

Microwave Assisted Synthesis of CdS & CdS/ZnS Core-Shell Nanoparticles and Their Characterization

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Abstract: *In this paper we report successful synthesis CdS quantum dots & CdS/ZnS core-shell nanoparticles by Microwave assisted method. A domestic microwave oven (LG 8080) is used for synthesis of the nanocomposites. The as prepared samples were characterized by X-Ray Diffraction (XRD), High resolution Transmission Electron Microscopy (HRTEM), Scanning Electron Microscopy (SEM), Energy-Dispersive X Ray Spectra (EDX), UV-Visible and PL Spectroscopy. The HRTEM images confirm nanoformation of the prepared samples. The average particle size from the HRTEM study is found to be 3-5 nm for CdS quantum dots and 5-15 nm for CdS/ZnS core-shell nanoparticles. From HRTEM image core/shell formation of the as-synthesized samples are confirmed.*

Keywords: *Microwave irradiation, Core/Shell nanoparticles, Characterization, Quantum Dot.*

1. INTRODUCTION

CdS nanoparticles due to their interesting size dependent optical and electronic properties and potential applications in Photonics and Electronics have been the subject for several studies for a long time [1, 2]. The optical and electrical properties of CdS Quantum Dots and thin films have been extensively studied [3, 4, 5]. Many techniques are used for synthesis of CdS nanoparticles but most of these processes are costly, and require reaction condition and long reaction time. Microwave heating applied to material synthesis has shown very rapid growth due to molecular level heating which leads to homogeneous and quick thermal reactions than that of the conventional heating process [6]. Due to these advantages, Microwave assisted methods are now widely used for synthesis of semiconductor quantum dots [7, 8, 9], nanocrystalline films for Solar cells [10], Core-Shell Quantum Dots [11, 12], Nanosized metal oxides [13] etc.

Core/shell nanoparticles are formed when two dissimilar materials are placed into contact with each other. As the lattice constant, energy gaps, doping concentrations and affinity of core and shell material differences, the properties of core/shell material is modified. The small lattice mismatch of 7.3% between CdS and ZnS make it possible for epitaxial growth of CdS/ZnS core-shell nanoparticles. These type I core-shell nanoparticles are widely used in light emitting diode (LED) & biological labeling.

There are many parameters for controlling the size, shape and properties of core-shell nanoparticles. In this paper, we describe a simple one-step aqueous synthesis method to produce CdS and CdS-ZnS nanocrystals using 3-mercaptopropionic acid (MPA) as the capping molecule. The structural and optical properties of the nanoparticles samples are investigated precisely. Using microwave assisted method we can synthesize highly pure, nano particles with narrow size distribution [14].

2. EXPERIMENTAL

2.1. Synthesis

Synthesis of CdS nanoparticles is carried out by using a domestic microwave oven (LG 8080). The system operates at 2.45 GHz frequency and can operate at 0-100% of full power (900 W). Cadmium Acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.99%) and Sodium Sulphide (Na_2S , 99.99%) were purchased from Sigma and used without further purification. Double Distilled water is used for the experiments. For CdS/ZnS core-shell nanoparticles Zinc Acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) is used as Zinc source.

Synthesis of MPA capped CdS & CdS/ZnS core-shell nanoparticles:

In a typical procedure solution of cadmium acetate and MPA were mixed, titrated to pH value 8.2, 9.2, 10.2, 11.2 & 12.2 with NH_4OH . This solution is then saturated with nitrogen for 1 h. An aqueous solution of Na_2S is then added quickly to this solution keeping the Cd^{2+} : MPA: S^{2-} molar ratio fixed at 1:2:1. The size and structure of nanocrystals depends upon pH [15]. Then the flux was placed inside the microwave oven. The reactional mixture was heated at 900 W for 2 minutes and then air cooled at room temperature [Table 1].

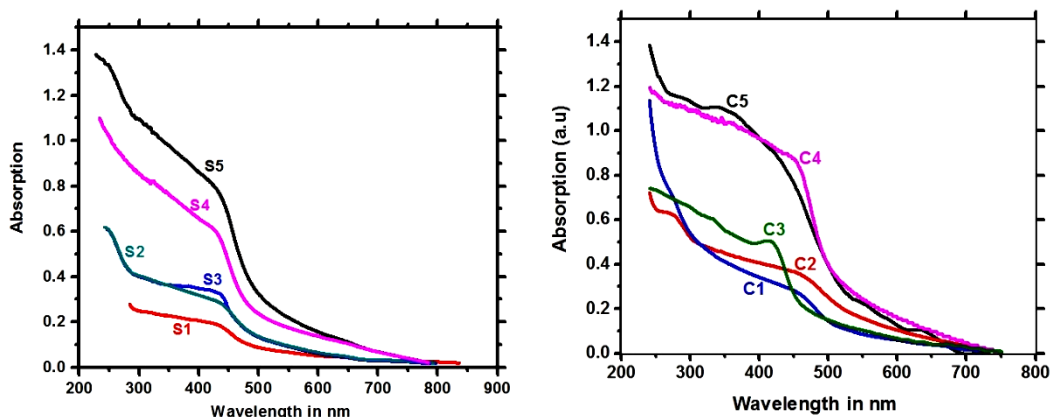
Table1. Different pH values and heating schemes of the samples

Serial No.	Sample Name	Sample Code	pH value	Heating Temperature	Heating Time
1	CdS 1	S1	8.2	90° C	2 min
2	CdS 2	S2	9.2	90° C	2 min
3	CdS 3	S3	10.2	90° C	2 min
4	CdS 4	S4	11.2	90° C	2 min
5	CdS 5	S5	12.2	90° C	2 min
6	CdS/ZnS 1	C1	8.2	90° C	2 min
7	CdS/ZnS 2	C2	9.2	90° C	2 min
8	CdS/ZnS 3	C3	10.2	90° C	2 min
9	CdS/ZnS 4	C4	11.2	90° C	2 min
10	CdS/ZnS 5	C5	12.2	90° C	2 min

For ZnS shell growth, solution of zinc acetate and MPA were mixed, titrated to pH 8.2, 9.2, 10.2, 11.2 & 12.2 with NH_4OH , and saturated with nitrogen for 1 hr. Then $(\text{Zn}(\text{CH}_3\text{COO})_2)$ solution is added to CdS solution and Na_2S were added slowly. Then the mixture was placed inside the microwave oven for some time and finally air cooled at room temperature.

3. RESULTS & DISCUSSION**3.1. UV-Visible Spectra**

The optical absorption of the samples is carried observed using double beam automated spectrometer (HITACHI-U3210). From the absorbance edges blue shift of the samples with respect to bulk CdS is confirmed. The band gap estimated from Tauc's formula for the CdS samples are found to be higher than that of bulk band gap of CdS. From the Fig. 1(a) & Fig.1 (b) it is clear that with increase in pH values the emission intensity of the samples also increased.

**Fig1(a).** UV-Vis spectra of CdS samples**Fig1(b).** UV-Vis spectra of CdS/ZnS Core-shell samples

The pH value of the thiol group of MPA is about 8.3. At higher pH more thiol groups became dehydrogenated, which was expected as the strength of the covalent bonding between MPA and Cd^{2+} on the surface of the QDs increased. In addition, the higher pH promoted the negative charge of the carboxyl groups of MPA and helped to disperse the nanoparticles better [16]. Fig. 1(b) shows the UV-Vis spectra of CdS/ZnS core-shell nanoparticles. ZnS shell formation is evident from the UV-Visible spectra as the absorption edge of CdS/ZnS samples is shifting towards lower energies (i.e higher wavelength) due to the leakage of exciton into the ZnS shell [17].

3.2. Photoluminescence Spectra

The luminescence spectra of the as-fabricated samples (Fig. 2(a) & Fig. 2(b)) are obtained using F-2500 Fluorescence Spectrophotometer (Make: Hitachi) at an excitation wavelength 360 nm. From the

emission spectra it is clear that samples with higher pH values has the highest emission intensity. For CdS/ZnS core-shell samples emission peaks are stronger than CdS samples because of the luminescence quench effect.

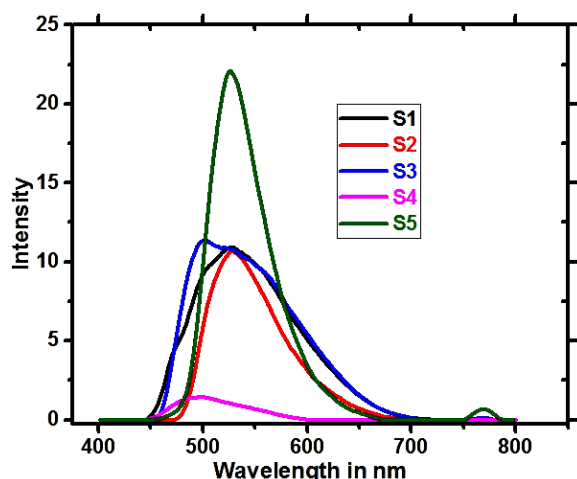


Fig2(a). PL spectra of CdS samples

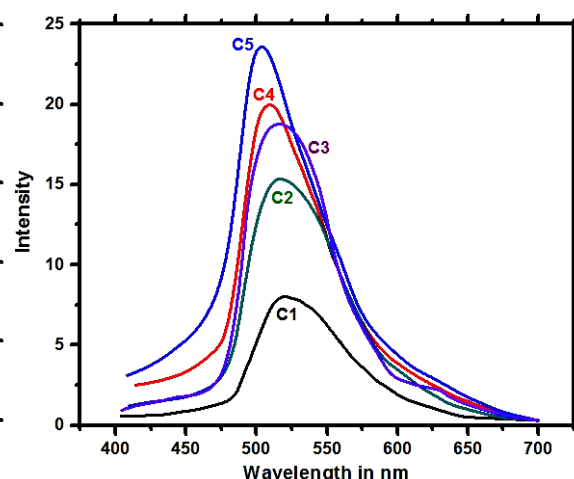


Fig2(b). PL spectra of CdS/ZnS core-shell Samples

3.3. XRD Study

The as prepared samples were characterized by X-ray powder diffraction (Philips X' pert) operating at 40kV-30ma. The radiation source used was CuK α ($\lambda = 1.542 \text{ \AA}$) and a Nickel filter was used to block K β radiation. Fig. 3 shows the XRD patterns of MPA capped CdS & CdS/ZnS core-shell quantum dots at room temperature. The XRD peaks can be indexed to the hexagonal structure of CdS [18]. As shown in the Fig.3, the main peaks are obtained at (111), (102) and (202) plans. The peaks are broad compared to the bulk peaks of CdS which confirms nanoformation of the samples. For CdS/ZnS core-shell samples no peaks are observed for free ZnS particles and the position of diffraction peaks are closer to bulk CdS compared to bulk ZnS which means no alloy is formed otherwise the peaks will be closer to ZnS bulk [19]. The average crystallite size (D) from X-ray line broadening has been calculated using the Scherrer equation.

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

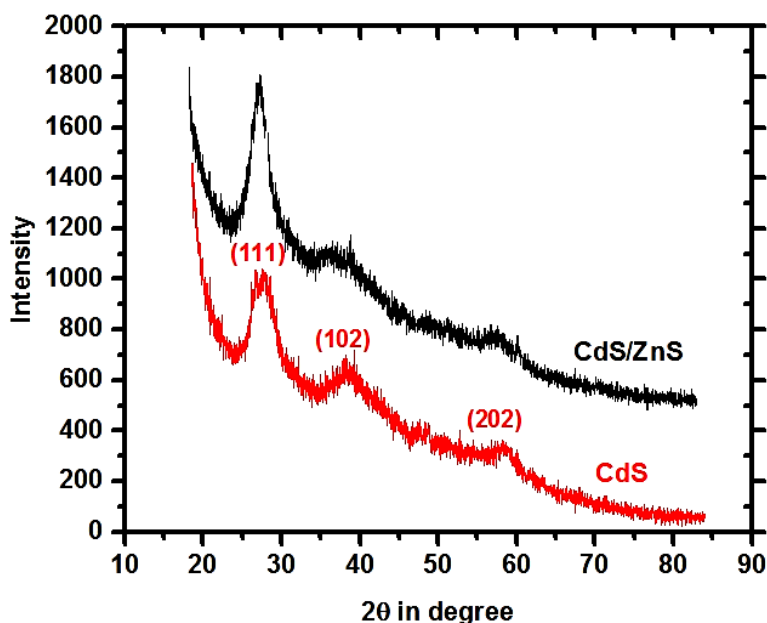


Fig3. XRD patterns of MPA capped CdS and CdS/ZnS core-shell Quantum dots at room temperature

Where λ is the wavelength of the X-ray beam, β is the full width at half maximum (FWHM) in radian and θ is the Bragg angle. The average crystallite size of CdS and CdS/ZnS nanoparticles calculated is about 5.2 nm and 7.5 nm respectively.

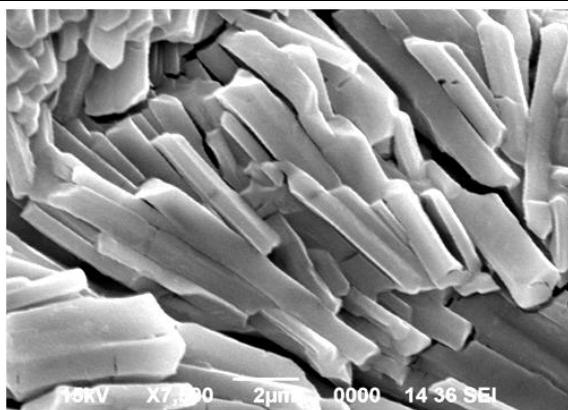


Fig4. SEM image of CdS nanoparticles

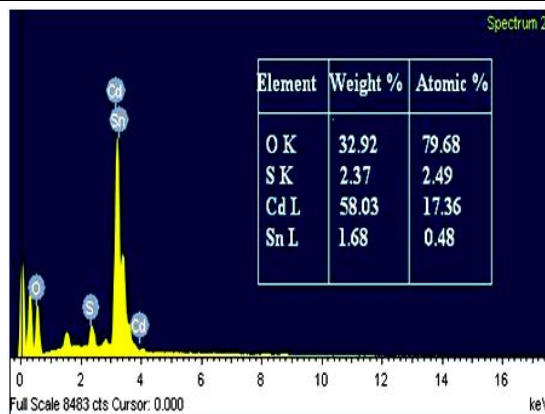


Fig5. EDX analysis of CdS nanoparticles

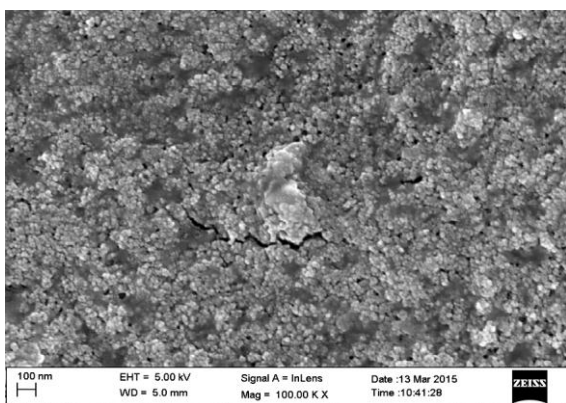


Fig6. SEM image of CdS/ZnS nanoparticles

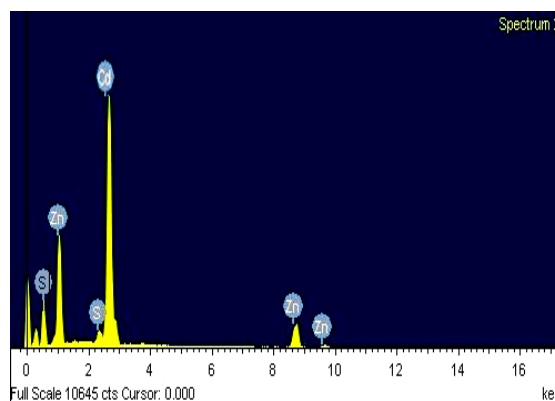


Fig7. EDX analysis of CdS/ZnS nanoparticles

3.4. SEM & EDX

The surface morphology of the prepared CdS and CdS/ZnS samples are studied by SEM characterization. In addition EDX was used to investigate the elemental characterization of the surface of the samples. As shown in Fig.4 we observe nano rod like structure for CdS samples. EDX analysis of CdS samples are shown in Fig. 5 and presence of Cd and S can be seen clearly. The SEM image of CdS/ZnS sample is shown in Fig.6. From the EDX analysis of CdS/ZnS sample (Fig.7) presence of Zn, Cd and S is confirmed. The EDX results also show that the samples are of high purity and very less amount of impurity is present in the sample.

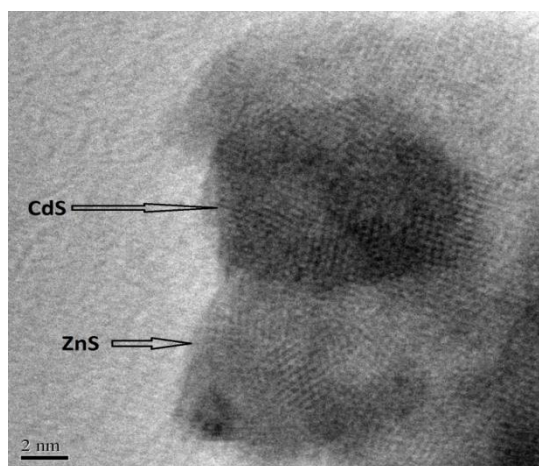


Fig8. HRTEM image of CdS/ZnS sample

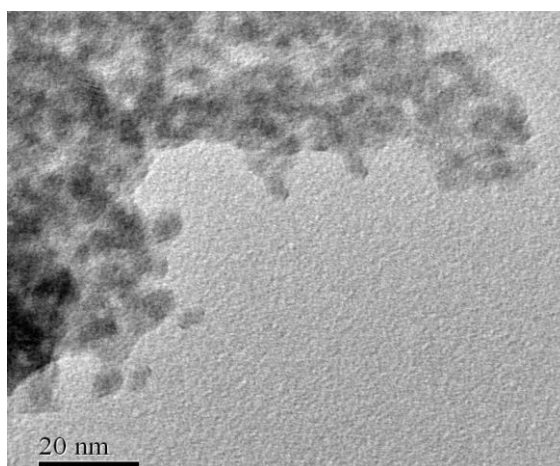


Fig9. HRTEM image of CdS sample

3.5. HRTEM of CdS and CdS/ZnS Nanoparticles

High Resolution Transmission Electron Microscopy (HRTEM, JEM-2100, 200 kV, JEOL microscope) results for CdS/ZnS and CdS samples are given in Fig.8 & Fig.9 respectively. The particle size of the samples is calculated by measuring an average of 50 nanoparticles per micrograph. The average particle size estimated for CdS and CdS/ZnS samples is about 5 nm and 8.5 nm. Core-

shell formation for CdS/ZnS samples can be confirmed from fig.8. From the image we can see the light gray shell of ZnS surrounding the dark gray CdS core.

4. DISCUSSION & CONCLUSION

UV-Visible spectra confirm blue shift of the as prepared samples. EDX of the as synthesized samples shows very less amount of impurity is present. It is found that particle size obtained from XRD and HRTEM are in good agreement. As size of the samples are less than 5 nm (exciton Bohr radius for CdS = 2.8 nm), strong confinement is achieved for CdS samples which are therefore Quantum Dots.

Thus we have prepared good quality, small size CdS and CdS/ZnS core-shell nanocomposites with 3-mercaptopropionic acid (MPA) as a capping agent and at a very short reaction time. It is also evident that pH values of the samples plays an important role in the formation of particles and it also controls different optical and chemical properties of the samples. The preparation is done in a domestic microwave oven so the process is also very cost effective. The resulting samples are found to be very small in size from HRTEM results. The prepared CdS core has hexagonal phase and the average crystallite size of CdS and CdS/ZnS core-shell nanoparticles were 5.2 nm and 7.5 nm respectively. From HRTEM the core-shell formation of CdS/ZnS samples can be confirmed. The ZnS shell thickness can be varied by varying the amount of shell precursor solution. So we can say that we have successfully synthesized small size & good quality CdS and CdS/ZnS core-shell nanocomposites with low cost and efficient microwave assisted synthesis technique.

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