and these were found to be co existent with the hexagonal phase of ZnO. The samples with nano sized particles were proved by the broadening of diffraction peaks of CdS [5]. They have observed the SEM image of the bare ZnO and ZnO/CdS nanocomposites by using thiourea and TAA as a sulfur source and they found that the bare ZnO was in the form of solid nano spheres with diameter of about 400 nm. When thiourea was used as a sulfur source they found that the CdS nano rods having diameter of 40 – 50 nm and length 300 nm covered the surface of the ZnO core. When TAA was used as sulfur source, the ordinary core/shell nanostructures with average size of 600 nm were obtained. The HRTEM image revealed the interplanar spacing of 0.33 nm for (002) plane of hexagonal phase CdS over ZnO core. The polycrystalline shells were revealed from the HRTEM image. It was observed that the ZnO core nanostructures were covered by CdS shell having the interplanar spacing of 0.33 nm and 0.36 nm corresponding to the lattice spacing (002) and (100) for hexagonal phase of CdS respectively [5, 6].

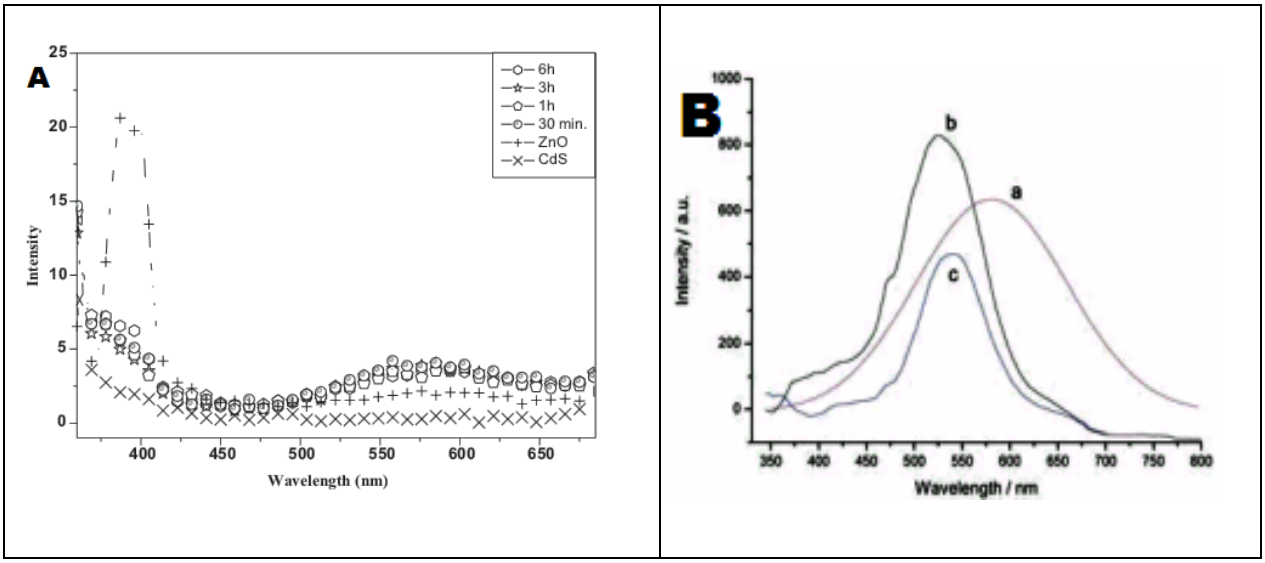
Avinash Rakade et al. studied the SEM image of as prepared ZnO and ZnO/CdS core/shell nanostructures and found that the ZnO was in the form of nano rod with hexagonal wurtzite structures. They also revealed that the ZnO core was covered by CdS nanoparticles forming the ZnO/CdS core/shell nanostructures. The average diameter and

length of as prepared ZnO nanorods were found to be 140 nm and 1600 nm. The ZnO/CdS core/shell nanostructures having average diameter and length of 250 nm and 1700 nm respectively were obtained [9].

Youngjo Tak et al. studied the structural properties of bare ZnO nanowires and ZnO/CdS heterostructures by using XRD and they have prepared the nanostructures by using SILAR method. The peaks of bare ZnO are found at (002) while the peaks of ZnO/CdS nanowires are found at CdS (111), ZnO (002), CdS (220), ZnO (102) and CdS (311). In case of ZnO/CdS nanowires, cubic phase of CdS are observed at 26.5^0, 44.0^0, 52.2^0 for plane CdS (111), (220), (311) (JCPDS file no. 80 – 0019) [13]. The remarkable outcome was that by increasing the number of SILAR cycles, the intensity of the prominent peak CdS (111) was enhanced. They have studied the SEM and HRTEM images of bare ZnO and ZnO/CdS core/shell nanocomposites with the SILAR cycles. They found that the ZnO nanoparticles were in the form of nano wires with average diameter of 100 nm and length 10µm. The cubic phase CdS nanoparticles of thickness ~5nm were found to be covered uniformly over the ZnO nano wire arrays. Some cracks were observed in the SEM image of ZnO/CdS core/shell nanostructures and were prominent with the SILAR cycles from 30 to 120. The HRTEM image revealed the increase in thickness of CdS shell in ZnO/CdS core/shell nanostructures with the increase of SILAR cycles from 10 to 120 [13-16]. The CdS shell of thickness 3 nm was observed for SILAR cycles of 10 and the CdS shell thickness increased to 11.5 nm for the SILAR cycles of 120.

The XRD analysis of ZnO/CdS core/shell nanomaterials by Garine Guerguerian et al. revealed the planes of ZnO at (10$\underline{1}$0), (10$\underline{1}$1), (0002), (10$\underline{1}$2), (11$\underline{2}$0), (10$\underline{1}$3) and (11$\underline{2}$2) which corresponds to the hexagonal phase of ZnO (JCPDS file no. 05 – 0664). The CdS planes with broad peak were found at (111) which gave the cubic phase of CdS with very small crystallites on the surface of ZnO nanorods. The average crystallite size using the Debye-Scherrer formula, $D = \frac{0.94\lambda}{\beta\cos\theta}$ for CdS at (111) and it was calculated as (8 – 10) nm [17]. They have studied the SEM and HRTEM images of ZnO and ZnO/CdS core/shell nanocomposites. The SEM image revealed the nano rod arrays of ZnO with the diameter of 200 – 300 nm and average length of 1.8 µm. When the CdS were deposited on the ZnO surface by SILAR method, the surface of hexagonal ZnO nano rods were found to be roughened confirming the formation of CdS shell over the ZnO core [17-20]. The TEM image revealed the ZnO core was covered by CdS shell of thickness 6 – 8 nm. The HRTEM image also revealed the average diameter of 7 nm CdS shell covering the ZnO core which was consistent with the SEM and TEM images.

4. Comparative studies of optical properties



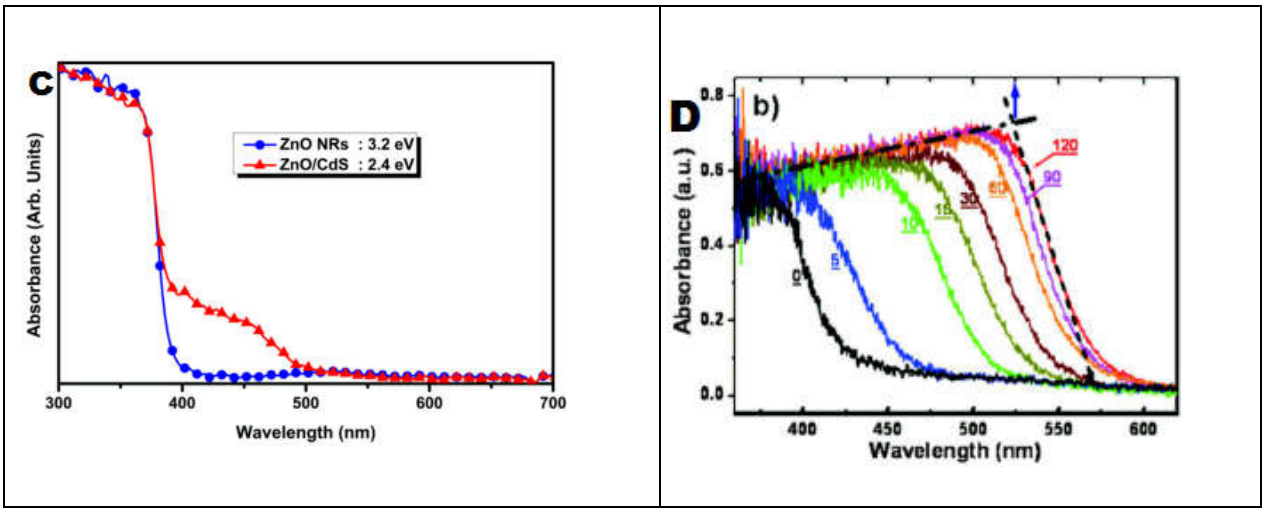


Figure 3. (A) PL spectra of the ZnO/CdS double quantum dots (courtesy to M. Sharma); (B) PL spectra of (a) ZnO nanospheres, (b) ZnO nanosphere@ CdS nanorod and (c) ZnO nanosphere@CdS nanoparticle (courtesy to J. Geng); (C) UV-Visible absorption spectra of ZnO and ZnO/CdS core/shell nanostructures (courtesy to A. Rokade); (D) Absorbance spectra of ZnO nanowire and ZnO/CdS core/shell nanowire arrays with increasing shell thickness (courtesy to Y. Tak).

Manu Sharma et al. studied the PL spectra of ZnO and ZnO/CdS core/shell nanostructures with increasing the SILAR cycles and the mechanism of ZnO/CdS core/shell nanostructure formation were explained. The PL spectra of bare ZnO showed two emission peaks centered at 380 nm and 575 nm. The emission at 380 nm was attributed to the near band edge emission and that of 575 nm was due to the oxygen vacancies[1]. The bare CdS nanoparticles showed the low intense emission at 575 nm. The two emission peaks were shown by the ZnO/CdS nanocomposites. The PL emission of near band edge emission due to ZnO was found to be decreased where as the intensity of 575 nm due to CdS increased with the SILAR cycles [1,2]. The increase in the PL spectra for CdS nanoparticles in the nanocomposites were attributed to the emission from defect states like cadmium interstitials or sulfur vacancies in the CdS nanostructures [1-4]. The mechanism for the formation of ZnO/CdS core/shell nanocomposites were chemically given as

$$CdSO_4 + H_2O = Cd(OH)_2 + H_2SO_4$$

$$ZnO + Cd(OH)_2 = ZnO - Cd(OH)_2$$

$$ZnO - Cd(OH)_2 + CH_3CSNH_2 = ZnO - CdS + H_2O + CH_3CONH_2$$

The PL spectra of ZnO and ZnO/CdS core/shell nanocomposites have been studied by Jun Geng et al. and found the emission peak of bare ZnO was centered at 581 nm, CdS at 525 nm and additional shoulder peak at 473 nm and the PL peak for ZnO/CdS core/shell nanostructures was found to be at 540 nm[5]. Compared with bare ZnO and CdS the intensity of emission peak of ZnO/CdS core/shell nanocomposites were reduced [5-8]. This reduction in PL peak of CdS in ZnO/CdS core/shell nanostructures were attributed to the quenching effect of the interfacial charge transfer. They also suggested that the rod-like crystals on the surface had larger defects due to faster 1D crystal growth. They explained the sensitivity of growth condition on the luminescence properties on the surface state and structural defects. They opined the interaction between the two semiconductors ZnO and CdS could be responsible for the shift in emission peak in the PL spectra [5].

The UV Vis spectra of ZnO and ZnO/CdS core/shell nanostructures as studied by Avinash Rakade et al. revealed that the ZnO/CdS core/shell nanostructures were red shifted with respect to the bare ZnO nano rods[9]. The band gap calculation by them revealed the band gap of pristine ZnO as 3.2 eV and ZnO/CdS core/shell nanostructures as 2.4 eV. The red shift in the absorption peak reveals the formation of type – II core/shell nanostructures [9-12].

Youngjo Tak et al. studied the UV Vis spectra of ZnO and ZnO/CdS core/shell nanostructures with respect to the SILAR cycles and found the red shift in the absorption spectra revealing the formation of type – II core/shell nanostructures [13-15]. They found that the absorption edge of bare ZnO nano wire was 3.2 eV and with increase in SILAR cycles the absorption peak shifted and finally reached at 2.4 eV[13]. According to them, the CdS were deposited on the ZnO core as an island growth followed by subsequent coalescence to form the CdS shell layer over the ZnO core [13-15].

The structural, morphological and optical studies of ZnO/CdS core/shell double quantum dots are explained in this work. The structural properties are investigated by using XRD, SEM, FESEM, TEM and HRTEM where as the optical properties are investigated by using UV-Vis and PL spectra by the previous workers. A systematic comparative study is carried on for relating the effect of growth parameters with their particles sizes of the nanostructures as well as other structural properties. Some remarkable results were reported by the workers. The ZnO/CdS hierarchical nanocomposites have been successfully synthesized by M. Sharma et al. by using a simple solution based method at room temperature, without using any ligang, surfactant or chelating agent. The XRD study revealed the wurtzite structure for core ZnO and cubic phase for CdS shell materials. The XRD peak intensity due to ZnO is decreased and that of CdS increased in the ZnO/CdS nanocomposites due to the increase of CdS shell thickness. The average particle grain size of ZnO is calculated as 28 nm while that of CdS as 2.2 nm in ZnO/CdS double quantum dots. The CdS shell thicknesses are found to be increased from 2.1 nm to 2.3 nm when the reaction times are increased from 30 min to 6h. The FESEM image also supported the XRD result [1]. The ZnO/CdS core/shell double quantum dots could be prepared by J. Geng et at. by using a facile sonochemical method, using the different precursors as a sulfur source. The XRD analysis revealed hexagonal wurtzite phase of ZnO core and a consistent hexagonal phase of CdS shell on the ZnO in ZnO/CdS core/shell double quantum dots. When thiorea and TAA was used as sulfur source the size of ZnO/CdS core/shell are found to be 600nm and 500 nm respectively. The HRTEM image supported to the XRD result. The SEM and TEM images revealed ZnO nanospheres core and polycrystalline CdS Shell on the ZnO core [5]. The heterostructures of ZnO/CdS core/shell double quantum dots are prepared by two steps solution based method by Y. Tak et al. They have used SILAR method to deposit the CdS layer on core ZnO nanostructures. The cubic phase of CdS was observed and they have also reported little evidence of any morphological change of ZnO core nanoparticles by the deposition of CdS shell on it. Their XRD results were supported by the SEM images. The shell thickness played an important role for the electrical and optical properties of these core/shell nanostructures [13-16]. They have also suggested that the thickness of the shell were increased with cycle number regardless of the sample area and dipping time for better result. The color of the sample was also changed from grey to orange with increasing the thickness of the CdS shell [13]. The ZnO/CdS core/shell nanoarrays are fabricated by two step method by G. Guerguerian et al. They have used SILAR method to deposit the CdS shell material on the ZnO core nanorod arrays. The XRD result revealed the hexagonal wurtzite phase of ZnO core and cubic phase of CdS shell material. The average grain sizes of crystallites are calculated to be 8 – 10 nm. The HRTEM images supported to the XRD results. Also the CdS shells of mean diameter of about 7 nm are found to cover uniformly over the ZnO core nanorods [17-20]. Again, the optical studies revealed the formation of type- II band alignment for ZnO/CdS core/shell double quantum dots.

5. Conclusion

The comparative studies on the structural and optical properties of ZnO/CdS core/shell double quantum dots with respect to the different growth conditions were carried out and the physics behind the core/shell nanostructures formation were explained. The shape and the shell thickness dependent on the growth mechanism of the ZnO/CdS core/shell nanostructures were reported by the various workers. In this work, we have reviewed the different synthesis procedures for the preparation of ZnO/CdS core/shell double quantum dots and the comparative studies of their structural and optical properties have been done to identify the best method for their synthesis. Again, the increase in shell thickness with SILAR cycles is revealed in this work.

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