Morphology-dependent space charge polarization and dielectric relaxation of CdO nanomorphotypes

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A versatile approach signifying the morphology-dependent dielectric polarization and relaxation mechanisms of cadmium oxide (CdO) nanosphere, nanoflakes and nanoparallelepiped morphotypes as a function of frequency and temperature is presented. Variation of dielectric property is observed due to the changes of space charge/interfacial polarization resulting from the variations of surface to volume ratio of nanomorphology. Accordingly, colossal dielectric constant value has been observed in CdO nanosphere having larger surface to volume ratio. The order of dielectric constant (dc) values observed for the present nanomorphologies is: dc of sphere > dc of flakes > dc of parallelepiped resembles the order of surface to volume ratios of the present morphologies respectively. The experimental data of complex impedance values are numerically fitted using theoretical models which provide the information of role of grain resistance on dielectric polarization and Cole–Cole type mechanism of dielectric relaxation process. The activation energies for electron transport are found to be 0.087 eV for spheres, 0.074 eV for flakes and 0.067 for parallelepiped nanomorphotypes of CdO. The dielectric and impedance spectroscopic analysis of the present material opens up wide scope for morphology-dependent tuning of nanomaterials for electrical applications.

Keywords: CdO nanomorphotype; space charge polarization; impedance spectroscopy; Cole–Cole dielectric relaxation.

1. Introduction

In the recent years dielectric properties of metal oxide semiconductor nanomaterials have caught additional attention because of its high dielectric constant values at nanosize range. The large surfaces to volume ratio and quantum confinement effect have altered dielectric and conductivity behavior of nanomaterials much compared with its bulk materials. In addition, researchers generally believe that the morphology of nanomaterials is an important parameter for modifying the entire physical properties like optical, electrical, magnetic and nonlinear behavior. Over the past decades many researchers have satisfactorily examined electrical transport and dielectric behavior of semiconductor metal oxide nanomaterials with various parameters including temperature, particle size, structural defects, effect of pH, doping, etc. Liao *et al.* presented the surface state effect on electron transport in individual ZnO nanowires and confirm that the surface states have greatly affected the electronic transport in single ZnO nanowires.¹ Dang and co-workers examined the dielectric properties and morphologies of composites filled with whisker and nanosized ZnO.² They claim that dielectric constant and losses increase with increasing w-ZnO content in composites. Suresh conducted the study of dielectric relaxation behavior of CdS nanoparticles and found that dielectric properties of CdS nanoparticles significantly enhanced specially in the low frequency range due to confinement.³ Velayutham *et al.* presented the theoretical and

experimental approach on dielectric properties of ZnO nanoparticles and polyurethane/ZnO nanocomposites.⁴ El-Sayed and co-workers carried out a study on synthesis, characterization, optical and dielectric properties of polyvinyl chloride/Cadmium oxide (CdO) nanocomposite films.⁵ They concluded that optical and dielectric properties are reinforced by adding the CdO nanoparticles in PVC matrix. Tripathi *et al.* studied the dielectric relaxation and ac conductivity mechanism of CdO nanoparticles recently and suggests that the electron transport mechanism obeys the universal power law.³¹ Out of these important literatures, we observe that very little studies are carried out to dig out the dielectric property of CdO semiconductor nanomaterial.

CdO is an n-type IIB-VIA, semiconductor metal oxide with direct bandgap of 2.5 eV and indirect bandgap of 1.98 eV.^{6,7} Recently many researchers have shown interest on synthesis of CdO nanomaterials especially in diverse morphotypes, because of its potential applications in electronic storage devices, optoelectronics, gas sensing, solar cells and flat panel displays.^{8–11} However, no report is observed on the study of dielectric properties of nanostructures as a function of different morphologies. In the present study, electrical property of three different morphologies of CdO (sphere, flakes and parallelepiped) nanostructures are compared and concluded that the morphology is a parameter that have control over electrical properties of materials. In addition to this we have employed the impedance spectroscopy to determine the

electrical resistance of electrode, grain and grain boundary and confirm which of them is responsible for dielectric polarization process and also analyze the dielectric relaxation mechanism. To the best of our understanding this is the first ever made report to study the dependence of dielectric property of CdO nanostructure on surface morphologies.

2. Experimental Procedure

2.1. Synthesis of CdO nanomorphotypes

We have already reported the chemical synthesis route and growth mechanism for fabricating CdO nanomorphotypes through chemical precipitation and hydrothermal method using $(\text{CH}_3\text{COO})\text{Cd}\cdot 2\text{H}_2\text{O}$ and NaOH as starting materials.¹⁴ In brief, the chemical precipitation method is used for synthesizing the spherical nanomorphotype. The solutions of reactants in double distilled water are prepared in 1:1 ratio. NaOH solution is added to $(\text{CH}_3\text{COO})\text{Cd}\cdot 2\text{H}_2\text{O}$ solution dropwise with constant stirring using a magnetic stirrer for 30 min. By the addition of NaOH, a milky turbid solution is formed due to the precipitation of $\text{Cd}(\text{OH})_2$ spherical precursor nanostructure. The flake and parallelepiped morphotypes have been prepared by hydrothermal method. A specific amount of capping agent $\text{C}_6\text{H}_{15}\text{NO}_3$ (TEA), is added (1 mL per 100 mL solvent) to the same precursor solution and the mixture is poured into a Teflon lined stainless steel autoclave. It is then heated at 200°C for 8 and 24 h for the formation of $\text{Cd}(\text{OH})_2$ nanoflakes and $\text{Cd}(\text{OH})_2$ parallelepiped precursor nanostructures, respectively. At the end of chemical precipitation and hydrothermal treatment, white precursors are obtained which are then dried at 60°C for 4 h. The yellowish colored CdO nanomorphotypes are obtained by annealing the precursors at 500°C for 5 h in air. The variation of morphologies at various stages of synthesis is shown with the help of transmission electron microscope images presented in Fig. 1.

2.2. Analysis techniques

The crystal structure (X-ray diffraction analysis- Bruker AXS D8 Advance with X-ray source Cu $\text{K}\alpha 1$, Wavelength $1.5406 \text{ \AA}$), BET surface area analysis (Micromeritics Gemini 2375 V5.01, USA), Sample morphologies and size dimensions (high resolution transmission electron microscope- JEM-2100, 200 Kv, Jeol) and the fundamental optical bandgap (optical reflection spectroscopy-T90+UV/Vis spectrometer) are already reported in our recent publication.¹⁴ For electrical analysis, the prepared powder samples are pelletized at a pressure of 2.5 tons for 5 min using a KBr hydraulic press. The pellet is then sintered at temperature of 400°C for 10 h for densification to avoid the voids/air traps between the grains/grain boundaries. The disc shaped pellet has a radius of 0.65 cm and thickness of 0.18 cm. The density of sintered pellet is 8.49 g/cm^3 which is much closer to the density 8.15 g/cm^3 of crystalline CdO material. When the pellets are prepared by pressing powdered sample using hydraulic press, there are chances to form many voids or air gaps within the pellet. Such air gaps can affect the measurements of electrical/dielectric properties of the material. The sintering process reduces the air gaps or voids inside the pellet and the pellet becomes highly dense. The higher density of the pellet is due to sintering and close packing of nanoparticles.^{32,33} Silver paste is coated on both sides of the pellet for creating better contact between the pellet and the electrodes. The pellets are placed in a furnace for determining the effect of dielectric property on temperatures. The dielectric and impedance spectrum measurements are carried out using HIOKI 3532-50 LCR HiTESTER instrument having frequency range 50 Hz to 5 MHz.

The XRD spectra¹⁴ given in Fig. 2(I) shows that the diffraction peaks of the samples are very sharp and highly intense which reveals the well-defined crystalline nature and phase purity of the prepared nanostructures. The diffraction pattern of CdO at (111), (200), (220), (311) and (222) planes

Fig. 1. Transmission electron microscope images of CdO nanomorphotypes annealed at 500°C for 5 h in air: (a) nanosphere, (b) nanoflakes and (c) nanoperallelepiped morphologies, respectively.

Fig. 2. (I) XRD pattern of CdO: (a) sphere, (b) flakes, (c) parallelepiped. (II) BET (isothermal curve) surface area analysis of CdO nanomorphotype.

Table 1. Parameters obtained from BET surface area analysis.

	Sphere	Flakes	Parallelepiped
Single point surface area (m^2/g)	12.3464	9.2851	7.6702
BET surface area (m^2/g)	12.5955	9.5109	7.7606
Langmuir surface area (m^2/g)	20.4812	15.5189	12.5074
Micropore area (m^2/g)	0.6818	0.2945	0.8439
External surface area (m^2/g)	11.9137	9.2165	6.9167
Micropore volume (cm^3/g)	0.000233	0.000055	0.000380
BJH adsorption average pore diameter (Å)	74.0469	67.1888	76.9408

match well with the JCPDS card No. 05-0640 of CdO having lattice constant $a = 4.695 \text{ \AA}$. The BET spectra¹⁴ given in Fig. 2(II) indicates that the surface area is maximum in the case of spherical shape and that the surface area of flakes structure is in between spherical and parallelepiped nanostructures. The surface area measurements¹⁴ are given in Table 1. The BET surface area analysis of the materials confirm the morphology-dependent variation of nanostructures surface area.

3. Results and Discussion

3.1. Dielectric polarization and relaxation

A dielectric material is made up of large number of atoms/molecules that possess different types of electric polarizations such as electronic, atomic/ionic, dipolar, orientational or hopping and space charge polarizations. The space charge, orientational and atomic/ionic polarizations are significant only in low frequency AC field, whereas electronic polarizations are more significant in high frequency AC field.¹⁵ Therefore in the present study we analyze the dielectric property of CdO nanostructure as functions of frequency and temperature. The frequency-dependent dielectric constant and loss factor ($\tan \delta$) at room temperature and temperature-dependent dielectric constant at 55 Hz and 100 kHz are represented in Fig. 3. It is noteworthy that the observed dielectric value of CdO nanosphere is about 6530 whereas the

dielectric constant of bulk CdO is about 21.¹² As the dielectric constant $\epsilon_r > 10^3$ is termed as Colossal,¹³ the value of dielectric constant obtained for CdO spherical nanomorphotype can be termed as colossal. The colossal value of room temperature dielectric constant of CdO nanostructures has never been reported earlier. Meanwhile, for each morphology, $\tan \delta$ exhibit clear loss peaks corresponding to the frequency at which dielectric constant is maximum. The larger value of dielectric constant and loss factor in CdO spherical morphology is due to the larger surface to volume ratio of the spherical shapes. In the present study, we are attempting to elucidate the dependency of dielectric polarization and relaxation of CdO nanostructures on the surface morphology based on dielectric measurement and BET surface area analysis (Fig. 2(II)).¹⁴ We have also reported on theoretical and experimental grounds that spherical nanomorphology have maximum surface to volume ratio compared to that of CdO flakes and parallelepiped morphology.¹⁴ In addition to this we have evidently proved that the size dimension of CdO nanomorphotypes increases as morphology changes from spherical to flakes and to parallelepiped shape whereas, the surface to volume ratios decreases with increase in particle size dimensions.¹⁴ The exact reason for change in the dielectric constant behavior with morphology is not clearly understood. However, we explain the dependency of morphology on dielectric behavior of nanomaterials on the basis of particle size dimension as well as surface to volume ratios. For a spherical nanostructure, the general relation for the ratio between surface area to volume (S/V) is $3/R$ (i.e., $3:R$) and for parallelepiped structure, it is $6/L$ (i.e., $6:L$) where R and L are particle size dimensions for spherical and parallelepiped nanostructures, respectively. In the present case nanosphere has lesser size than the remaining morphologies.¹⁴ Hence, the nanospheres possess maximum surface to volume ratio. Since nanoflakes are similar to parallelepiped shape with one of the dimensions very small, their surface to volume ratio will lie between that of nanosphere and nanoparallelepiped structures. BET analysis also confirms that the surface to volume ratio of flakes is in between that of sphere and parallelepiped nanostructures. Because of small size of

Fig. 3. (I) and (II) Frequency-dependent dielectric constant (ϵ_r) and loss factor ($\tan \delta$) respectively at room temperature. (III) and (IV) Temperature-dependent dielectric constant at 55 Hz and 100 kHz, respectively.

the nanoparticles, more charge carriers reach the surface of the particles.^{34–36} Accordingly, due to the higher surface to volume ratio, there is maximum density of the distribution of charges on the surface of spherical nanostructures. Hence, stronger size selective surface charge effect is possible in spherical morphotypes than that of flake and parallelepiped structures. Consequently, the higher surface charge density creates higher surface charge polarization in the nanosphere compared to other cases. Hence, dielectric constant of nanosphere must be larger than the other morphologies of the present material. It is evident from the measurements that dielectric constant of parallelepiped morphotype shows almost same nature as that of dielectric value of CdO bulk material whereas the dielectric constant of flakes appears in between that of sphere and parallelepiped nanostructure. Similar morphology-dependent optical, surface plasmons, catalytic activity and electrical behaviors are seen in literatures.^{37–39}

The dielectric constant of CdO morphotypes as a function of temperature at 55 Hz and 100 kHz are shown in Figs. 3(III) and 3(IV), respectively. In the case of all morphologies the dielectric constant value increases with temperature. The increment of dielectric constant with increase in temperature is due to the temperature-dependent dielectric polarization of nanoparticles. In all these results the dielectric constant of spherical CdO morphotype has relatively higher value compared to other morphotypes. The order of the dielectric constants obtained is: dielectric constant (d.c.) of nanosphere > d.c. of nanoflake > d.c. of nanoparallelepiped. Hence it could be robustly concluded that the dielectric constant of CdO nanostructures are significantly dependent on the

morphology. The morphology-dependent dielectric analysis in the present study strongly agrees to our previous report on morphology-dependent nonlinear optical behavior of CdO nanomorphotype.¹⁴ Moreover based on the observed dielectric constant values, the CdO spherical morphology is a good candidate for using in the energy storage devices.

3.2. The complex impedance spectrum

The impedance spectroscopy shows the frequency dependence of real part (Z') and imaginary part (Z'') of the impedance. The complex impedance spectrum of the present study helps us to reconfirm the picture of morphology-dependent dielectric behavior of the present material. It shows the dielectric polarization/relaxation mechanism and contribution of electrode, grain or grain boundary resistance to the dielectric property of CdO nanomorphotypes.^{16–18} Generally, the dielectric polarizations can be grouped into two: the polarization in resonance region and the polarization in relaxation region.¹⁹ The polarization associated with vibration of electrons or vibration of atoms/ions belongs to resonance region because resonances will occur when the frequency of excited field is close to the natural frequency of oscillation system. Polarizations by orientational polarization or hopping and space charge polarization belong to the relaxation region. The relaxation phenomena occur only when the time required for the charge carriers to overcome the inertia is available. The Cole–Cole (Z' versus Z'' with frequency) plot of CdO nanosphere, nanoflakes and nanoparallelepiped morphologies at 30 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$, 150 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$ are given in Figs. 4(a)–4(c), respectively. The impedance

Fig. 4. The complex impedance spectrum: (a) nanosphere, (b) nanoflakes and (c) nanoparallelepiped shapes, respectively. (d) R-CPE equivalent circuit. (The dotted line indicates experimental data points and solid line indicates numerical fitting to the experimental data point by equivalent circuit).

analysis of crystalline materials can be explained by fitting the experimental data of impedance value to an equivalent circuit model consisting of a parallel combination of an ohmic resistor R and a capacitor C . The Nyquist (Cole–Cole plot) diagram of such a circuit gives one to three semicircular plots. Usually the diameter of low frequency side arc (high Z') represents the electrode resistance (R). The next arc gives the grain resistance and the high frequency side arc gives the grain boundary resistance. However, in some cases the experimental data show a deviation from this simple R – C behavior and the diagram need not be a semicircle plot. In such cases, we can generally use parallel R-CPE equivalent circuit instead of parallel R – C circuit.^{20,21}

For the present impedance spectra, the experimental data are fitted to an equivalent circuit consisting of a resistor and a constant phase element (CPE) instead of a capacitor having capacitance C . The proposed equivalent circuit used for simulating the experimental data in the present work is shown in Fig. 4(d).²⁶ Here the total impedance is given by the relation^{23–26}

$$Z^* = \left(\frac{1}{R} + \frac{1}{Z_{CPE}} \right)^{-1}, \quad (1)$$

where $Z_{CPE} = Q(i\omega)^n$, i is the imaginary unit, Q is the pre-factor for CPE and n is its exponent. The exponent n of CPE varies from 0 to 1. $n=1$ defines the impedance of ideal capacitor. $n < 1$ shows the departure from the ideal capacitor behavior, commonly known as Cole–Cole type relaxation behavior of dielectric materials.

$$Z' = \frac{R(1 + RQ\omega^n \cos(n\pi/2))}{1 + 2RQ\omega^n \cos(n\pi/2) + (RQ\omega^n)^2} \quad (2)$$

and

$$Z'' = -\frac{R^2 Q \omega^n \sin(n\pi/2)}{1 + 2RQ\omega^n \cos(n\pi/2) + (RQ\omega^n)^2}. \quad (3)$$

According to the above relations, the real capacitance can be calculated by the relation

$$C = R^{(1-n/n)} Q^{(1/n)}. \quad (4)$$

The impedance spectrum (Figs. 4(a)–4(c)) shows that at all temperatures Z' versus Z'' curve appears like a ‘depressed single semicircle’, indicating the contribution of grain resistance R_g and grain capacitance C_g in dielectric polarization of the nanomaterials. In other words, the diameter of these depressed semicircular arcs represents the resistance (in $k\Omega$ range) contributed by the grain resistance.^{27,28}

Table 2. The grain parameters of CdO nanomorphotype by numerical fit to the experimental data points.

Sphere	$R_g(\Omega)$	$C_g(F)$	$\sigma_g(S/cm)$	$\tau_g(s)$	'n' values
30°C	9.48×10^6	3.93×10^{-11}	9.54×10^{-7}	3.73×10^{-4}	0.78
100°C	4.84×10^6	4.37×10^{-11}	1.87×10^{-6}	2.12×10^{-4}	0.73
150°C	2.33×10^6	4.58×10^{-11}	3.88×10^{-6}	1.07×10^{-4}	0.69
200°C	1.10×10^6	5.89×10^{-11}	8.22×10^{-6}	6.48×10^{-5}	0.63
Flakes					
30°C	2.99×10^6	2.54×10^{-11}	3.03×10^{-6}	7.59×10^{-5}	0.76
100°C	3.05×10^6	2.93×10^{-11}	2.97×10^{-6}	8.94×10^{-5}	0.71
150°C	1.12×10^6	4.69×10^{-11}	8.08×10^{-6}	5.25×10^{-5}	0.68
200°C	2.39×10^5	8.99×10^{-11}	3.78×10^{-5}	2.15×10^{-5}	0.63
Parallelepiped					
30°C	7.24×10^5	2.34×10^{-11}	1.25×10^{-5}	1.69×10^{-5}	0.69
100°C	2.38×10^5	2.48×10^{-11}	3.80×10^{-5}	5.90×10^{-6}	0.64
150°C	9.58×10^4	2.99×10^{-11}	9.44×10^{-5}	2.86×10^{-6}	0.59
200°C	4.35×10^4	3.45×10^{-11}	2.08×10^{-4}	1.50×10^{-6}	0.54

The value of R_g is obtained from the diameter of impedance semicircle on X-axis. The mean relaxation time is obtained from the relation $\tau_g = R_g C_g$,²¹ which is the inverse of the most intense frequency ω_g of the impedance spectrum. The electrical parameters of CdO nanomorphotypes obtained by fitting the experimental data to the equivalent circuit are reported in Table 2. The resistances obtained in all temperatures are due to grain response which also indicates the polycrystalline nature of the prepared material.

It is noticed from Table 2, that the grain interior resistance and relaxation time are decreased with corresponding increment in temperatures. The variations of fitted n values and relaxation time for different temperatures are evidences for Cole–Cole type relaxation mechanism in CdO nanomorphotypes or the departure from Debye behavior, which is further supported by Fig. 5. In Fig. 5, the relaxation frequency is shifted with respect to increase in temperature which is the sign or evidence of the Cole–Cole type relaxation mechanism in dielectric materials.²³

The activation energy of CdO nanomorphotypes are calculated by fitting the data through Arrhenius equation^{29,30}

$$\sigma_g = \sigma_0 e^{(E_a/k_B T)}, \quad (5)$$

where E_a is the activation energy for conduction. The activation energy is the energy required for a material to once start the conduction process which mainly depends on temperature, size and shape of the nanomaterial.³¹

In Fig. 6, the conductivity values (corresponding to the temperature-dependent resistance values) are plotted against $1000/T$. The values of activation energy of grain response for CdO nanomorphotypes are calculated from the slope of the conductivity versus $1000/T$ curve and are of the order of 0.087 eV for sphere, 0.074 eV for flakes and 0.067 eV for

parallelepiped nanomorphotypes. In the present context, the activation energy can be explained as the minimum energy required for a material to start up the electrical transport mechanism. It is activated by thermal and electrical process. Dielectric semiconductor materials with high activation energy indicate that the material is more resistive against electron transport and also have high dielectric polarization/dielectric constant value.^{40–43}

As the resistance increase, the high dielectric polarization energy in the materials gets dissipated in the form of heat which causes large dielectric loss values in the material. In the present study, the higher activation energy in spherical morphology is due to its large grain resistance and dielectric loss values over flakes and parallelepiped morphotypes. It may be noted that the impedance spectroscopic studies given above show larger grain resistance for spherical morphology. Therefore, the calculated activation energy also supports our claim for morphology-dependent dielectric properties for CdO nanomorphotypes. Hence we strongly conclude that the dielectric relaxation time and grain interior resistance value obtained from impedance spectroscopic analysis also supports our claim of morphology-dependent electric polarization. As observed in Table 2, R_g value is highest for spherical morphology which decreases with increase in temperature in all morphologies.

The σ_g value is lowest for spherical morphology which increases with increment of temperature in all cases. Similarly, the relaxation time τ_g is highest for spherical morphology which decreases with increment of temperature in all cases. All these electrical parameters of CdO nanomorphotypes obtained by fitting the experimental data to Eq. (4) also suggest that the dielectric constant of CdO morphotypes depends strongly on morphology.

Fig. 5. Z'' versus frequency plot of CdO nanomorphotypes: (a) sphere, (b) flakes and (c) parallelepiped.

Fig. 6. Arrhenius plots of grain conductivity (σ_g (S/cm)) data: (a) sphere, (b) flakes and (c) parallelepiped nanomorphotype.

4. Conclusions

In summary, we have evidently proved that the dielectric polarization and relaxation of CdO nanosphere, nanoflakes and nanoparallelepiped morphotypes are dependent on morphology. As the spherical nanomorphotypes has the maximum surface to volume ratio and surface area, the surface charge is maximum in it. Consequently the maximum surface/space charge polarization takes place in spherical nanomorphotype. The order of the dielectric constants obtained is: dielectric constant (d.c.) of nanosphere > d.c. of nanoflakes > d.c. of nanoparallelepiped. It is to be noted that

the surface area of these morphotypes are also in the same order. The order of dielectric relaxation time and grain resistance values obtained from impedance spectroscopy are also in the same order. Therefore, the dielectric relaxation time and grain interior resistance value obtained from impedance spectroscopic analysis also strongly supports our claim of morphology-dependent electric polarization. The dielectric relaxation analysis suggests that the Cole-Cole relaxation mechanism is valid in the CdO morphotypes. The electrical study indicates that spherical CdO spherical nanomorphotype can be used as potential material candidate for new era of energy storage electronic devices.

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