CHEMICAL ROUTE TO NANOTECHNOLOGY

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ABSTRACT

There are various routes to nanotechnology, namely, physical, chemical, biological and nature's self assembly. Chemical route to nanotechnology is simpler, cheaper and allows fabrication of nanomaterials at bench top conditions. We followed chemical route of reverse micelles, co-precipitation, solvo-thermal, sol-gel and seed growth technique to prepare quantum dots, nanorods and nanoneedles of Barium Carbonate, Barium Oxalate, Iron Oxalate, Barium hexaferrite, Zinc Oxide, Cadmium Sulphide, Cadmium Oxide and Silver. All these nanomaterials were characterized by using XRD, SEM/TEM, FTIR and UV-Vis spectroscopy. In this review, synthesis of nanomaterials by chemical route will be described briefly.

KEYWORDS: Chemical synthesis, Nanotechnology, Quantum dots, Nanorods, Reverse micelles, Quenching, Seed growth.

INTRODUCTION

On December 29, 1959, Richard P. Feynman gave the talk at a meeting at Caltech of the American Physical Society. He presented a vision of the precise manipulation of atoms and molecules so as to achieve amazing advances in information technology, mechanical devices, medical devices, and other areas. Most nanotechnology historians date the conceptual birth of nanotechnology to physicist Richard Feynman's seminal speech in 1959, "There's Plenty of Room at the Bottom," in which he described the profound implications and the inevitability of engineering machines at the level of atoms: "The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It would be, in principle, possible. . . .for a physicist to synthesize any chemical substance that the chemist writes down. .

.How? Put the atoms down where the chemist says, and so you make the substance. The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed – a development which I think cannot be avoided." The concept of nanotechnology was given by a Physicist, Richard Feynman in 1959, but it was left to Eric Drexler of MIT, the Chemist, to found the modern field of nanotechnology, with a draft of his seminal Ph.D. thesis in the mid 1980s. His 1991 doctoral thesis at MIT was revised and published as the book *"Nanosystems Molecular Machinery Manufacturing and Computation"* (1992), which received the Association of American Publishers award for Best Computer Science Book of 1992. Drexler's vision cut across many disciplinary boundaries, and was so far reaching, that no one was daring enough to be his thesis

advisor. Drexler's doctoral thesis (premiered in his book, *Engines of Creation* in 1986 and articulated technically in his 1992 book *Nanosystems*) laid out the foundation of nanotechnology and provided the road map still being pursued today. In fact, modern nanotechnology is an interdisciplinary area of research involving physical, chemical, biological sciences and information technology [1, 2]. There are various routes to nanotechnology, namely, physical, chemical, biological and nature's self assembly. Chemical route to nanotechnology is simpler, cheaper and allows fabrication of nanomaterials at bench top conditions. We followed chemical route of reverse micelles, co-precipitation, solvo-thermal, sol-gel and seed growth technique to prepare quantum dots, nanorods and nanoneedles of Barium Carbonate, Barium Oxalate, Iron Oxalate, Barium hexaferrite, Zinc Oxide, Cadmium Sulphide, Cadmium Oxide and Silver. Readers are advised to refer to any standard text book of analytical chemistry to learn about the procedures involved in these chemical methods of synthesis. We shall describe briefly the techniques used for fabrication of nanomaterials in our laboratory.

CHEMICAL SYNTHESIS OF NANOMATERIALS

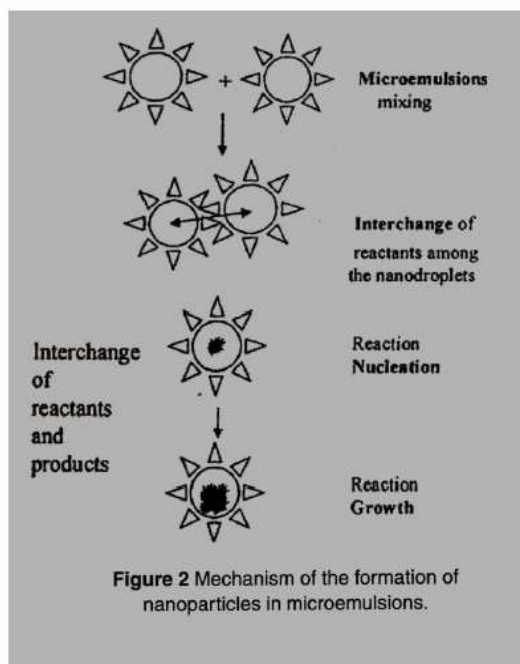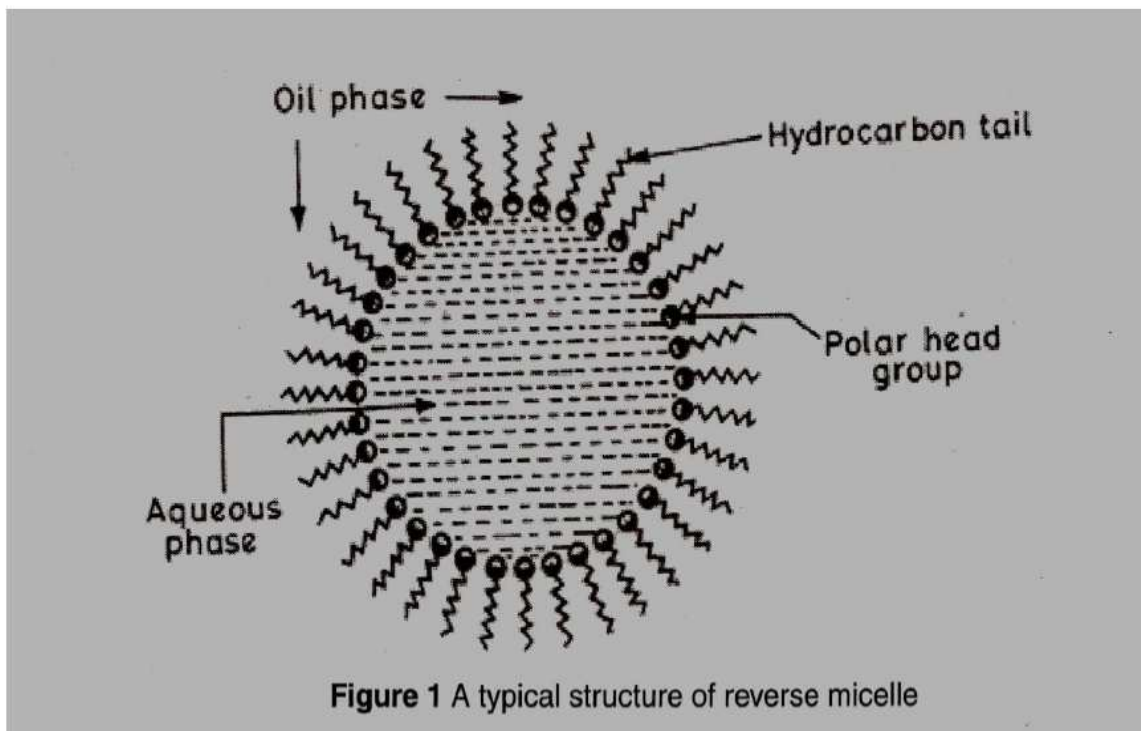### 1. Reverse Micelle Technique of Nanofabricaton

Among all chemical processes shape and size controlled growth of inorganic materials using reverse micelles or micro emulsions has received considerable attention during the recent past and demonstrated as a versatile method to produce a variety of nanoparticles owing to its diverse application potential in areas such as catalysis, medicine, pigments, cosmetics and separation technology [3, 4]. Here the precipitation is carried out in aqueous cores (nanoreactor) or reverse micelles that have the typical diameter of the order of 5-6 nm. The reverse micelle route of synthesis yields monodisperse nanoparticles with a very high degree of homogeneity as compared with other low temperature routes of synthesis. The mechanism for the formation of nanocrystalline materials using reverse micelles (Figs.1 & 2) has been explained in literature [5-9] by considering the synthesis of a simple compound like metal oxalate and carbonate. Colloidal synthesis is by far the cheapest and has the advantage of being able to occur at benchtop conditions. A microemulsion system consists of an oil phase, a surfactant and an aqueous phase. It is a thermodynamically stable isotropic dispersion of the aqueous phase in the continuous oil phase. Microemulsion A should be metal ion and B should be oxalate in case of metal oxalate and in case of metal carbonate, B should be carbonate. These two microemulsions are mixed by constant stirring and the droplets continuously collide, which results in the exchange of reactants. During this process, the reaction

takes place inside the nanoreactor. In microemulsion system, the reverse micelles of metal oxalate/ carbonate form the fused dimer which finally breaks down into two stable smaller droplets because surface tension becomes high due to large surface area and dimer is unable to sustain its geometry [8].

Figure 1 A typical structure of reverse micelle

Figure 2 Mechanism of the formation of nanoparticles in microemulsions.

(a) Synthesis of Barium Carbonate/Oxalate and Iron Oxalate Nanoparticles

The mechanism for the formation of nanocrystalline material using reverse micelles has been described elsewhere [10]. In a typical experiment, at room temperature, the barium carbonate and oxalate were synthesized by using the reverse micellar route with CTAB as a surfactant, n-butanol as the co-surfactant and iso-octane as the non-polar solvent. For the synthesis of barium carbonate two different microemulsions, A and B were used. Microemulsion A (25ml) is prepared by adding 2.5ml of 0.1M aqueous solution of barium nitrate, 3.5ml of n-butanol as co-surfactant, 15ml of iso-octane as the non-

polar solvent and 4.20g of cetyl trimethylammonium bromide (CTAB) as surfactant. Microemulsion B (25ml) is prepared by adding 2.5ml of 0.1M aqueous solution of ammonium carbonate, 3.5ml of n-butanol as co-surfactant, 15ml of iso-octane as the non-polar solvent and 4.20g of cetyl trimethylammonium bromide (CTAB) as surfactant. Both the microemulsions (A and B) were stirred separately, then mixed slowly and then kept for stirring overnight using a magnetic stirrer. The product was separated from microemulsions by centrifugation and washed with 1:1 mixture of chloroform and methanol and dried at room temperature. The flow chart for the synthesis of nanocrystalline barium carbonate is shown in Fig. (3).
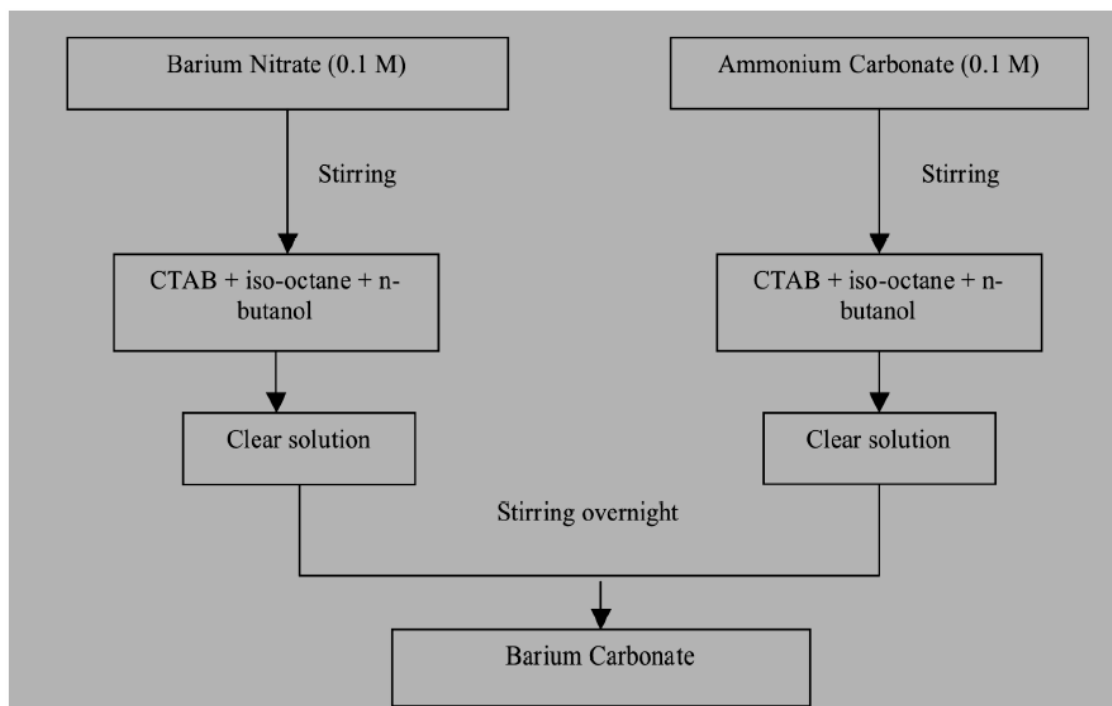

Fig. 3. Flow chart for synthesis of nanocrystalline barium carbonate.

The synthesis of barium oxalate was achieved in a similar manner as discussed above for barium carbonate except that the microemulsion B contains 0.1M aqueous solution of ammonium oxalate instead of ammonium carbonate. The weight fractions of various constituents in these microemulsions are as follows [6]: 16.76% of CTAB, 13.90% of n-butanol, 59.29% of isooctane and 10.05% of the aqueous phase. The composition, chemical formulae and purity of components used in microemulsions are given below in Table1. TEM micrographs are shown in Fig. 4(a, b) and Fig. 5.

Table 1. Composition, Chemical Formula and Purity of the Components of the Microemulsion

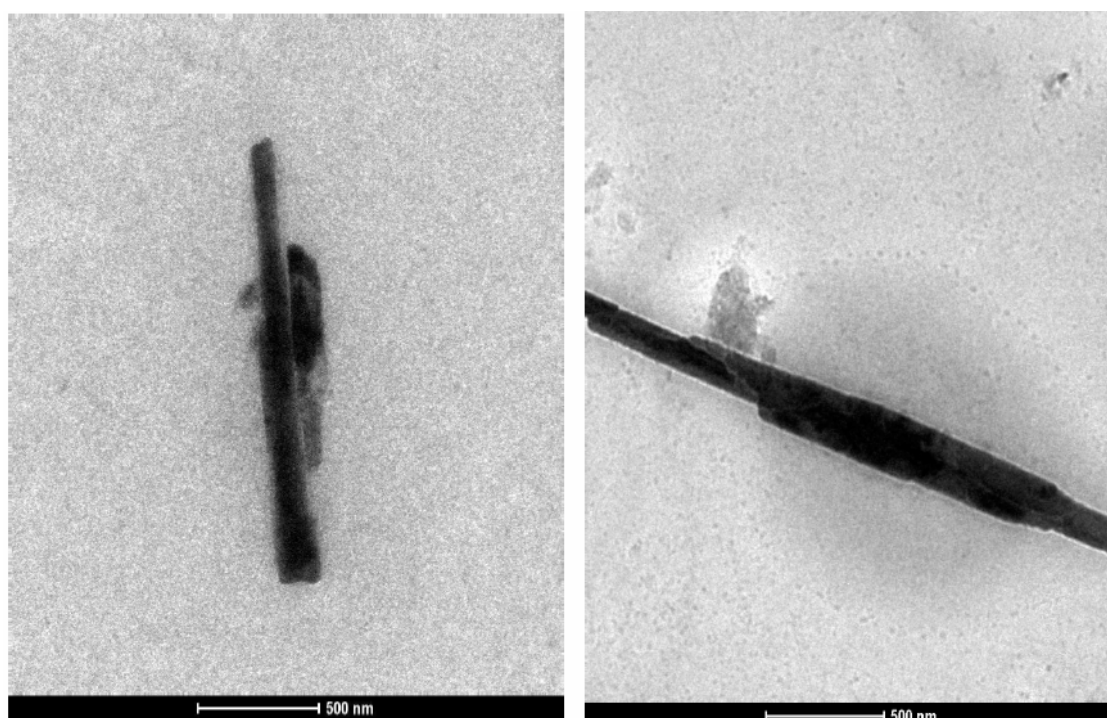| S. No.	Chemical Name	Chemical Formula	Purity
1	Iso-Octane	C_8H_{18}	99%
2	n-butanol	$C_4H_{10}O$	99%
3	Ammonium Carbonate	$NH_4HCO_3 + NH_2CO_2NH_4$	95%
4	Ammonium Oxalate	$(COONH_4)2H_2O$	99%
5	Barium Nitrate	$Ba(NO_3)_2$	99%
6	CTAB (Cetytrimethylammoniumbromide)	$C_{19}H_{42}BrN$	99%
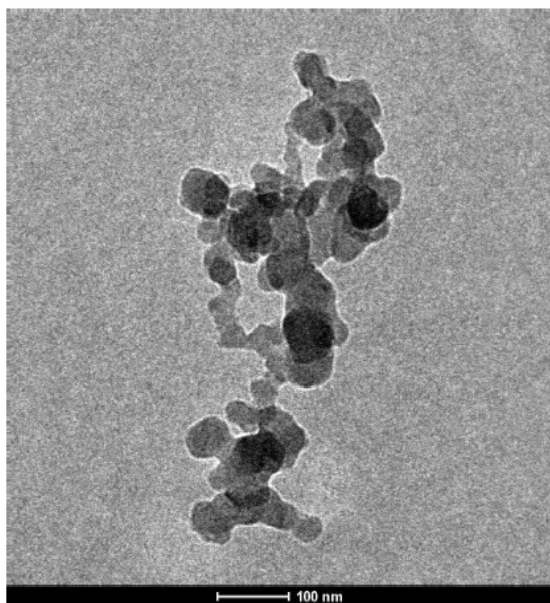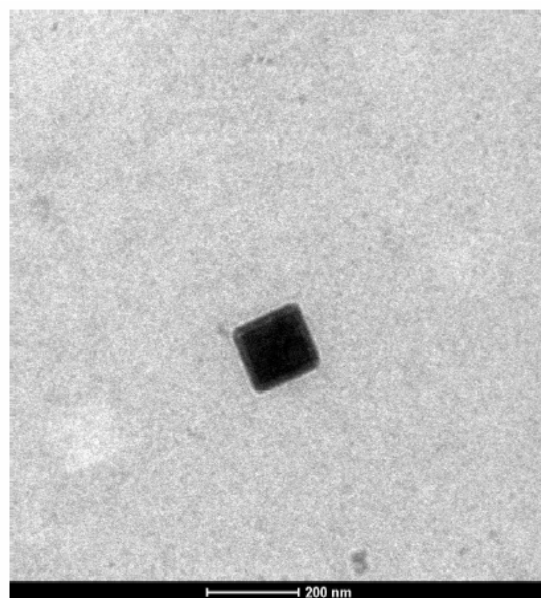
(a)   (b)

Fig. 4. TEM micrographs (a) Nanocrystals of Barium Oxalate, and (b) Iron Oxalate

**Fig. 5. TEM micrographs of nanorods of Barium Carbonate**

(b) Synthesis of Cadmium Sulphide Nanoparticles and Nanoneedles

For the synthesis of CdS nanocrystals, first microemulsion solution of 10 ml butanol, 25 ml cyclohexane and 0.1M $CdCl_2.H_2O$ was prepared and strongly stirred. A second microemulsion of Na_2S was prepared, replacing 0.1M $CdCl_2$ by 0.1M Na_2S and using n-butanol in a similar way. Then, these two microemulsions were mixed slowly and stirred to obtain yellow solution of CdS. This solution is incubated for 2 days and then centrifuged to get CdS nanoparticles. If the whole process is repeated, substituting n-butanol co-surfactant by n-hexanol, we obtain CdS nano-needles instead of nanoparticles.

The TEM result indicates that the synthesized CdS nanoparticles are of variable morphology. It should be noted that there were some significant changes in the morphology of the synthesized CdS nanoparticles when different co-surfactants were used with different molar ratios, w_o. At $w_o = 5$, comparison of TEM micrographs reveal that spherical nanoparticles were formed in both cases. However, at $w_o = 10$, significant morphological changes were observed when n-butanol was replaced by n-hexanol, and spherical/cylindrical nanoparticles were converted to nanoneedles (Fig. 6).
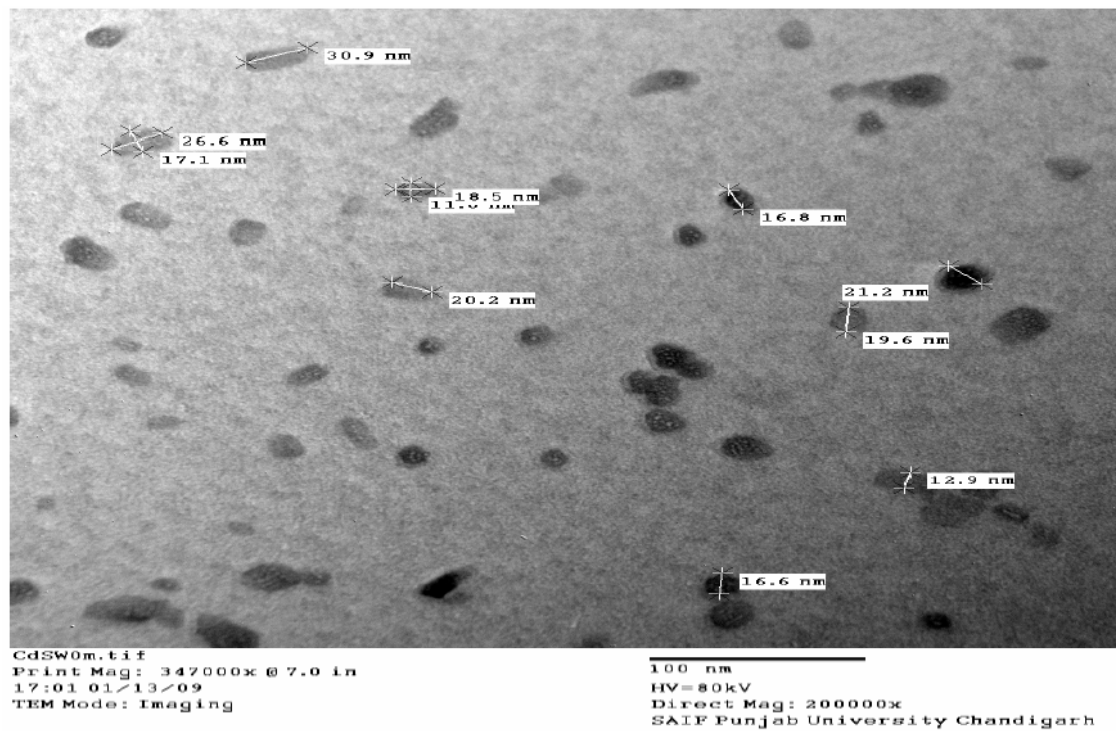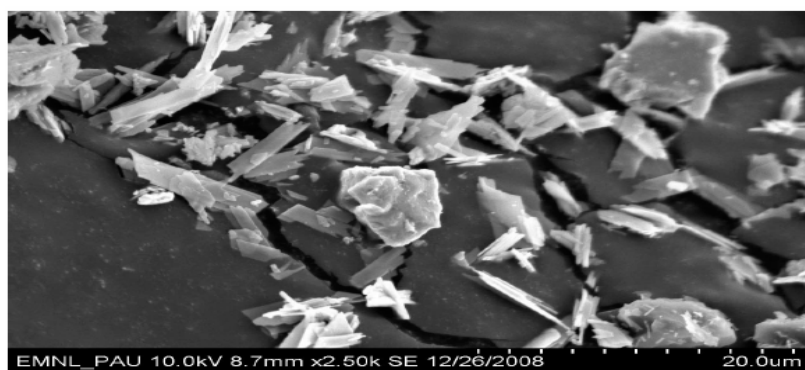
(a)
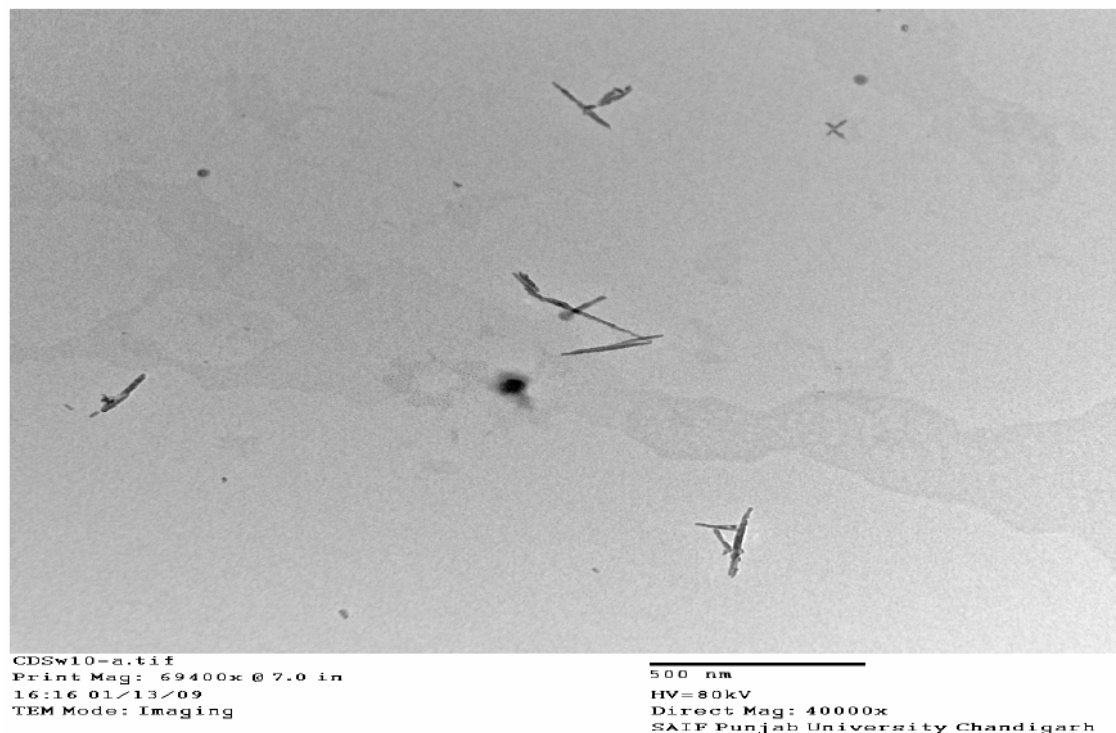
(b)

Fig. 6. TEM micrographs of (a) CdS quantum dots, and (b) CdS nanoneedles

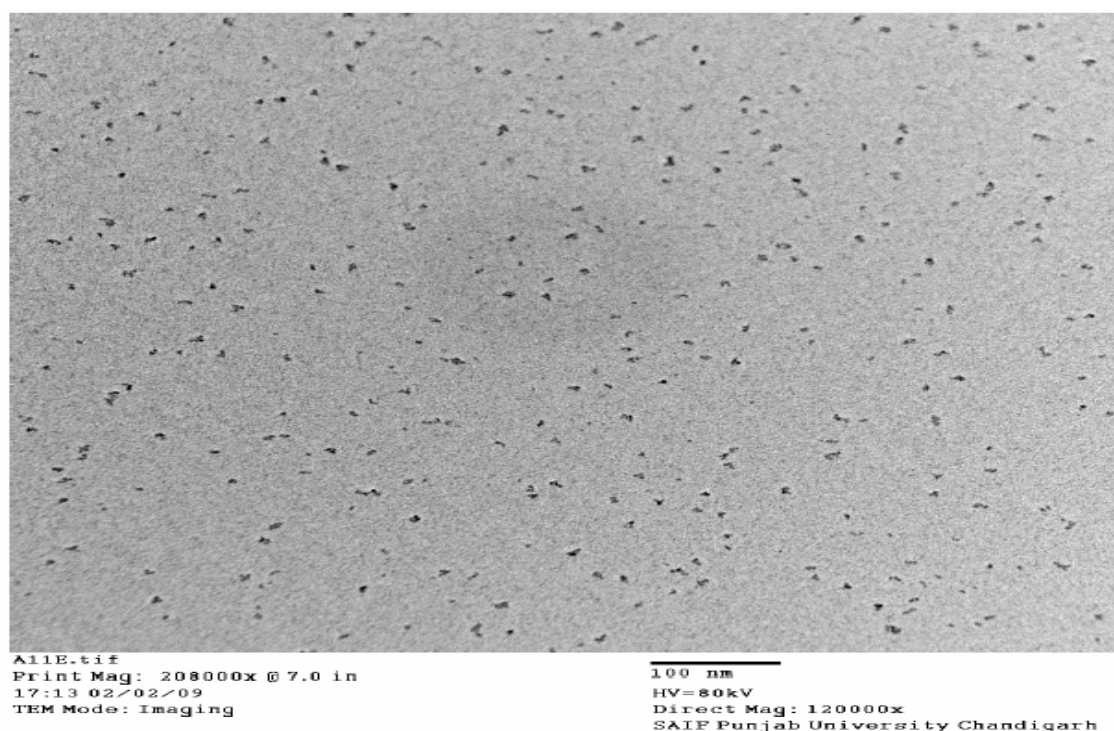**(c) Synthesis of Barium hexaferrite Micro/nanoparticles**

Barium ferrite has been extensively studied for advanced recording applications like computer data storage, high density perpendicular magnetic and magneto-optic recording, disk driver and video recorder because of its high intrinsic coercivity, large saturation magnetisation, high Curie temperature, fairly large megnetocrystalline anisotropy constant, excellent chemical stability and corrosion resistivity [11-12]. M-type barium hexaferrite with hexagonal molecular structure $BaFe_{12}O_{19}$ is a high performance permanent magnetic material. The technological applications require barium hexaferrite particles with good chemical homogeneity, and narrow particle size distribution. The magnetic properties of hexaferrite strongly depend upon particle size, method of preparation etc. A.R. Grade barium nitrate $(Ba(No_3)_2.6H_2O)$, ferric nitrate $(Fe(No_3)_3.9H_2O)$, and cetyltrimethyl ammonium bromide (CTAB) were used as starting materials. Appropriate amounts of barium nitrate, CTAB (0.01 M surfactant in 100 ml de-ionized water) and ferric nitrate were dissolved, one by one, in 100 ml of de-ionized water. Ammonium hydroxide (NH_4OH) solution (30%) was added slowly in the mixture to adjust pH of 8. Barium hexaferrite particles were prepared by water in oil microemulsion technique involving cetyltrimethyl ammonium bromide (CTAB) as a surfactant, n-butanol as the co-surfactant, isooctane as the solvent (oil phase) and aqueous solution as water phase. The aqueous phase in microemulsion-I was a solution of 0.1 M barium hydroxide and 1.2 M ferric nitrate (5ml aqueous solution in 42.5ml microemulsion). The aqueous phase in microemulsion-II was a solution of ammonia (w/v=25%) as the precipitator agent (5 M aqueous solution of ammonia in 42.5 ml microemulsion). In order to obtain precipitation of barium hexaferrite particles, microemulsion-II was added drop wise in microemulsion-I under vigorous stirring for 2 hours; then the solution was aged for 12 hours.

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(a)

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(b)

Fig.7. (a) SEM image of BaFe$_{12}$O$_{19}$ hexaferrite, and (b) TEM image of nanoparticles

2. Synthesis of CdO and ZnO Quantum Dots by Quenching Method

Fabrication of quantum dots has emerged as an important area of research in the field of nanotechnology during recent years [13-17]. Cadmium oxide (CdO) is a n-type semiconductor and finds applications in photodiodes, photovoltaics, liquid crystal displays, IR detectors, electrodes of storage batteries, phosphors, pigments and ceramic glazes [18]. A major use of CdO is as an ingredient for electroplating baths and in pigments [19]. A number of synthetic routes have been used to synthesize CdO nanoparticles and nanowires [20-21]. We employed a simple technique of sintering CdO powder and quenching it in ethyl alcohol to prepare quantum dots. In a typical synthesis, 4g of CdO powder (purity 99.5% CDH make) was sintered at 900 ^{0}C in a muffle furnace for 5 hrs. and then quenched into 7 wt. % aqueous ethyl alcohol kept at ice cold temperature followed by moderate stirring. The resulting solution contains CdO quantum dots (Fig. 8a). The second portion of quantum dot solution was transferred into a stainless steel autoclave and heated slowly to 100 ^{0}C and maintained at this temperature for 24 hours. The resulting suspension was centrifuged to retrieve the end product, washed and then vacuum dried. Ethylenediamine was added to the reaction mixture obtained above, which resulted in the formation of nanorods (Fig. 8b).
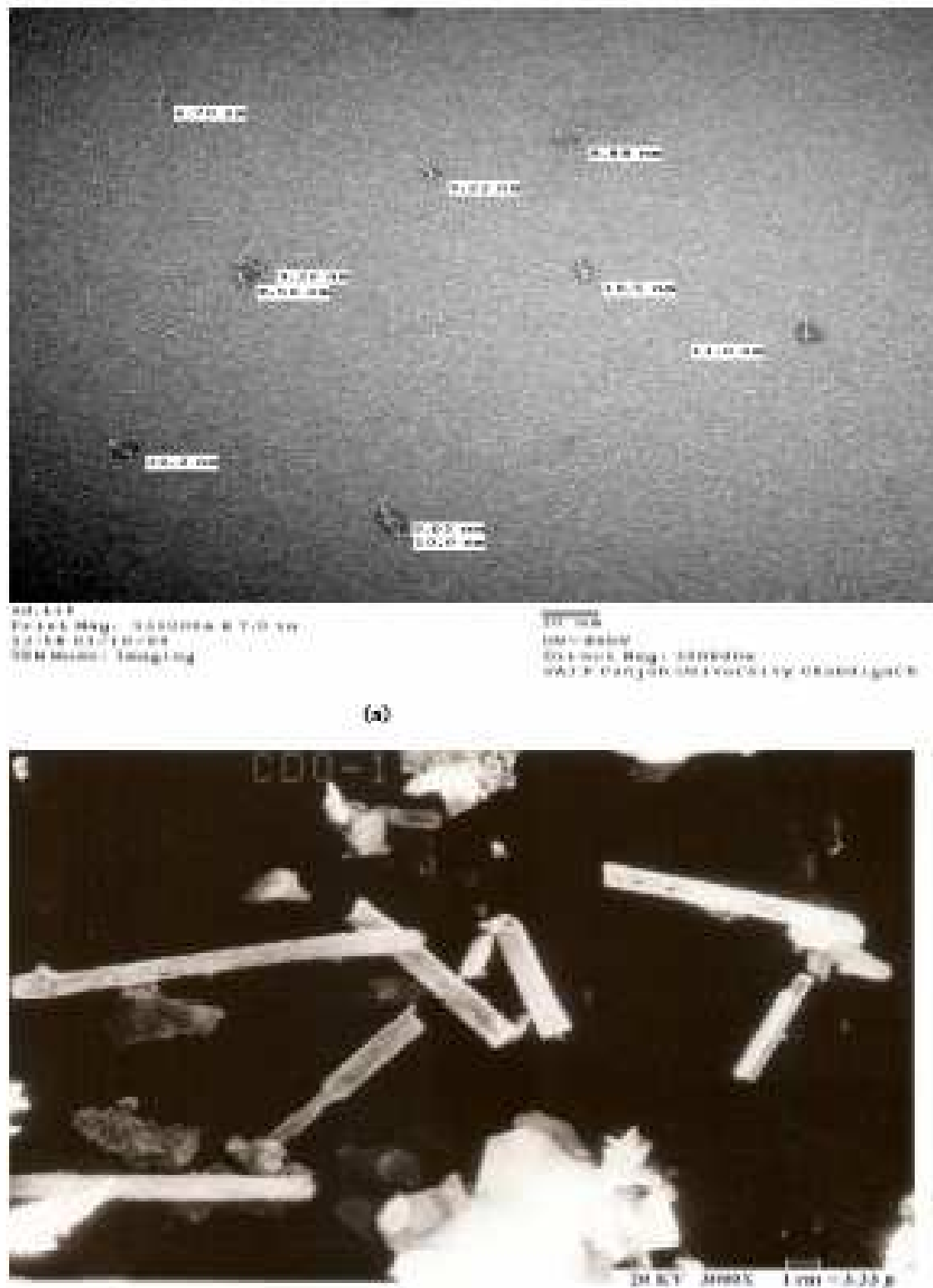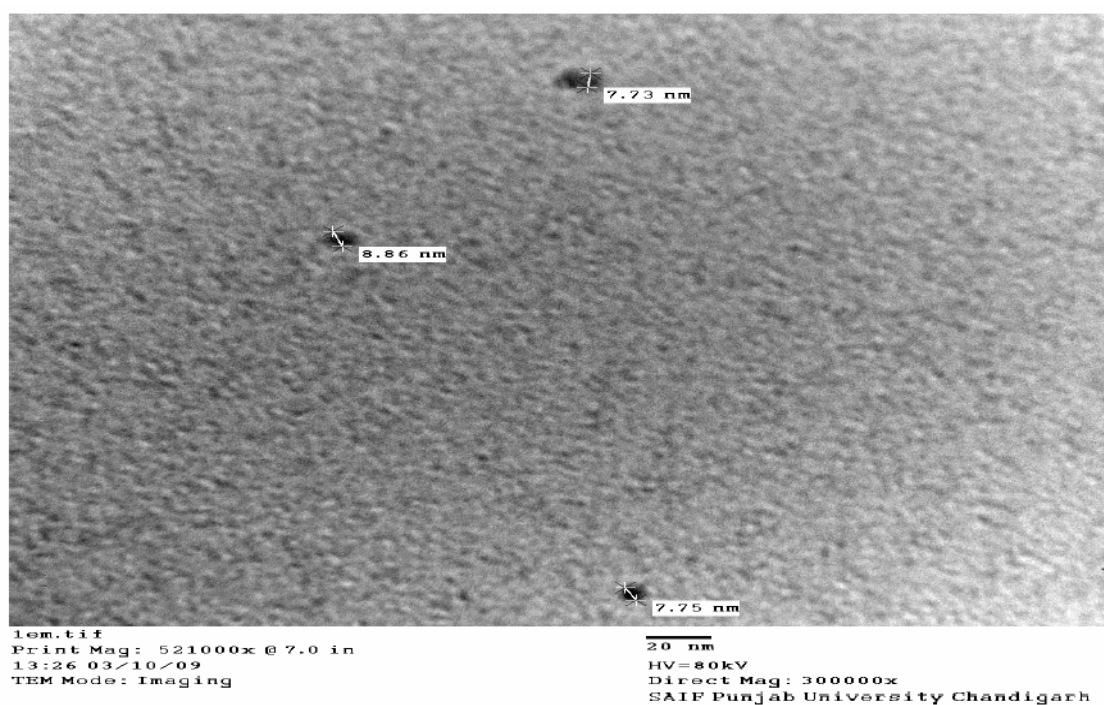
Fig. 8(a) TEM micrograph of CdO quantum dots and (b) nanorods on adding EDA
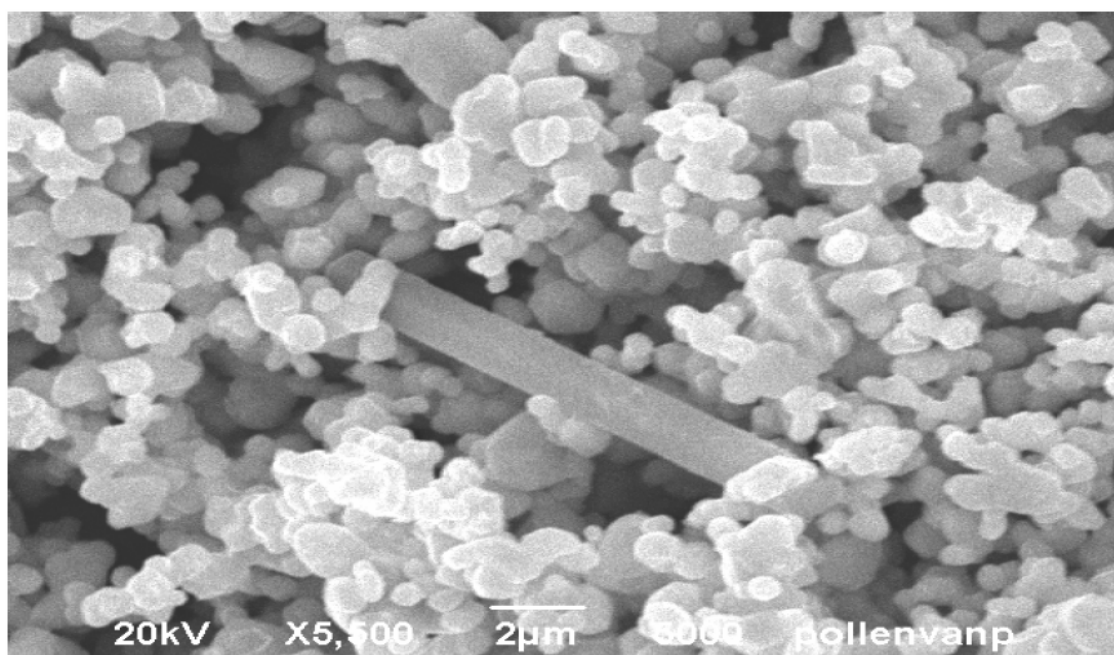
Zinc oxide (ZnO) is one of the most important semiconducting materials, having a wide range of potential applications [22]. ZnO is an important electronic and photonic material because of its wide direct based gap of 3.37 eV. In recent years, ZnO nanocrystals have been used for solar cell applications [23], gas sensors [24], ultraviolet lasing action at room temperature [25] and photoelectronics [26]. Nanocrystals of ZnO have been prepared using both physical and chemical methods; among them sol-gel chemistry, spray pyrolysis, microemulsion, precipitation, solvothermal and hydrothermal methods are being extensively used [27-32]. Generally, most of these methods of synthesis require relatively high temperatures or involve the use of expensive chemicals or apparatus. It is therefore advisable to find simple methods to produce ZnO nanocrystals using commonly available chemicals.

5 mg of ZnO powder (CDH grade, 99.5 % purity) was heated at 800^0C for 6 hrs. and quenched in 10 ml of ice cold ethanol to prepare nanoparticles. ZnO nanocrystals (Fig.9a)   are produced by quenching process. The resulting suspension is centrifuged to retrieve the product, washed with alcohol and dried. ZnO nanorods (Fig.9b) were prepared by addition of 1ml of ethylenediamine to one part of this mixture at the room temperature.


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(a)

(b)

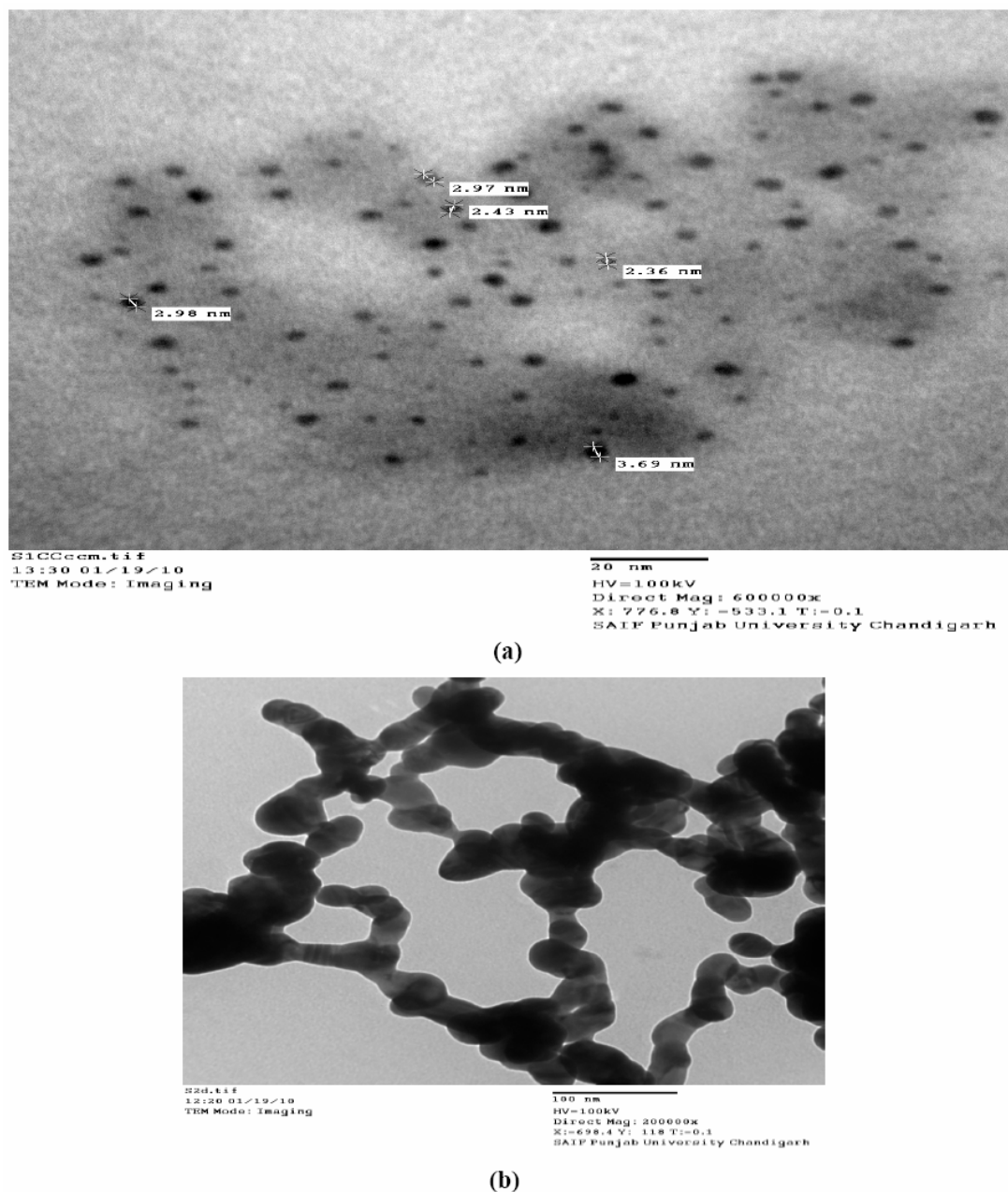**Fig.9 (a) TEM micrographs of ZnO quantum dots and (b)nanorods on adding EDA**

3. Synthesis of Silver Nanoparticles by Seed Growth Method

An aqueous phase room temperature synthesis of such materials is highly significant so as to have maximum yield and diverse applications. Several studies [33] have demonstrated the use of surfactants as capping and stabilizing agents to develop 1D nanostructures such as nanorods and nanowires by using seed mediated approach. In this method [34, 35] small seeds are first obtained by reducing the metal cations by strong reducing agent like NaBH4, then they are used to grow into long nanorods or wires under slow reducing growth conditions. The crystal growth is very well controlled by selectively adsorbing surfactant monomers in the form of a monolayer on certain low atomic density crystal planes such as {100} or {110} in the case of face centered cubic

geometry. An appropriate choice of a surfactant is a key factor and not all surfactants provide 1D nanostructures [36]. Here, the chemical structure of a surfactant molecule plays a vital role. Synthesis of Triton X-100 capped silver nanoparticles was followed by Seed-growth method essentially similar to that reported by Murphy et al. [34] and Bakshi [36]. Briefly, 25ml of seed solution was prepared by keeping silver nitrate $[AgNO_3] = 0.5mM$ and sodium citrate $[Na_3Cit] = 0.5mM$, which was followed by the addition of 0.6 ml of aqueous sodium borohydride ($[NaBH_4] = 0.1mol\ dm^{-3}$) solution under constant stirring. A growth solution consists of $[TritonX-100] = 1mM$ in 5ml water along with $[AgNO_3] = 0.5mM$, 0.2ml of freshly prepared ascorbic acid (AA) aqueous

solution ([AA] = 0.1M), and different quantities (i.e., 0.5, 0.25 and 0.125ml) of previously prepared seed solution. The color of each sample was yellowish brown when TritonX-100 was used as the capping surfactant. The samples were kept for 24 hrs. at room temperature in the dark. Then samples were centrifuged and washed with water until complete surfactant is removed. The silver nanoparticles obtained were redispersed in 1ml water for TEM analysis (Fig.10).

(a)

(b)

Fig.10. TEM micrographs of Ag (a) quantum dots, and (b) embedded nanoparticles

4. Synthesis by Sol-gel, Co-precipitation, Solvo-thermal and Sonochemical Methods

Sol-gel method involves the formation of a concentrated suspension of a metallic oxide or hydroxide (sol), which is subsequently dehydrated by evaporation or solvent extraction, resulting in a semi-rigid mass (gel). A wide range of pure and mixed oxides can be produced on controlled heating of this gellated material. This process gives a good control over composition and particle size, and a substantial reduction in the formation temperature. Almost mono size metal nanocrystals can be produced from a hydrosol, i.e., a colloidal dispersion in water, but this method is limited in applicability.

The co-precipitation technique is a useful method for the preparation of ceramic oxide powders. In the case of a multi-component system, this technique is usually limited to the cations of chemically similar properties. In the co-precipitation method, the required amount of the aqueous solution of desired metal ions were mixed together. The pH is adjusted somewhere in the region where the metal ions gets precipitated by adding aqueous solution of ammonia, ammonium hydroxide or ammonium carbonate. The precipitate was washed with distilled water, dried and ground to obtain particles of sizes smaller than 5 nm. An advantage of the co-precipitation method is that the calcination temperature may be raised without agglomerating the particles. In co-precipitation method, it is sometimes possible to achieve high degree of homogenization together with a small particle size and thereby speed up the reaction rate. The main disadvantage of the method is that it produces materials with broad size distribution. The method does not work well in the following cases:

- The two reactants have very different solubilities in water.

- The reactants do not precipitate at the same time.

In the solvothermal method, nanophase materials are produced by chemical reactions in an aqueous or organic medium under the simultaneous application of heat and pressure in the presence of an alkali or acid. A number of fundamental properties of solvents are greatly affected by pressure and temperature, for example, the viscosity or dielectric constant are considerably reduced; this has major implications on the solubility of solid reagents under reaction conditions. Synthesis under solvo-thermal conditions offers some significant advantages over other chemical methods. First, it is easy to control particle size and morphology by varying the synthesis conditions (temperature, pressure, time, concentration, pH, shearing forces, nature of additives). Secondly, many nanomaterials can be directly synthesized (one step synthesis) in the desired crystalline phase at relatively low temperature. Solvo-thermal process opens a fruitful route for improving the synthesis of well-known nanomaterials, furthermore, allowing the preparation of

nanophase materials which are difficult to obtain by other methods.

An acoustic cavitation process can generate a transient localized hot zone with extremely high temperature gradient and pressure. Such sudden changes in temperature and pressure assist the destruction of the sonochemical precursor (e.g., organometallic solution) and the formation of nanoparticles. Sonochemical decomposition of volatile organometallic precursors has shown to produce nanostructured materials in various forms with high catalytic activities. This has proved extremely useful in the synthesis of a wide range of nanostructured inorganic materials for industrial applications, including high surface area transition metals, alloys, carbides, oxides, and sulfides, as well as colloids of clusters. Another important application has been the sonochemical preparation of biomaterials, most notably protein microspheres. These protein microspheres have a wide range of biomedical applications, including uses for in vivo thermography, in vivo oximetry, MRI contrast agents, and drug delivery.

CONCLUSIONS

Chemical synthesis of nanomaterials has been described using reverse micelles, quenching method and seed growth techniques in our laboratory. It has been established that chemical route to nanotechnology is most convenient, cheap and efficient for production of a variety of nanomaterials, for example, quantum dots, nanowires and nanorods. CdS, CdO and ZnO nanoparticles prepared by microemulsion and quenching techniques show interesting morphology. The morphology of nanoparticles is dependent on nature of surfactant and co-surfactant used. 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. ZnO nanocrystals can be prepared at room temperature by using a simple technique known as quenching method. EDA acts as a shape directing agent and produces nanorods of ZnO. Characterization of nanoparticles has been done using XRD, SEM, TEM and FTIR analysis but our focus in this paper is on synthesis of nanomaterials.

ACKNOWLEDGEMENTS

REFERENCES

1. Ratner M & Ratner D, "*Nanotechnology: A gentle introduction to the next big*

Idea", Pearson Education Publication, London, 2003.

2. Cao G Z, *"Nanostructures and Nanomaterials"*, Imperial College Press, London, 2004.

3. Pileni M P, Gulik-Krzywicki T, Tanori J, Filankembo A, Dedieu J C, *Langmuir*, **14**, 7359 (1998).

4. Rees G D, Evans-Gowing R, Mammond SJ, Robinson B H, *Langmuir*, **15**, 1999(1993).

5. Ahmad T, Chopra R, Ramanujachary K V, Lofland S E, Ganguly A K, *Nanosci. Nanotechnol,* **5**, 1840 (2005).

6. Ahmad T, Ramanujachary K V, Lofland S E, Ganguly A K, *J. Mater. Chem*, **14**, 3406 (2004).

7. Ahmad T, Vaidya S, Sarkar N, Ghosh S, Ganguly A K, *Nanotechnology*, **17**, 1236 (2006).

8. Ganguly A K, Ahmad T, *J. Nanosci Nanotechnol*, **7**, 2029 (2007).

9. Macketta J J, *Encycyclopedia of chemical processing and design*. Marcel Dekker, New York, pp. 51, (1997).

10. Sharma P and Virk H S, *The Open Surface Science Journal,* **1,** 23 (2009).

11. Paul K B*, Physica B: Condensed Matter*, **388**, 337 (2007).

12. Yu H, Liu P C, *J. Alloys Compounds*, **416**, 222(2006).

13. Bailey R E, Nie S, *J. Am. Chem. Soc*., **125**, 7100 (2003).

14. Ledentsov N N, Ustinov V M, Shuchukin V A, Koplev P S, Alferov Z I, Bimberg D, *Semiconductors*, 32343, (1998).

15. Tuan A C, Bryan J D, Pakhomov A B, Shutthananadan V, *et al*. *Phys. Rev. Lett. B*, **70** 054424 (2004).

16. Timp G, *"Nanotechnology"*, Springer Verlag, New York, p. 276 (2005).

17. Bandyopadhyay S, Nalwa H S, (Eds.) *"Quantum Dots and Nanowires"*, American Scientific Publishers, NY, 2003.

18. Lockhande B J, Patil P S, Uplane M D, *Mater. Chem. & Phys*., **84**, 238 (2004).

19. Clifford A, Gessner H, Hawley G, *"The Encyclopedia of Chemistry"*, *3rd ed*., Hawley, p.169,(1973).

20. Radi P A, Brito-Madurro A G, Madurro J M, Dantas N O, *Brazilian J. Phys*. **36,** 412 (2006).

21. Peng X S, Wang X F, Wang Y W, Wang C Z, Meng G W, Zhang L D, *J. Phys. D.: Appl. Phys*., **35,** L101 (2002).

22. Wang Z L, Kong X Y, Ding Y, Gao P, Hughes W L, Yang R and Zhang Y, *Adv.Funct. Mater.,* **14**, 943, (2004).

23. Li Q, Kumar V, Li Y, Zhang H, Marks T J and Chang R P H, *J. Am. Chem. Soc*., **17**, 1001 (2005).

24. Singh R C, Singh O, Singh M P and Chandi P S, *Sensors and Actuators B*, 1**35**, 352 (2008).

25. K Tang, Wang G K L, Yu P, Kawasaki M, Ohtomo A, Koinmua H and Segawa Y, *Appl. Phys. Lett*. **72**, 3270 (1998).

26. Lao J Y, Wen J G, Ren Z F, *Nano Lett*., **2**, 1287 (2002).

27. Xu C, Xu G, Liu Y and Wang G, *Solid State Commun*., **122,** 175 (2000).

28. Guo L, Ji Y L, Xu H, Simon P, Wu Z, *J. Am. Chem. Soc*., **124,** 14864 (2002).

29. Liu L, Ge M, Liu H, Guo C, Wang Y, Zhou Z, *Colloids and Surfaces A: Physicochem. & Engg. Aspects*., **348**, 124 (2009).

30. Liu B, Zeng H C, *J. Am. Chem. Soc*., **125**, 4430 (2003).

31. Pahchakarla L S, Govindaraj A, Rao C N R, *J. Cluster Sci*., **18**, 660 (2007).

32. Wang J, Zhang S, Yu J, Yan H, Li Z, Jing X, Zhang M, *Bull. Mater. Sci*., **31**, 597(2008).

33. Chen J, Wiley B J, Xia Y, *Langmuir,* **23**, 4120 (2007).

34. Murphy C J, Sau T K, Gole A M, Orendoff C J, Gao J, Gou L, Hundayi S E, Li T J, *Phys. Chem. B*, **109**, 13857 (2005).

35. Murphy C J, Gole A M, Hundayi S E, Orendoff C J, *Inor. Chem*., **45**, 7544 (2006).

36. Bakshi M S, *J. Nanoscience and Nanotechnology*, **10**, 1 (2010).