

Effect of co-surfactant and water to surfactant molar ratio on the CdS nanoparticles in microemulsion

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Abstract

CdS nanoparticles have potential applications in many diverse fields such as optoelectronic devices, lasers, electrochemical cells and photocatalysis. Cadmium Sulphide (CdS) nanoparticles were prepared using microemulsion technique. The obtained nanoparticles were characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Ultra-Violet-Visible (UV-Vis) absorption. XRD analysis shows that CdS nanoparticles of hexagonal phase are formed. The TEM result indicates that the synthesized CdS nanoparticles are of variable morphology, namely, spherical, elliptical, nanorods and nanoneedles. UV-Visible spectroscopy reveals that as prepared CdS nanoparticles show a quantum confinement effect with shift in band gap. The band gap varies from 2.72 eV to 2.85 eV. It is also found that water to surfactant molar ratio (w_0) and the nature of co-surfactant is a vital factor in the morphology and optical properties of CdS nanoparticles.

Keywords: Microemulsion, CdS nanoparticles, quantum confinement, molar ratio, co- surfactant.

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1. Introduction

In recent years, semiconductor nanoparticles have attracted much attention in both fundamental research and technical applications owing to their unique size dependent electronic,¹⁻⁴ optical,⁵⁻⁷ catalytic,⁸⁻⁹ and electrochemical¹⁰ properties compared to their bulk forms. Such behavior arises due to quantum size effects that are manifested only in the case of particles below a certain critical size limit.¹¹ Semiconductor nanoparticles that show these quantum size effects are called quantum dots. Among various semiconductors, CdS nanoparticles have potential applications as optoelectronic devices,¹²⁻¹³ laser,¹⁴ photocatalysts,¹⁵ electrochemical cells,¹⁶ fluorescent labeling of cell organelles,¹⁷ etc. These exciting applications have focused attention on the synthesis and size control of nanoparticles. Many synthetic methods have been used to prepare CdS nanoparticles such as solid state

reaction, sol-gel process,¹⁸ sonochemical preparation,¹⁹ microwave heating,²⁰ and photo-etching²¹ but microemulsion synthesis²² has been recently used to obtain nanoparticles with dimensions in 1-10 nm range. Microemulsion is an isotropic, thermodynamically stable dispersion of oil, water, surfactant and often co-surfactant, which is normally alcohol. Microemulsion is the co-existence of an excess water phase and the surfactant molecules which aggregate in the oil phase in the form of reverse micelles. It is well known that these micelles could perform as nano-scaled reactors²³. Once two microemulsions of which one contains the precursor and the other contains the precipitating agent are uniformly mixed, the reaction will occur in controlled manner in the micelles which have the size in order of nanometers, resulting in the formation of nanoparticles

of controlled characteristics. It is also known that addition of co-surfactant, especially low molecular weight alcohols, can reduce the surfactant concentration in microemulsion preparation. The amphiphilic nature of co-surfactant could also enable them to distribute between the aqueous and oil phase²⁴. In our investigation, we have employed microemulsion technique and synthesized CdS nanoparticles using different co-surfactants and molar ratios, w_o .

2. Experimental details

2.1 Materials

Cadmium chloride (CdCl_2), Sodium sulphide (Na_2S), cyclohexane, n-butanol, n-hexanol and cetyltrimethylammoniumbromide (CTAB) used in this experiment are analytical grade and used without any further purification. De-ionized water was used for sample preparation.

2.2 Synthesis of CdS nanoparticles

The CdS nanoparticles were synthesized by using the reverse micellar route reported elsewhere²⁵. The four-solvent reverse micelle system was prepared by adding in sequence of 15 ml cyclohexane, 4.20 gm surfactant (CTAB), 2.5 ml of 0.1M aqueous $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, 3.5ml n-butanol or n-hexanol as co-surfactants. The concentration ratio of Surfactant /Co-surfactant was kept =1, while w_o varied over the range 5, 10, and 15 in different experiments. Solution was mixed vigorously at approximately 3000 rpm for 15 min. The same experiments with the same solvents were also performed by replacing $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ with $\text{CdCl}_2\cdot 5\text{H}_2\text{O}$ of equal molarity (0.1M). Then equal volumes of two microemulsions with the same surfactant, one containing S^{2-} and the other containing Cd^{2+} , were mixed together followed by gentle shaking for another 3 min. The final solution was let to sit at room temperature for 12 h to allow for the formation

of nanomaterials with different morphologies. The precursor precipitate was separated in a superspeed centrifuge at 10000 rpm for 10 min. The precipitate was then washed in a 1:1 mixture of methanol and chloroform followed by 100% methanol to remove residual cyclohexane and surfactant from the particles. The particles were then dried at 100 °C for 2 h in an electric oven to obtain the yellow precipitates of CdS nanoparticles.

2.3 Characterization

The optical absorption spectra of as prepared samples were carried out on colloidal suspension formed in the wavelength range 200-850 nm to determine band gap and particle size using UV (Thermoevolution) spectrometer. Transmission Electron Microscopy (TEM) studies were performed using (HRTEM, Hitachi, H 7500) with accelerating voltage 80 kV for surface morphology and particle size determination. For TEM analysis, CdS nanoparticle suspension was centrifuged and washed several times with de-ionized water. Finally they were dispersed in acetone and ultra-sonicated for 10 min. and then a drop of solution was taken on a carbon coated copper grid and used for TEM analysis under ultra-high vacuum conditions.

The above colloidal solution is then centrifuged and air dried to get sample in powder form. The CdS powder obtained was characterized by X-Ray Diffractometer (X'Pert PRO PANalytical, Netherland) using $\text{Cu K}\alpha$ radiation source of $\lambda = 1.5406 \text{ \AA}$, operated at 45 kV for structural and phase analysis.

3. Results and Discussion

In order to investigate the effect of co-surfactant, n-butanol and n-hexanol were selected and added individually into different microemulsion systems with concentration ratio of CTAB/Co-surfactant =1, while w_o varied over the range 5, 10, and 15. The

reactant concentration was kept constant at $0.1\text{ mol}/\text{dm}^3$. All synthesis work was conducted at room temperature.

3.1 X-Ray Diffraction analysis

It has been observed²⁶ that CdS nanoparticles display both cubic and hexagonal structures depending upon the synthesis technique used. Phase transition²⁷ from cubic to hexagonal occurs due to thermal annealing with resultant band gap shift in CdS. It is very difficult to differentiate the cubic from the hexagonal because the cubic (111) and the hexagonal (002) main peaks

almost overlap, coinciding within 1%. Patterns corresponding to the hexagonal phase show a preferred orientation along the (002) direction. It has been reported²⁸ that CdS nanoparticles are also produced in β -CdS phase of cubic crystal system with (111) main peak in XRD spectrum.

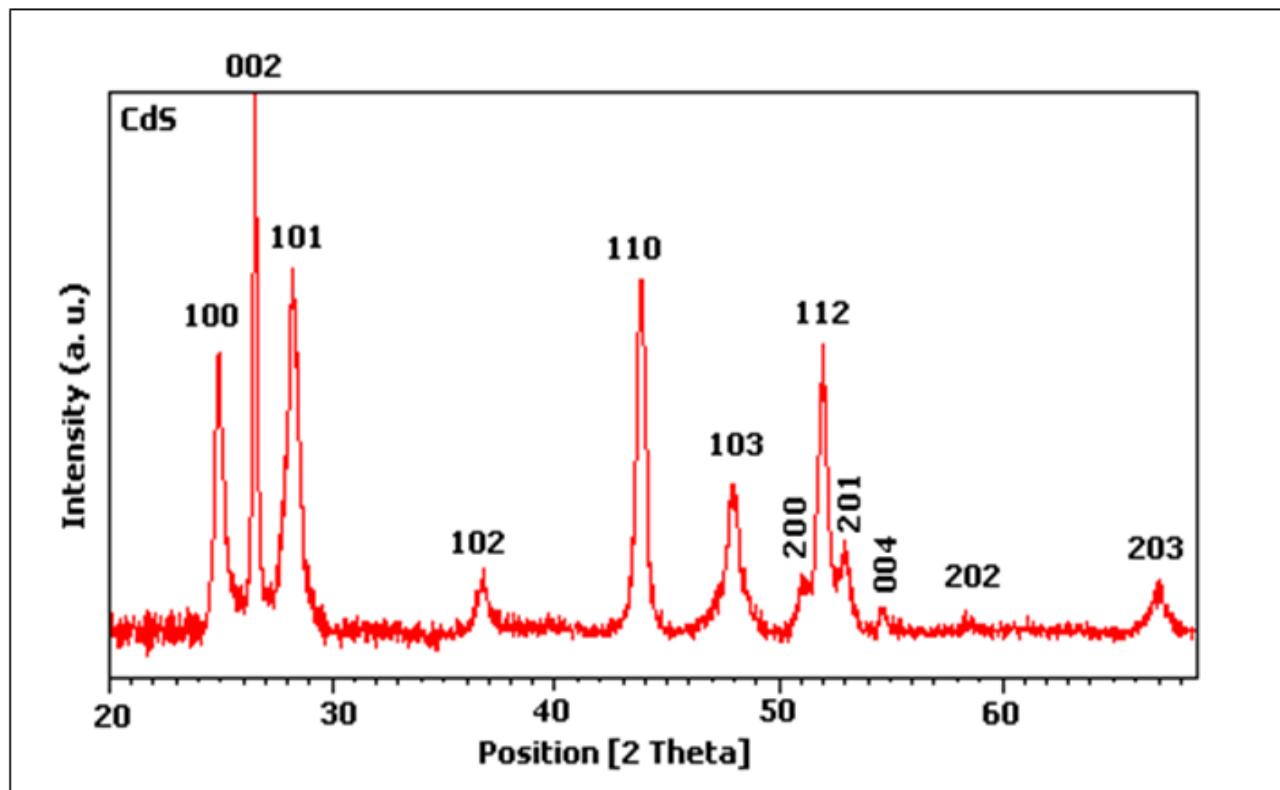


Fig. 1: XRD of typical CdS nanoparticle samples obtained from w/o microemulsion

XRD spectra of CdS nanoparticles synthesised in our experiments reveals 12 peaks corresponding to Miller indices (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202) and (203) as shown in Figure 1. The spectrum shows five prominent peaks at

$2\theta = 24.8671, 26.5687, 28.2424, 43.8178$, and 51.9481 corresponding to Miller indices (100), (002), (101), (110) and (112), respectively. The most prominent peak at $2\theta = 26.5687$ corresponds to hkl (002) with lattice constants, $a = 4.14 \text{ \AA}$ and $c = 6.72 \text{ \AA}$. All the

peaks can be indexed to hexagonal CdS, consistent with the literature data of JCPDS 41-1049 card. It clearly shows that CdS nanoparticles crystallize in hexagonal structure. Table 1 summarizes the XRD analysis result of some prominent CdS peaks, which

were compared with the standard diffraction pattern (JCPDS 41-1049). XRD spectra do not show any peaks of impurities, indicating the high purity of the product.

Table 1: Assignment of Miller indices to CdS nanocrystals

Sr. No.	Pos. [$^{\circ}$ 2Th.]	d-spacing [Å]	hkl
1.	24.8671	3.58064	100
2.	26.5687	3.35506	002
3.	28.2424	3.15991	101
4.	43.8178	2.06613	110
5.	51.9481	1.76028	112

3.2 UV-Visible analysis

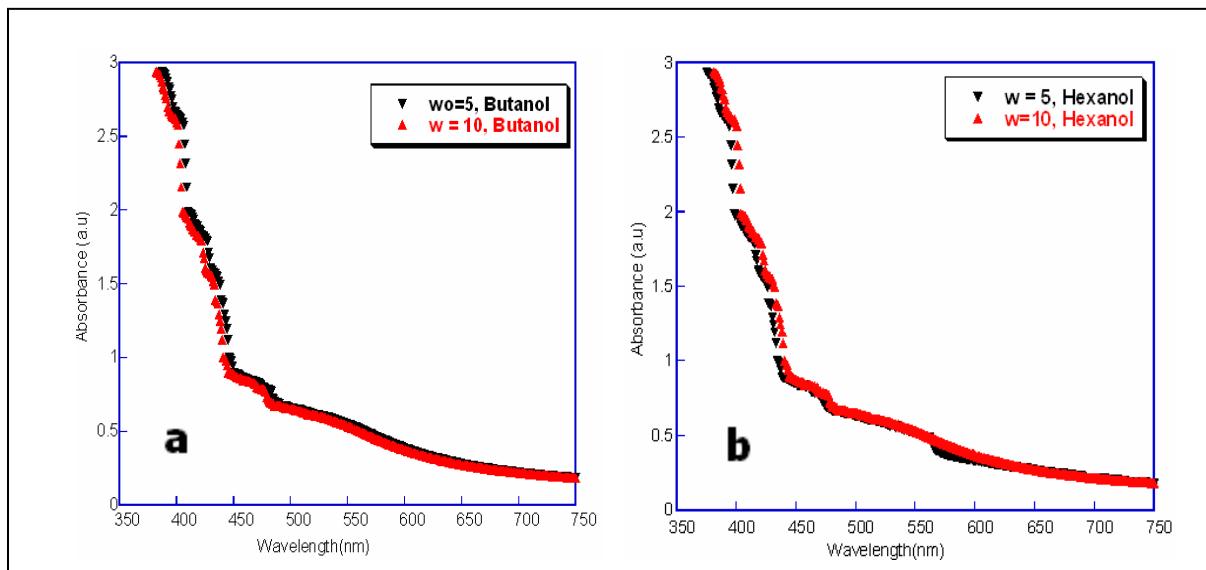


Fig. 2: Absorption spectra as a function of wavelength at $w_0 = 5$ and 10, (a) n- butanol (b) n-hexanol

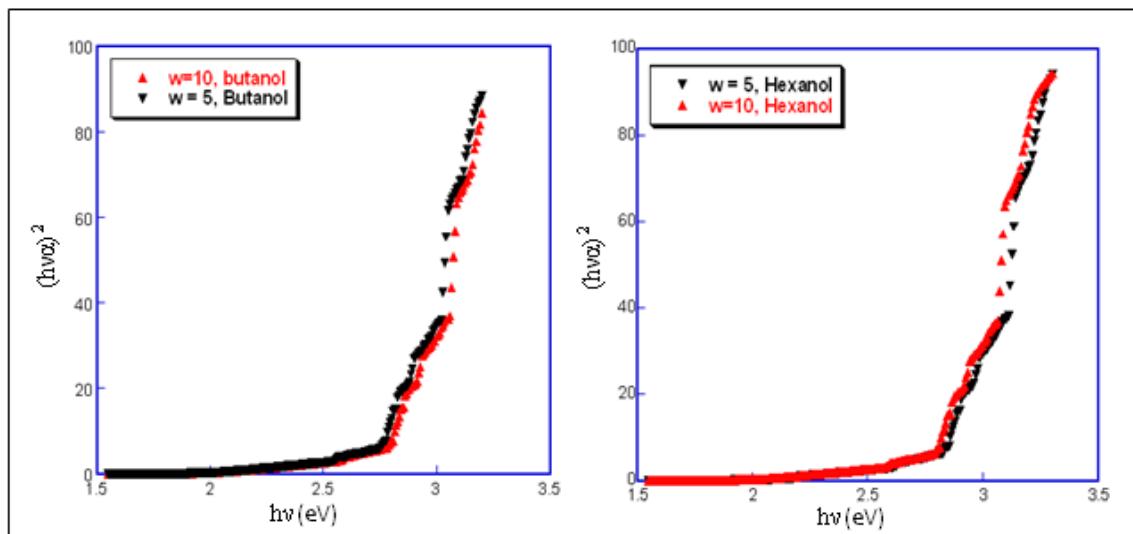


Fig. 3: Plot of $(hv\alpha)^2$ versus (hv) at $w_0 = 5$ and 10 , (a) n-butanol (b) n-hexanol.

Figure 2(a,b) shows the absorption spectra for the CdS nanoparticles (in CTAB/iso-octane/different co-surfactants, i.e. n-butanol and n-hexanol) for w_0 of 5 and 10. As compared to the band gap 2.42 eV of bulk CdS, the absorption spectra clearly show a blue shift due to the quantum confinement effect, with the absorption edge shifting to large wavelength region with increase in the value of w_0 . The optical spectra of the CdS particles formed indicate that the particles formed are in the nanoparticle regime. Band gap values were obtained from the linear fit for $(hv\alpha)^2$ versus (hv) plot shown in figure 3(a, b) for $w_0 = 5$ and 10. The band gap of the CdS nanoparticles is a function of size under tight binding approximation (TBA) as well as effective mass approximation (EMA). TBA fits better for particles with diameters smaller than 4nm whereas EMA fits for all range of sizes.²⁹ The relationship between the particle size and band gap is given by equation (1):

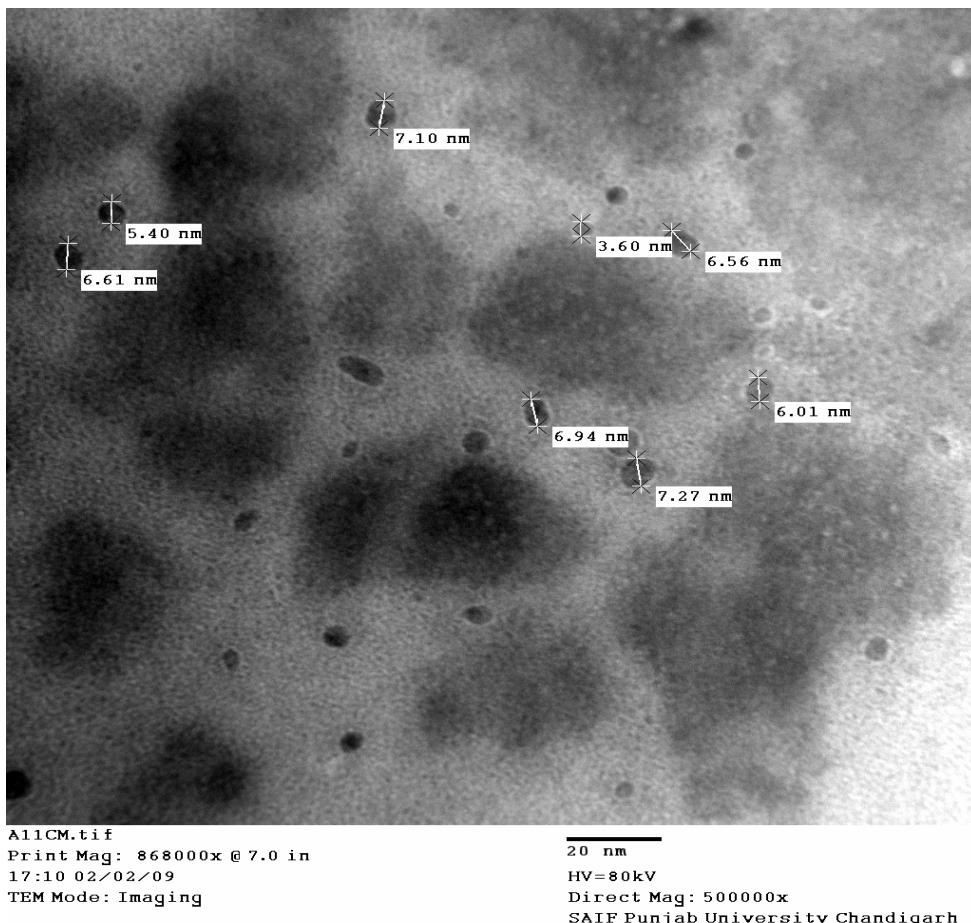
$$E_g = E_g(0) + \alpha/d^\beta \quad (1)$$

where $E_g(0)$ is band gap of bulk CdS (2.42 eV), α and β being constants. The values of α and β were obtained as 13eV/nm² and 2, respectively, using EMA fitting³⁰ and from the data taken from Lippens and Lannoo³¹ for the relationship between band gap and particles size. The band gap values of the nanoparticles formed with different co-surfactants and w_0 along with the particles size estimated using equation (1), are given in Table II. However, for accurate size assessment by UV-Visible absorption spectroscopy,³² particles should be exactly spherical in shape. But it is evident from TEM images that most of the particles of various samples are not spherical in shape. We believe that due to non-spherical shape, exact size determination by absorption spectroscopy is not possible and only the approximate particle size calculation has been possible from this study whereas TEM images give a better assessment.

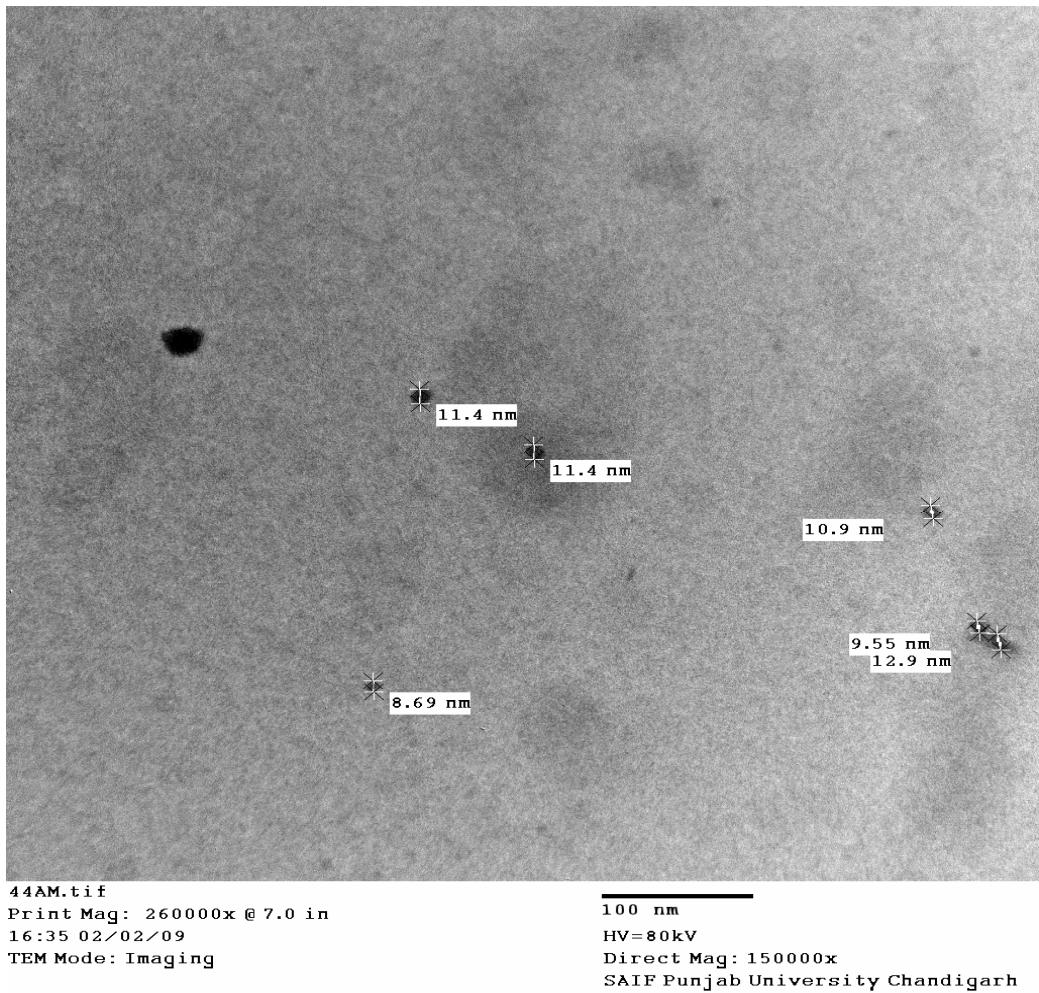
Table 2. Band gap values and particle sizes of CdS nanoparticles formed at $w_o = 5, 10$ with n-butanol and n-hexanol as co-surfactants.

Co-surfactant	Molar ratio (w_o)	UV-Visible		TEM
		Band Gap (eV)	Particle Size (nm)	Mean Particle Size (nm)
n-butanol	$w_o = 5$	2.77	6.05	6.20
	$w_o = 10$	2.72	6.25	10.80
n-hexanol	$w_o = 5$	2.85	5.49	7.00
	$w_o = 10$	2.75	6.27	10.05

3.3 TEM analysis



(a) $w_o = 5$, mean dia.=6.2 nm

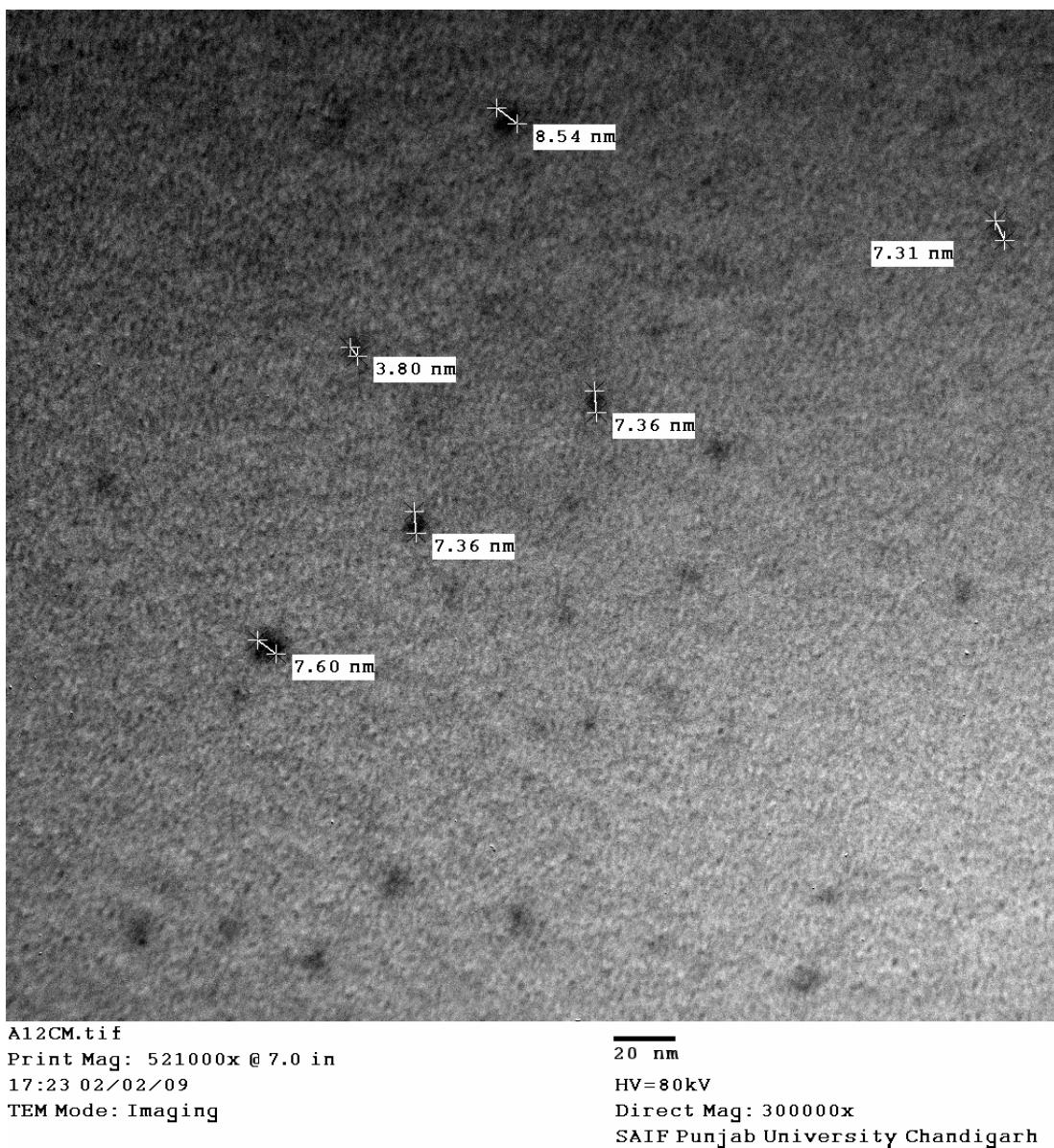


(b) $w_o = 10$, mean dia.=10.8 nm

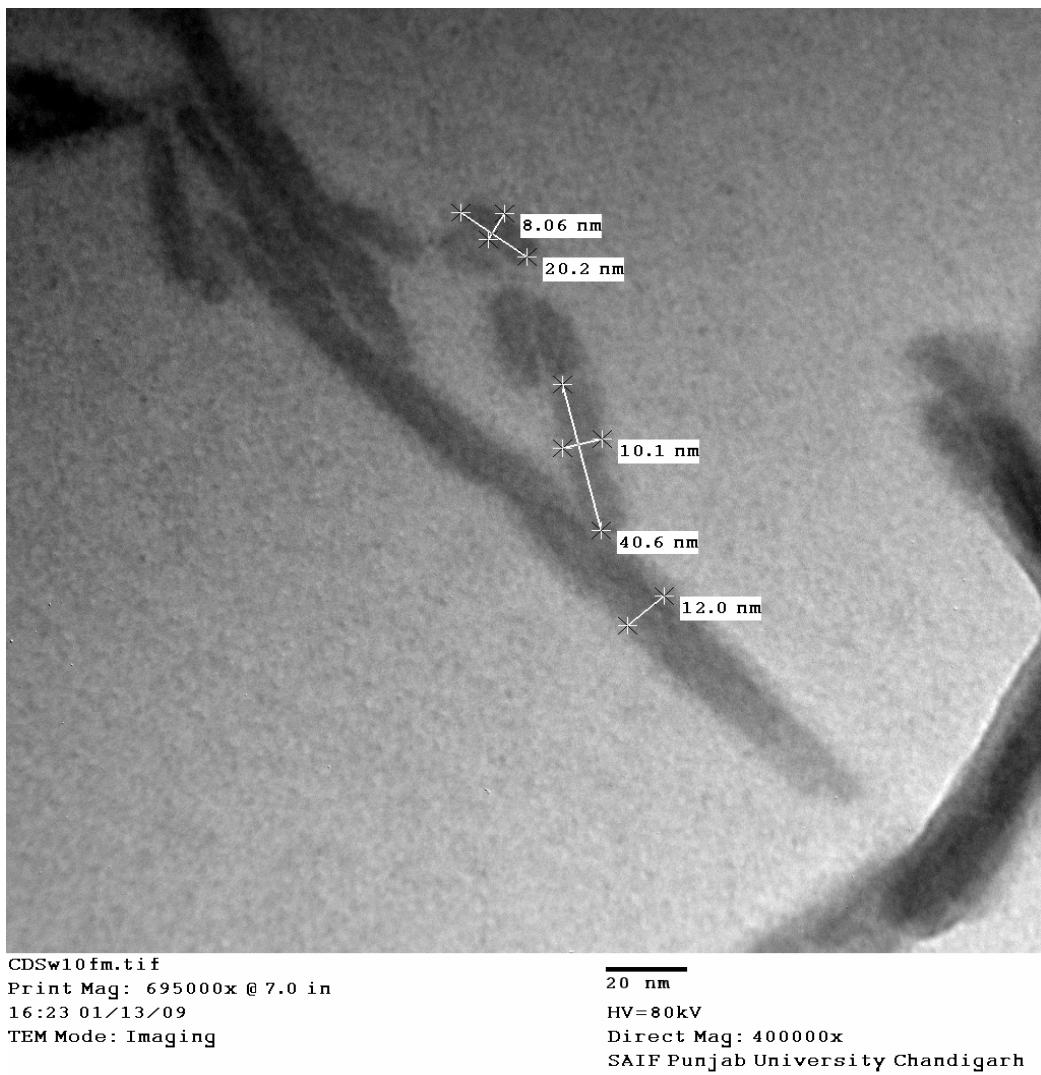
Fig.4 (a,b): TEM images of CdS nanoparticles synthesized in microemulsion with n-butanol as a co- surfactant

By employing n-butanol as a co-surfactant at relatively low $w_o = 5$, TEM image in Figure 4(a) shows that the synthesized product consists of uniform nanoparticles or quantum dots with mean diameter of 6.2 nm. The smaller size of quantum dots leads to their higher efficiency of light emission and because of this, it is reasonable to expect that the synthesized product could potentially be used in electroluminescent applications upon doping.

Figure 4(b) shows elliptical shaped nanoparticles with mean diameter 10.8 nm at $w_o = 10$. Similarly, using hexanol at $w_o = 5$, spherical nanoparticles of mean diameter 7.0 nm are formed (Fig. 5a). However, significant morphological change is observed at $w_o = 10$ for hexanol, where instead of spherical nanoparticles, nanoneedles with length 20-40 nm and mean diameter 10.05 nm are formed (Fig. 5b).



(a) $w_o = 5$, mean dia.=7.0 nm



(b) $w_o = 10$, mean dia.=10.05 nm

Fig.5 (a,b): TEM images of CdS nanoparticles synthesized in microemulsion with n-hexanol as a co- surfactant.

It should be noted that there were some significant changes in the morphology of the synthesized CdS nanoparticles when different co-surfactants were used. At $w_o = 5$, comparison of Figures 4(a) and 5(a) reveals that spherical nanoparticles are formed in both cases. However, comparing Figures 4(b) and 5(b) at $w_o = 10$, significant morphological changes were observed with n-butanol and n-hexanol where elliptical shaped

nanoparticles and nanoneedles were formed, respectively, in place of spherical particles. Finally, when n-butanol was used as a co-surfactant with $w_o = 15$, the morphology change is predominant yielding nanorods (Fig 6) of mean aspect ratio of 8.0. The morphology change in case of butanol co-surfactant follows a regular pattern from spherical to elliptical to nanorods with change of molar ratio, w_o . However, it is more sudden in case of hexanol as a co-surfactant.

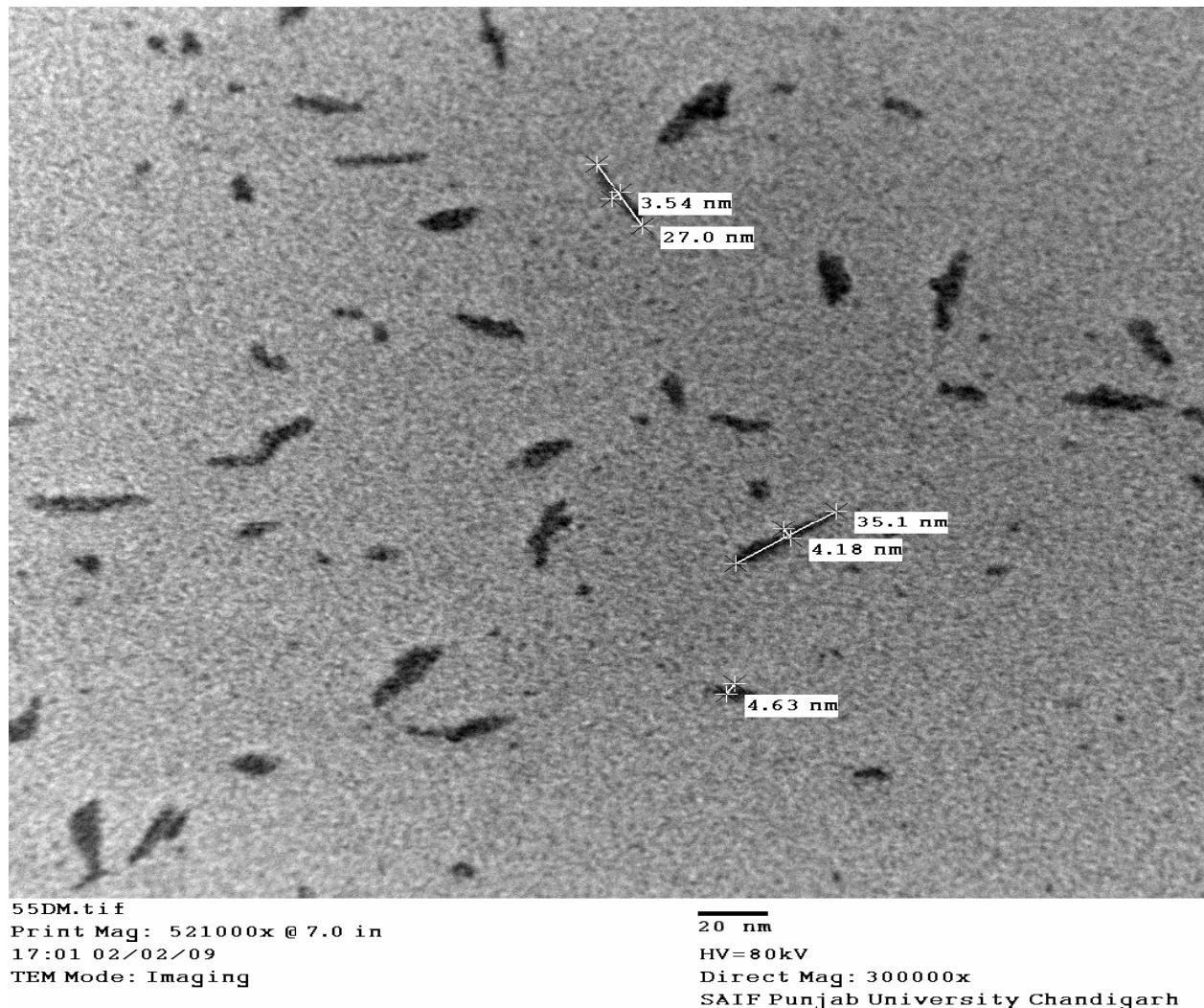


Fig. 6: TEM image of CdS nanorods synthesized in microemulsion with n-butanol as a co- surfactant and $w_0 = 15$.

4. Conclusion

CdS nanoparticles, synthesized in w/o microemulsion system using different co-surfactants, show an interesting morphology. It is clearly shown by TEM images that the size and the morphology of CdS nanoparticles are dependent on the nature of co-surfactant and water to surfactant molar ratio (w_0). Co-surfactant with larger molecular size such as n-hexanol could provide higher possibility to synthesize

CdS nanoparticles with high aspect ratio like nanoneedles or nanorods. However, observable morphological change has been observed at $w_0 = 10$. The elliptical nanoparticles formed using n-butanol as a co-surfactant are replaced by long nanoneedles using n-hexanol. Optical absorption spectra also supports the results as band gap shifts are observed at $w_0 = 5$ and 10 using different co-surfactants. However, exact size

assessment was not possible by absorption spectra due to non-spherical shape of nanoparticles, the evidence for which is provided by the TEM images.

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References

1. Henglein A. *Chemical Reviews* 1989. 89. 1861 p.
2. Steigerwald M. L. and Brus. L. E. *Accounts of Chemical Research* 1990. 23. 183 p.
3. Wang Y. and Herron. N. *The Journal of Physical Chemistry* 1991. 95. 525 p.
4. Weller H. *Angewandte Chemie International Edition (English)* 1993. 32. 41 p.
5. Wang Y. *Accounts of Chemical Research* 1991. 24. 133 p.
6. Rosencher E. et al. *Science* 1996. 271. 168 p.
7. Hines M. A. and Guyot-Sionnest. P. *The Journal of Physical Chemistry B* 1996. 100. 468 p.
8. Bard A. J. *Science*. 1980. 207. 4427 p.
9. Yanagida S. et al. *The Journal of Physical Chemistry* 1990. 94. 3104 p.
10. Haram S. K. et al. *Journal of the American Chemical Society* 2001. 123. 8860 p.
11. Brus L. E. *Journal of Chemical Physics* 1984. 80. 4403 p.
12. Colvin V. L. et al. *Nature* 1994. 370. 354 p.
13. Dabbousi B. O. et al. *Applied Physics Letters* 1995. 66. 1316 p.
14. Pavesi L. et al. *Nature* 2000. 408. 440 p.
15. Graetzel C. K. and Graetzel. M. *Journal of the American Chemical Society* 1979. 101. 7741 p.
16. Hagfeldt A. and Graetzel. M. *Chemical Reviews* 1995. 95. 49 p.
17. Bruchez J. M. *Science* 1998. 281. 2013 p.
18. Mane R. S. and Lokhande. C. D. *Materials Chemistry and Physics* 2000. 1. 65 p.
19. Henshaw G. et al. *Chemical Communications* 1996. 27. 1096 p.
20. Wada Y. et al. *Journal of Materials Chemistry* 2001. 11. 1940 p.
21. Torimoto T. et al. *The Journal of Physical Chemistry* 2001. 105. 6838 p.
22. Guinier A. *X-ray diffraction* Freeman. San Francisco. CA. 1963.
23. Klabunde K. J. Ed. *Nanoscale Materials in Chemistry*. Wiley-Interscience. N.Y. 2001.
24. Alany R. G. et al. *International Journal of Pharmaceutics* 2000. 196. 145 p.
25. Yang X. H. et al. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2005. 264. 172 p.

26. Thongtem T. et al. *Materials Science Forum* 2007. 544-545. 777 p.
27. Zelaya-Angel O. et al. *Vacuum* 1995. 46. 1083 p.
28. Wang G. Z. et al. *Materials Letters* 2001. 48. 269 p.
29. Murakoshi K. et al. *Journal of the Chemical Society, Faraday Transactions* 1998. 94. 579 p.
30. Singh V. A. et al. *Physics of Semiconductor Devices* Narosa Publishing House. 1998. 69p.
31. Lippens P. E. and Lannoo. M. *Physics Review B* 1989. 39. 1035 p.
32. Nanda J. J. and Sarma. D. D. *Journal of Applied Physics* 2001. 90. 2504 p.