

# Synthesis and characterization of nano ZnO and CdO

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Nano ZnO synthesized with and without surfactant adopting Solid State Reaction (SSR) method, the later at four different temperatures and by Aqueous Chemical Method (ACM) is reported. CdO synthesized by ACM is also presented. The ZnO nanorods by SSR with surfactant are of hexagonal shape with diameter between 20–30 nm and lengths of about 350–500 nm, while that without surfactant does not exhibit rod like morphology. The particle size increases from 35 to 59 nm with temperature in the range 500 to 800°C. ACM resulted in a particle size of 15–35 nm whose SEM shows the nanoparticles forming flakes. Optical properties are studied. A blue shift is observed where the band gap increases from 3.37 (bulk) to 3.62 eV. The increase in band gap is due to quantum confinement effect. CdO synthesized by ACM was of size 30–70 nm. The XRD pattern of CdO reveals NaCl structure.

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## 1. Introduction

Semiconductors have been attracting the attention of scientists and technologists due to the challenges they pose in exhibiting various desirable properties. When the bulk semiconductors go nano, they show remarkable changes in their properties especially in optical properties due to quantum confinement.<sup>1)–4)</sup> The size effect and quantum confinement energy and their influence on energy gap following the blue shifts have been the topics of interest.<sup>5)–8)</sup> The behavior of nano semiconductors has aroused the curiosity of many because of the variations in the particle sizes and morphology with different preparatory conditions and temperatures.<sup>9)</sup> The present paper discusses the salient observations on two important nano oxides, ZnO and CdO. ZnO is prepared using solid state reaction method with and without Cetyl Trimethyl Ammonium Bromide (CTAB). The later procedure was pursued at four different temperatures, 500, 600, 700, and 800°C. These observations are compared with nano ZnO prepared by aqueous chemical method. CdO prepared using aqueous chemical method is also reported.

## 2. Experimental procedure

### 2.1 ZnO: solid state reaction (SSR) method

Zinc acetate dehydrate, CTAB and Sodium hydroxide were used without further purification. The precursors were mixed (molar ratio 1:0.4:3) and ground together in an agate mortar for 50 minutes at room temperature. The reaction started immediately during the mixing process accompanied by the release of heat. The mixture was washed with distilled water in an ultrasonic bath at a frequency of about 200 KHz for half an hour. The so-obtained mixture was diluted in ethanol. Wet powder was then dried in air in a muffle furnace at the temperature of 600°C for 2 hours.

### 2.2 ZnO: SSR without CTAB at different temperatures

1:1 molar ratio of Zinc acetate dehydrate and Sodium hydroxide were used without further purification. The same experimental procedure discussed earlier was followed except for not adding CTAB. The wet powder was dried in air in a muffle furnace at different temperatures, 500, 600, 700, and 800°C.

## 3. Results and discussion

### 3.1 ZnO nanorods by SSR method with CTAB

The XRD pattern shown in **Fig. 1** can be indexed to hexagonal wurtzite structure with cell constants  $a = b = 3.2431 \pm 0.0021 \text{ \AA}$  and  $c = 5.1856 \pm 0.0068 \text{ \AA}$  in agreement with the report of Zhi-Peng et al.<sup>10)</sup> The FESEM of the nanorods is shown in **Fig. 2** revealing a kind of flowering arrangement of nanorods.

Optical absorption spectrum is shown in **Fig. 3**. It clearly shows a blue shift of ~25 nm from the bulk (362 nm). The band

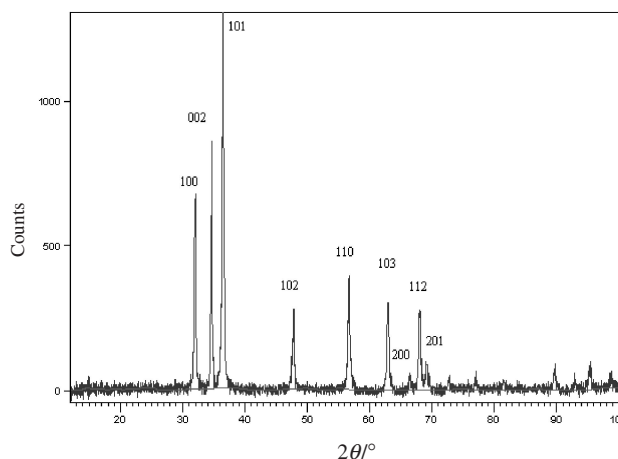


Fig. 1. XRD of nano ZnO.

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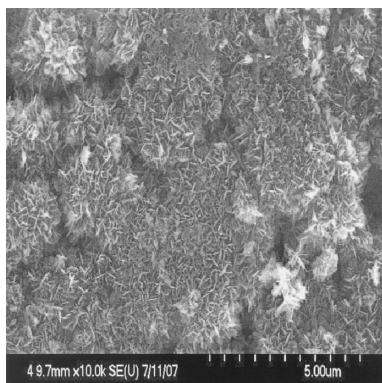


Fig. 2. FESEM image of ZnO (SSR with CTAB).

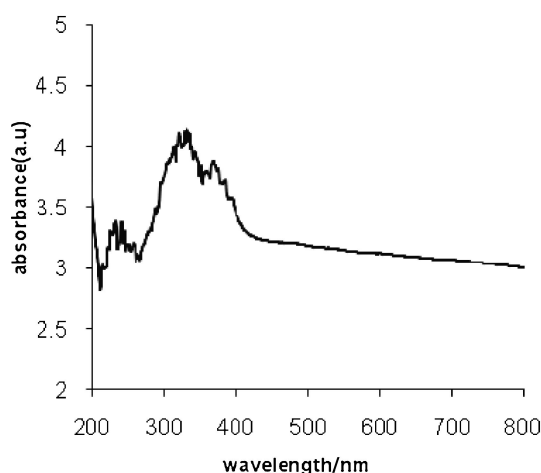


Fig. 3. UV-Vis spectrum of ZnO nanorod.

### PL Spectra of ZnO nanorods

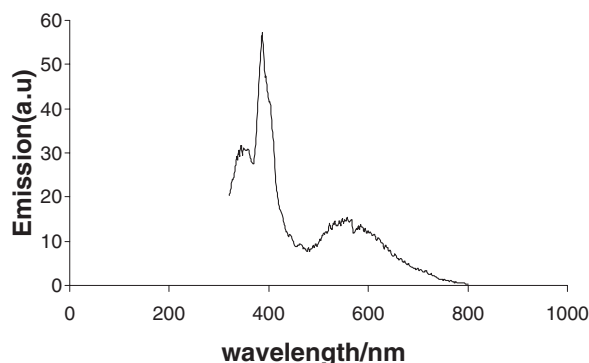


Fig. 4. Photoluminescence spectrum of ZnO nanorod.

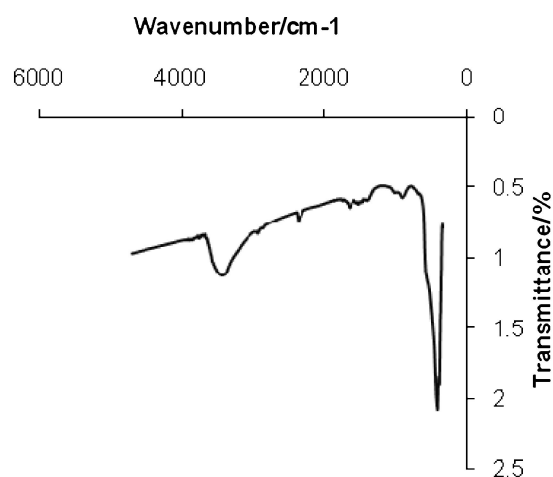


Fig. 5. FTIR spectrum of ZnO nanorod.

gap increases from 3.37 (bulk) to 3.62 eV due to quantum confinement effect. Photoluminescence spectrum of ZnO nanorod is shown in Fig. 4. It has two maxima which are typical for ZnO—a narrow intensive exciton peak at 388 nm and broad emission peak at 567 nm.

The strong emission is due to the exciton recombination related near band edge emission. It shows Stokes shift of 51 nm (0.43 eV). The emission peak at 567 nm is due to the single ionized oxygen vacancy in ZnO nanorods. This is also due to the recombination of a photon generated hole with a singly ionized charge of the oxygen vacancy. The FTIR spectrum of ZnO nanorods shown in Fig. 5 agrees well with the IR spectrum obtained by Zhijian Wang et al.<sup>11)</sup> using solid-state heat decomposition method at low temperature. The peak around 459 cm<sup>-1</sup> shows a distinct stretching mode of crystal ZnO.

### 3.2 ZnO nanorods by SSR method without CTAB

The XRD of nano ZnO by SSR method without CTAB at 500, 600, 700, and 800°C respectively is shown in Fig. 6. As the crystalline nature is observed at much lower temperature in SSR method (Fig. 1), we do not observe any significant change in the XRD pattern with change in temperature, though the tendency to increase in particle size is noticed which is in agreement with other reports using different methods of preparation.<sup>12),13)</sup> The particle size changes from 35 to 59 nm with rise in temperature in the range 500 to 800°C.

The SEM pictures at four temperatures are shown in Fig. 7. The SEM picture also reveals an increase in the particle size with increase in temperature. The surfactant, CTAB has played a role in development of nano rod morphology (Fig. 2) which is absent in Fig. 7. The FTIR is shown in Fig. 8. The Zn–O stretching is observed at 600 cm<sup>-1</sup>. Broadening of peaks is observed with an increase in temperature.

### 3.3 ZnO: aqueous chemical precipitation (ACP) method

The precursors used are zinc chloride and sodium hydroxide. The XRD pattern reveals hexagonal wurtzite structure with the lattice parameter comparable with the reported ones. The particle size was 15–35 nm using Scherer formula. The particles aggregate together and form nano flakes as seen from SEM shown in Fig. 9. FTIR spectrum showing strong absorption band between 500 and 450 cm<sup>-1</sup> can be attributed to the stretching modes of ZnO.

PL has a green band emission peak at 531 nm which is attributed to the radiative recombination of photo generated hole with an electron belonging to a singly ionized vacancy in the surface and subsurface. The blue shift observed in the ZnO nanostructures is due to size effect. The major difference between the two methods is in the resulting morphology of the nano particles.

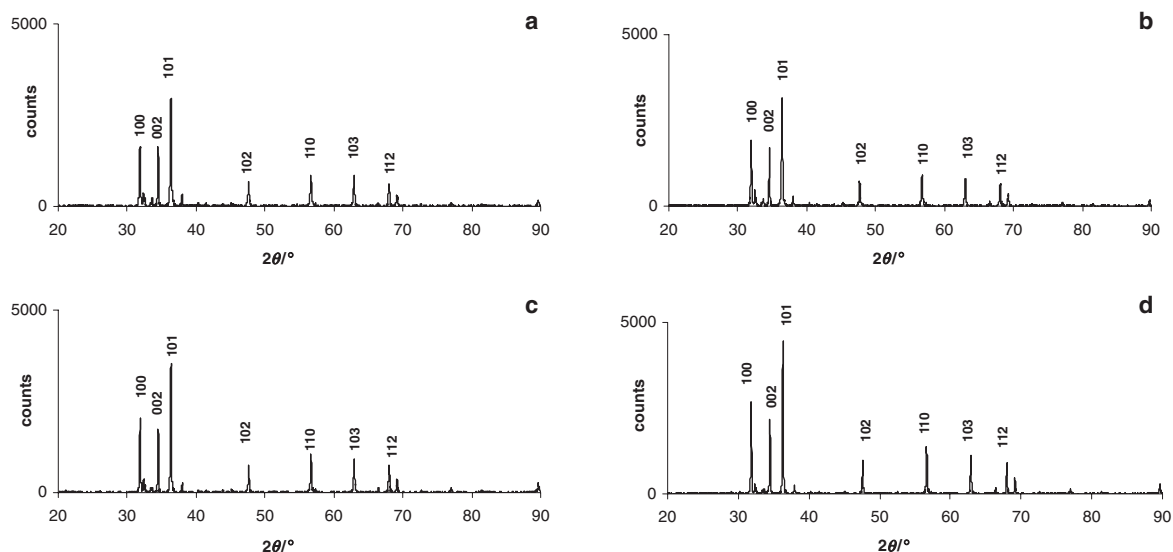


Fig. 6. XRD of ZnO at (a) 500, (b) 600, (c) 700, and (d) 800°C.

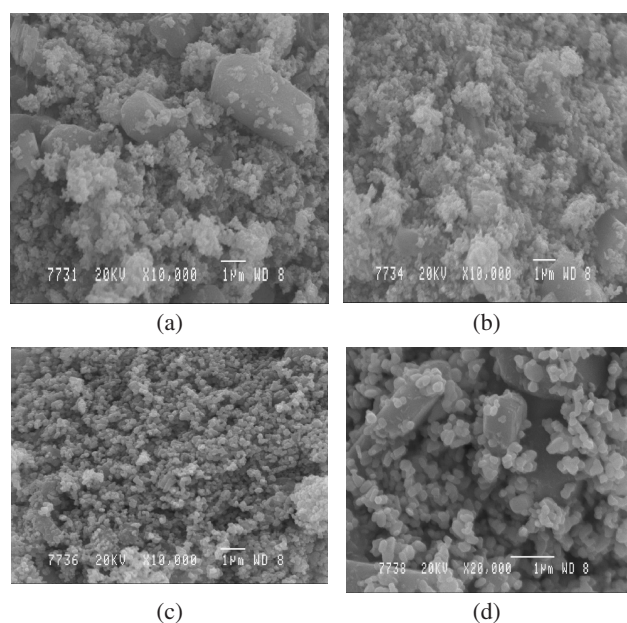


Fig. 7. SEM of ZnO (SSR with out CTAB) at (a) 500, (b) 600, (c) 700, and (d) 800°C.

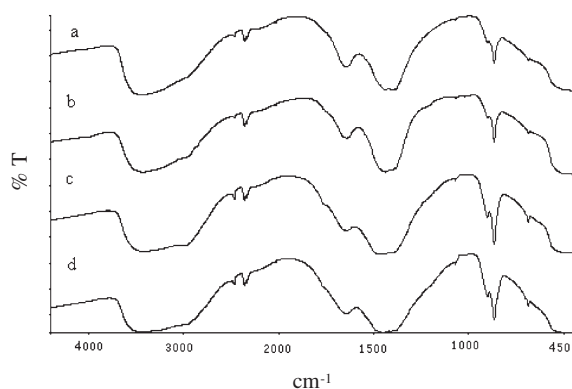


Fig. 8. FTIR of at (a) 500, (b) 600, (c) 700, and (d) 800°C.

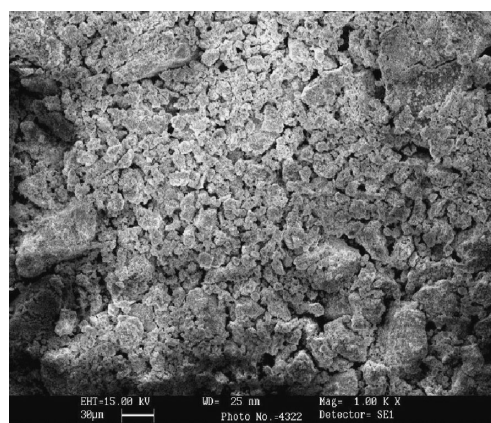


Fig. 9. SEM of ZnO (ACM).

#### 4. Nano CdO

Binary Oxides have distinctive properties and are now widely used as Transparent Conducting Oxide Materials (TCOS) and gas sensors.<sup>14),15)</sup> CdO is a direct band gap ( $\sim 2.3$  eV) semiconductor also reported as indirect compound with band gap of 1.98 eV. Due to its large linear refractive index ( $n_0 = 2.49$ ), it is a promising material for opto-electronic applications and other applications, including solar cells, phototransistors, photodiodes, transparent electrodes and gas sensors.<sup>16)</sup> Reduction in the dimensionality of such materials from the three Dimensional (3D) bulk phase to the zero Dimensional (0D) nanoparticles can lead to enhanced non linearity, determined by the quantum size effects and other mesoscopic effects. We report the results of CdO prepared using aqueous chemical method in the following session.

Aqueous solutions of Cadmium chloride hemipentahydrate ( $\text{CdCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$ ) and Sodium hydroxide (NaOH) were used. Precipitate was formed when the later was slowly added to the former while the mixture was stirred for 30 minutes at 50°C. Then the precipitate was washed several times using distilled water in the centrifugal and then dried in the temperature of 50°C.

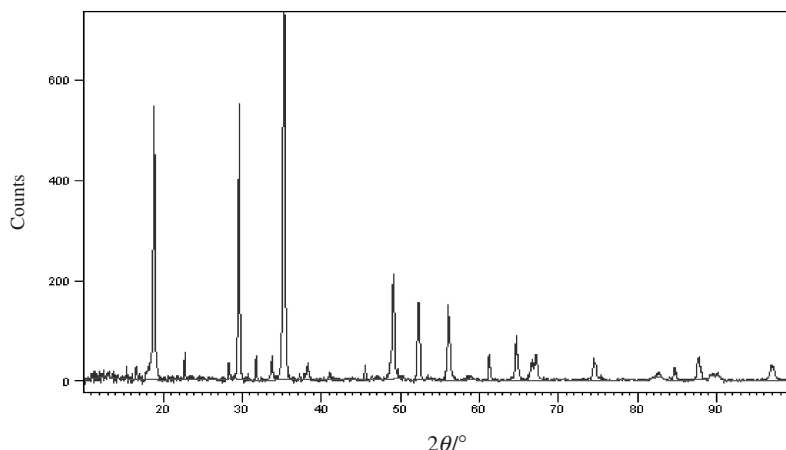


Fig. 10. XRD Pattern of CdO nanoparticles.

The structure and particle size analysis of CdO nanocrystals were pursued using powder X-ray diffraction. **Figure 10** shows the XRD pattern of CdO nanocrystals which reveals NaCl structure with six fine peaks having  $2\theta$  values equal to 18.904, 29.568, 35.293, 49.096, 52.328, and 56.171 degrees which is in agreement with that reported by Moumita Ghosh et al.<sup>17)</sup> The average particle size was estimated to be 35 nm using Debye–Scherrer formula.

## 5. Conclusion

ZnO prepared using solid state reaction method with and without the surfactant, CTAB and the later at four different temperatures, 500, 600, 700, and 800°C, and nano ZnO by aqueous chemical method is reported. We have successfully synthesized ZnO nanorods of band gap 3.62 eV by a rapid and low cost solid state reaction method. FESEM observation shows that the ZnO nanorods have diameters of about 20–30 nm and lengths of about 500 nm. The optical absorption spectrum shows a blue shift of ~25 nm in comparison with the bulk. The band gap of ZnO nanorod increases by 0.25 eV due to quantum confinement effect. The prepared nanorods show strong UV emission at 388 nm confirming an excellent optical property of ZnO nanorods. The nano ZnO synthesized by the same SSR method without CTAB reveals a different morphology as seen in the SEM pictures. Thus we conclude that the surfactant CTAB has played a role in developing rod like morphology. The SEM at four different temperatures 500, 600, 700, and 800°C shows increase in particle size which ranges from 35 to 59 nm. FTIR peak broadening with temperature is also observed. The ZnO synthesized by aqueous chemical method has particle size of 15–35 nm whose SEM shows the agglomeration of nanoparticles to form flakes. CdO synthesized by aqueous chemical method was of size 30–70 nm. The XRD pattern reveals NaCl structure. The optical spectra of nano particles are found to exhibit strong UV and PL and the peak positions are found to shift continuously towards lower wavelength side due to quantum confinement.

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