Luminescence and electrical resistivity properties of cadmium oxide nanoparticles

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Cadmium oxide (CdO) nanoparticles have been prepared by precipitation method using cadmium acetate and ammonia solution. The electrical resistivity ($\rho$) has been measured at low temperature using four-probe method which is found to be $0.351 \, \Omega \cdot \text{cm}$ at 7 K and $0.264 \, \Omega \cdot \text{cm}$ at 300 K, respectively. The decrease of resistivity with increasing temperature indicates the semiconducting behaviour. The activation energy values are found to be $0.06 \, \text{meV}$ in temperature range 7-15 K and $0.6 \, \text{meV}$ in 39-152 K from temperature dependent resistivity. Photoluminescence (PL) spectrum shows band edge emission at 395 nm and green emission at 550 nm. Green emission arises from the oxygen vacancy of CdO materials because of recombination of a photo generated hole in valence band with an electron in conduction band.

Keywords: Cadmium oxide, Resistivity, Photoluminescence, Nanoparticles

1 Introduction

Productions of mono disperse metal oxide nanoparticles have a special interest because it not only increases surface area, but also provides superior electrical conductivity as compared to other morphologies1,2. The brown CdO is, generally, formed by burning of Cd in air. The CdO is insoluble in water and absorbs CO$_2$ from air and can be reduced to the conducting oxides. It is one of the promising candidates for optoelectronics3. Cadmium oxide (CdO), a II-VI n-type semiconductor has interesting properties like large band gap, low electrical resistivity and high transmission in the visible region etc.; which makes it useful for a wide range of applications such as solar cells, photo transistors, photo diodes, transparent electrodes and gas sensors4-8.

CdO has 2.5 eV direct band gap9 and 1.98 eV indirect band gap10. The optical transmittance of CdO in the visible region of the spectrum has been reported to be low11. In the present paper, synthesis of CdO nanoparticles has been carried out and their photoluminescence and electrical resistivity properties have been studied.

2 Experimental Details

In the present work, we have synthesized cadmium oxide (CdO) nanoparticles by simple and low cost precipitation method using cadmium acetate and ammonium hydroxide as starting materials.

All chemicals used in the experiment were of analytic reagent (AR) grade. Cadmium acetate was purchased from Glaxo Smith Kline Pharmaceutical Ltd. (99.0%) and ammonia solution 25% GR from Merck, India. All chemicals were used as received without further purification. Deionized water was used during the experiment.

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During calcinations as prepared powder loses H$_2$O which is as follows:

$$400^\circ \text{C}$$

$$\text{Cd(OH)}_2 \longrightarrow \text{CdO} + \text{H}_2\text{O} \quad \cdots (2)$$
2.1 Characterization techniques

The powder X-ray diffraction (XRD) was recorded using Philips Holland, XRD system PW 1710 with nickel filtered CuKα (λ = 1.5405 Å) radiation. The average crystallite size (t) has been calculated from the line broadening using the Scherrer’s relation: 

\[ t = \frac{0.9\lambda}{B\cos\theta} \]

where, λ is the wavelength of X-ray and B is the half maximum line width. Scanning electron microscopy (SEM) was performed by JEOL JSM-5600 and the transmission electron microscopy (TEM) was performed with Tecnai 20 G under 200 kV. Samples were prepared by dispersing drop of colloid on copper grid, covered with the carbon film and the solvent was evaporated. To record Fourier Transform Infrared (FTIR) spectra, Bomem Hartmann and Braun MB Series Infrared spectrometer was used. CdO powder was crushed with KBr particles (1:5) and pressed into thin pellets. Photoluminescence (PL) measurements were performed by F-4500 FL spectrophotometer with 150 W xenon lamp at room temperature. Powder samples were spread over a glass slide and mounted inside the sample holder. The electrical resistivity of the sample (in the form of pellet) has been carried out using four probe method.

3 Results and Discussion

3.1 XRD study

XRD pattern of CdO nanoparticles calcined at 400°C is shown in Fig. 2. It confirms a face centered cubic (fcc) structure. Diffraction peaks observed were matched with standard JCPDS data (05-0640) and lattice parameters were calculated using the matched (hkl) values. The lattice parameters is found to be 

\[ a = 4.692 \text{ Å} \]

and unit cell volume \( V = 103.31 \text{ Å}^3 \). It is clear from Fig. 2, that all peaks corresponds to fcc structure of CdO and no any other impurity peaks are found, indicating high purity nature of the sample. The peaks are broad due to the nano-size effect. The average crystallite size of CdO nanoparticles is found to be 33 nm using Scherrr’s formula.

3.2 FT-IR study

Figure 3 shows IR spectrum of CdO nanoparticles heated at 400°C. There are O-H stretching (3450 cm\(^{-1}\)) and vibration (1660 cm\(^{-1}\)) bands in addition to Cd-O band. The broad peak at 620 cm\(^{-1}\) is attributed to CdO. O-H functional group is related to absorption of water during pellet formation.

3.3 Particle morphology study

Figure 4(a) shows SEM image of CdO nanoparticles heated at 400°C. It shows grain morphology. Some grains are small while some grains are larger. The shape of grain particles is spherical. Figure 4(b) shows TEM image of CdO nanoparticles.

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**Fig. 1 — Schematic diagram for preparation of CdO nanoparticles**

**Fig. 2 — (a) XRD pattern of CdO nanoparticles calcined at 400°C and (b) JCPDS file No. 05-0640**
Particle size from TEM is about 30 nm matched with the crystallite size (33 nm) indicating non-agglomeration of crystallites in a particle. Figure 4(c) shows the selected area electron diffraction (SAED) pattern of CdO nanoparticles calcined at 400°C. A cubic pattern of spots shows the highly crystalline nature of CdO.

3.4 Photoluminescence (PL) study

The room temperature photoluminescence spectra of CdO nanoparticles calcined at 400°C are shown in Fig. 5 after excitation at 250 nm. Three emission peaks are observed at 395 nm (violet), 469 nm (blue) and 550 nm (green) for CdO calcined at 400°C. The peak at 395 nm corresponds to the band-edge emission\(^\text{14}\). The peak at 469 nm is due to artifact. This arises because of Xenon lamp source. The peak at 550 nm arises from the oxygen vacancy of CdO materials because of recombination of a photo generated hole in valence band with an electron in conduction band\(^\text{15}\). Similar peaks in spectrum of CdO have been reported by Wu et al\(^\text{16,17}\).

Figure 6 shows excitation spectra of CdO particles heated at 400°C monitored at 420 nm. It is clearly observed that the band-edge absorption is found at 221 nm (3.4 eV), which is larger than the bulk\(^\text{18}\) CdO (2.5 eV).

3.5 Electrical resistivity measurement

Figure 7 shows the variation of resistivity with temperature in the range 7-300K. Resistivity is temperature dependent. The resistivity values at 7 and 300 K are found to be 0.351 and 0.264 Ω-cm, respectively. Choi et al.\(^\text{19}\) reported high resistivity of CdO (10\(^3\) Ω-cm) at room temperature. The resistivity decreases with increasing temperature due to increase of electron carriers.
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Fig. 6 — Excitation spectrum of CdO monitored at 420 nm emission

Fig. 7 — Variation of resistivity ($\rho$) with temperature (7-300 K) and fit to data of CdO using Arrhenius law is also drawn. Inset shows the $\rho$ versus $T^{-1}$

The temperature coefficient of resistivity (TCR) value for CdO is calculated using the relation:

$$ TCR = \frac{1}{\rho_{250}} \left( \frac{\Delta \rho}{\Delta T} \right) $$

It is found to be $-0.0377 \, K^{-1}$ and it is negative. This indicates that the prepared sample is behaving as semiconductor\textsuperscript{20-24}. Activation energy ($E_a$) of CdO nanoparticles is calculated using the equation:

$$ \rho = \rho_0 \exp \left( \frac{E_a}{kT} \right) $$

where $\rho$ is resistivity, $\rho_0$ is a parameter, $k$ is Boltzmann’s constant and $T$ is absolute temperature. Fitting to the data is not good using the Eq. (4). Then, we have plotted $\ln \rho$ versus $1/T$, which is shown as inset of Fig. 7. We found two slopes in range 7-15 K and 39-152 K. The former slope gives $E_a = 0.06 \, meV$ and the latter one gives $E_a = 0.6 \, meV$.

4 Conclusions

Face centered cubic structure CdO nanoparticles of average size of 33 nm is synthesized. The green emission at 530 nm is observed due to oxygen vacancy of CdO materials because of recombination of a photo generated hole in valence band with an electron in conduction band. The band-edge absorption is found at 221 nm (3.4 eV). The resistivity of CdO is found to be very low $0.351 \, \Omega \cdot cm$ at 7 K while it is $0.264 \, \Omega \cdot cm$ at 300 K. Two different activation energy values at different temperature ranges are obtained.

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