

Synthesis, structural, morphological, functional, optical and particle size enhanced cadmium oxide nanoparticles on electro-chemical applications

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The co-precipitation technique of cadmium oxide (CdO) nanoparticles in aqueous solutions at high temperatures was employed in this investigation. The potential for electrochemical activity was studied. Thus, a powder X-ray diffractometer was used to quantitatively evaluate the Scherer-calculated crystallite grain size and dislocation density. Scanning electron microscopy imaging and analysis revealed the distinct shape and structure of CdO nanoparticles. The above-mentioned nanoparticles were sorted into their respective functional groups by FTIR spectroscopy. The CdO nanoparticle size was measured in the nanometre range using a dilution-based particle size analyzer. There was a significant improvement in the CdO nanoparticles' ability to absorb UV-visible light. Their unique colours of light were made visible in the spectrum of their fluorescence emission, which allowed them to be clearly authenticated. An electrochemical probe into the phenomenon of super capacitance has revealed its fundamental characteristics. This CdO nanomaterial might be useful for scientific investigation.

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1. Introduction

The nanoscale range is a novel and continually growing field that involves the industrial processing and application of structures, electronics, and systems via the manipulation of the structures' shape and size. The nanoscale range has a length scale of less than one hundred nanometres. Large surface area, high crystallinity, chemical purity, and phase selectivity [1] are just a few of the characteristics that distinguish metal oxide nanoparticles from their bulk counterparts and explain why they have piqued the interest of many popular works throughout their synthesis. Title nanoparticles of CdO have an excellent linear refractive index ($n_o = 2.49$), a small optical band gap ($E_g = 2.5$ eV), high conductivity ($103 \text{ ohm}^{-1} \text{ cm}^{-1}$), and strong carrier mobility ($142 \text{ cm}^2/\text{Vs}$). Among the numerous applications for this material are solar cells, photo transistors, transparent electrodes, catalytic gases, chemical sensors, and lattice panel displays. Due to their low electrical resistance and optical transmittance in the visible region of the solar spectrum [2-3] given that cadmium oxide (CdO) is both a semiconductor and a piezoelectric, it is also an essential material. CdO is unique among semiconductors due to its low band gap energy of 4.05 eV and high exciton binding energy of 75 meV [4]. Physical properties suggest that cadmium oxide (CdO) nanoparticles might function as a densifying agent of the microstructure, leading to reduced porosity [5, 6]. Cadmium (Cd) nanoparticles, according to their high reactivity, may react with the calcium hydroxide generated by the hydration of calcium silicates, prompting the cement hydration process even more. It happens because the surface area is proportional to the response rate [7]. It has been postulated that various distinct chemical techniques may be used to synthesise cadmium oxide nanostructures (CdO). Physical and chemical methods for the synthesis of CdO have been reported by a limited number of research groups, including the hydrothermal procedure, sol-gel technique, simple synthesis, and microwave-assisted synthesis methodology. The chemical

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co-precipitation method, on the other hand, is illustrative of the synthesised methods since it offers a greater variety of practical benefits. This method was performed at low temperatures without the need for complex or expensive equipment [8]. Nanotechnology has allowed for the production of CdO in a variety of interesting forms, including rhombuses, nanosticks, nanoclusters, nanocrystals, nanowires, nanoparticles, and nanocubes [9]. In this case, CdO nanoparticles were synthesised using a co-precipitation technique. To produce the appropriate CdO nanostructures, it is essential to strike a balance between the amount and rate of addition of cadmium nitrate and sodium hydroxide throughout the synthesis process. After the nanoparticles were synthesised, they were analysed for their structural, morphological, functional, and optical properties using techniques like X-ray diffraction, Scanning electron microscopy, Fourier transforms infrared spectroscopy, Ultraviolet-visible spectroscopy, Vibrating sample Magnetometer, Fluorescence spectroscopy, and Particle size analyses. The present work aimed to prove that synthesised nanoparticles in a more malleable material had better electrochemical activity, with the ultimate goal of building a cheap and significant super capacitor.

2. Experimental

2.1. Synthesis

Producing cadmium oxide (CdO) nanoparticles using the co-precipitation method requires stoichiometrically combining highly pure cadmium nitrate [$\text{Cd}(\text{NO}_3)_2$] with sodium hydroxide pellets (NaOH) in deionized water. The first step included establishing a stoichiometric ratio of 1:1 by dissolving cadmium nitrate in a beaker using deionized water and sodium hydroxide pellets in a beaker of deionized water. It's possible that both solutions will maintain the pH value during their application. After six hours of sprinkling, the solutions were filtered, and the NaOH solution was added to the Cadmium Nitrate solution, drop by drop, until the two were well mixed and a precipitate developed, mostly due to the pellet of the magnetic stirrer. The white precipitate that formed was washed many times with deionized water and ethanol to remove any remaining unreacted compounds, then filtered and dried in an oven at 70 °C. After 3 hours of drying in a muffle furnace at 550 °C, the cadmium hydroxide precipitate was powdered using an agate mortar. Therefore, the powder we received was of Nano size. Making nano-sized CdO and colouring it brown allowed for further study.

2.2. Material Characterization

To get the powder XRD data, we used a MAC Science MXP18 diffractometer, irradiated the sample with $\text{CuK}\alpha$ radiation ($\lambda = 1.5405$) at 40 kV and 30 mA, and scanned the sample at a rate of 2 to 4 min^{-1} . The morphology of cadmium oxide nanoparticles' surfaces was studied using a scanning electron microscope operating at 10 kV (JSM-6330TF). Fourier transform interferometry could enable for vibrational absorption. To capture nanoparticles, a SHIMADZU Spectrophotometer was used in conjunction with the KBr pellet technique, which records wavenumbers from 4000 cm^{-1} to 400 cm^{-1} . With a molecular weight sensitivity of as low as 250 Da, the Nano plus Particle Size Analyser with Dilution Method may be used to measure the size of CdO nanoparticles in solutions with concentrations from 0.0001% to 40%. We were able to analyse the sample's UV-Vis absorption spectra with the use of a UV-Vis spectrophotometer (Model-Perkin-Elmer Lambda 35). For this purpose, the fluorescence spectrum was recorded using a Perkin-Elmer LS-55 spectrophotometer. It's a STAT MC that can switch gears electrochemical applications were tested using frequencies between 1 Hz and 1 MHz and a powder sample cell in situations where the voltage was higher than what the Nernst equation predicted.

3. Results and discussion

3.1. Powder X-ray diffraction Studies

The synthesised powder form of Cadmium Oxide nanoparticles was subjected to powder X-ray diffraction analysis as shown in Fig.1. The variable intensity of peaks is obtained as

diffraction in order to the angle of position 2θ . From Fig.1, we can see that peaks with (hkl) numbers (111), (200), and (220) have 2θ equal to 33.13° , 38.29° , and 55.33° for high intensity, whereas peaks with (hkl) numbers (311) and (222) are shown at 2θ equal to 66.00° and 69.30° , respectively for less intensity. Because of this, the fact that CdO nanoparticles exhibited such desirable peaks indicated that their structures were strong and their diffraction was intense. A cubic crystal structure with a space group of $Fm\bar{3}m$ a cell parameter of $a = b = c = 4.6958 \text{ \AA}$

was found to be in agreement with the detected peaks (JCPDS No: 75-0592) [1]. The Debye-Scherrer method was used to determine the average crystallite size of CdO nanoparticles from their position, Full Wave Half Maximum (FWHM), and incoming radiation. The following relation shows the association of average crystallite grain size D is,

$$D = k \lambda / \beta \cos\theta \quad (1)$$

The complete width at half maximum of the pattern peaks is denoted in radians and λ is proportional to the wavelength of the (CuK α) radiation ($\lambda=1.5405 \text{ \AA}$), where k represents the particle form factor (0.94), θ represents the Bragg's diffraction angle. [4, 13]. What's more, the crystallite size is proportional to the dislocation density in the crystalline space, as shown in the following relation:

$$\delta = 1 / D^2 \quad \text{lines / metre}^2 \quad (2)$$

All these structural parameters were tabulated in Table 1. And crystallite size and dislocation density were correlated with position in radians (Fig.2).

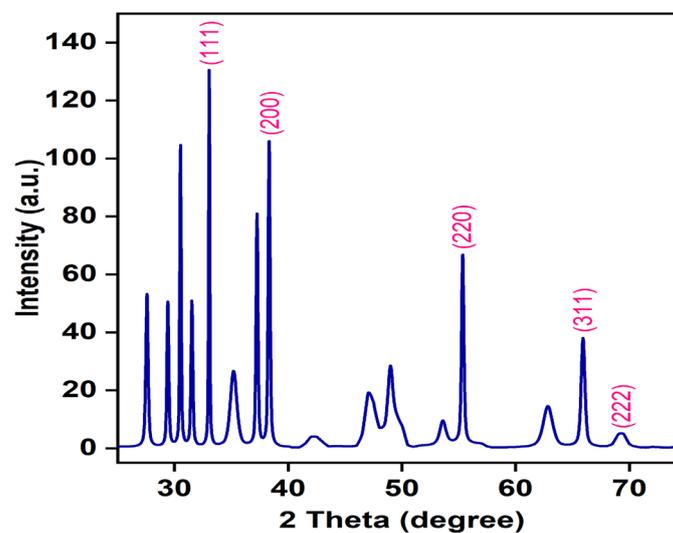


Fig. 1. Powder XRD pattern of CdO nanoparticles.

Table 1. Powder X-ray diffraction parameter of CdO nanoparticles.

2θ (radian)	(hkl)	d-spacing (Å)	β FWHM (deg.)	D Grain Size (nm)	δ Dislocation Density $\times 10^{-14}$ (Lines / metre ²)
33.13°	111	2.70831	0.12	72.09445962	1.9239608
38.29°	200	2.34698	0.192	45.73135498	4.7815848
55.33°	220	1.65870	0.24	39.02150673	6.5673767
66.00°	311	1.41573	0.384	25.74319571	15.089508
69.30°	222	1.35498	1.152	8.751433594	130.56946
Average Crystallite Size (D) *				38.26	
Ref [2]				42.0	
Ref [13]				35.5	

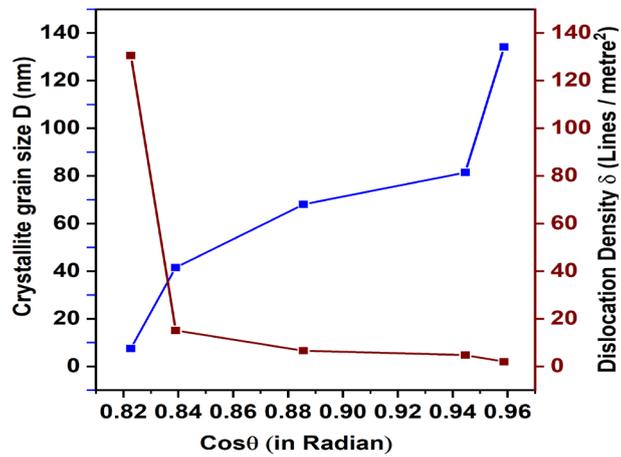


Fig. 2. Crystallite grain size vs. Dislocation density.

3.2. SEM Analysis

Scanning electron microscopy (SEM) is an analytical technique that involves scanning an electron beam over a sample to create a magnified visual image. With the use of a scanning electron microscope, nanoparticles may be studied in great depth, appearance and structure included. Image data from scanning electron microscopy (SEM) at various magnifications of the synthesised nanoparticles is shown in Fig. 3. The range of magnification in these photographs is from a. $1\mu\text{m}$ b. $2\mu\text{m}$ c. $3\mu\text{m}$ to d. $5\mu\text{m}$. When first examined at $1\mu\text{m}$ magnification, which showed the composite composed worms. The cadmium oxide nanoparticles resolved into distinct wires upon closer at $2\mu\text{m}$ of inspection. Gradual improvements in resolution ($3\mu\text{m}$) have revealed the CdO cluster comprised needles.

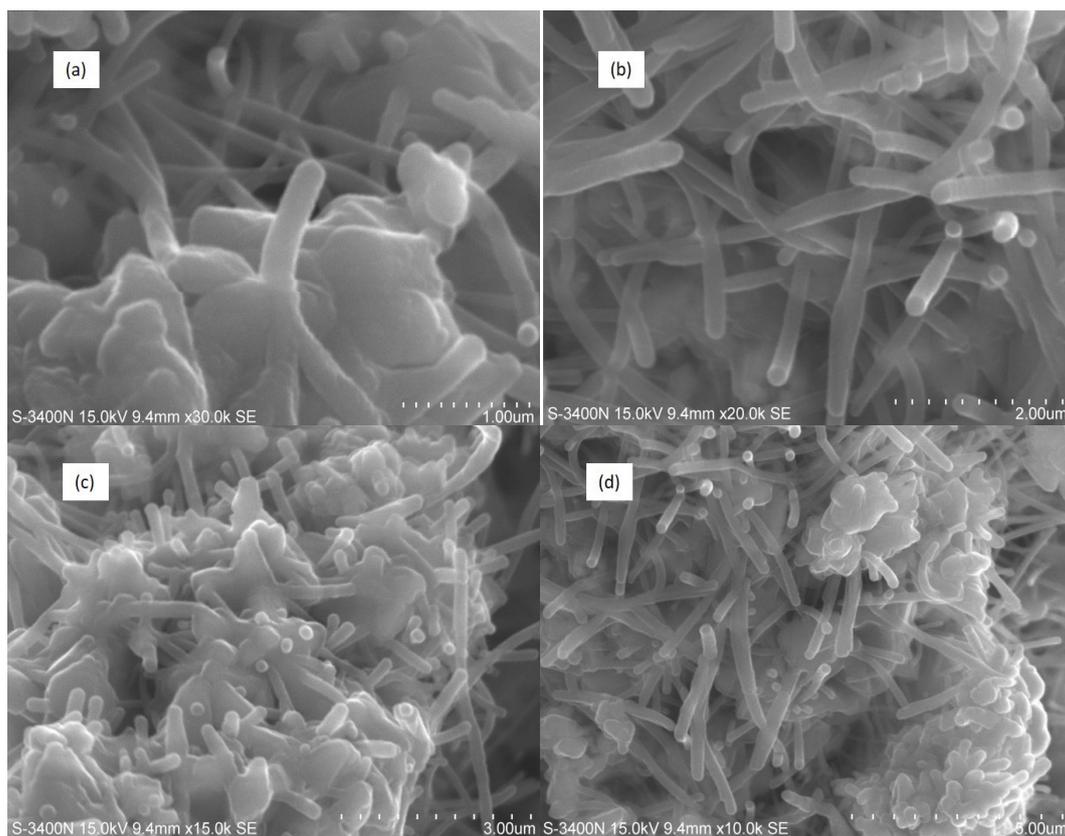


Fig. 3. SEM images CdO nanoparticles.

Finally the cylinder-shaped rod form ($5 \mu\text{m}$) of CdO nanoparticles interacting with porosity clusters. This SEM analysis at high magnification shows that particles get smaller when their size is decreased.

3.3. Fourier Transforms Infrared Spectroscopy

The CdO nanoparticles were analysed by FT-IR spectroscopy, and the findings are shown in Fig. 4. The peak in the absorption band at 460.4 cm^{-1} is due to the bonding of cadmium with oxygen. A lower peak at 838.9 cm^{-1} reflects the stretching vibrations associated with the Cd-O bond. A very sharp peak at 1383.6 cm^{-1} is evidence for C-H stretching vibrations, while a big peak at 1639.3 cm^{-1} is attributed to O-C-O stretching vibrations. The peak at 2925.0 cm^{-1} for the O-H bending mode is larger than that at 2426.3 cm^{-1} for the CO_2 inner atmospheric vibrations. The hydroxyl group in water molecules is thought to stretch at a frequency of 3456.1 cm^{-1} . There are two types of stretching vibrations in N-H bonds that contribute to the characteristic absorption peak at 3584 cm^{-1} [1, 5]. CdO nanoparticles have been proven to have a functional group through peaks in the FT-IR spectra.

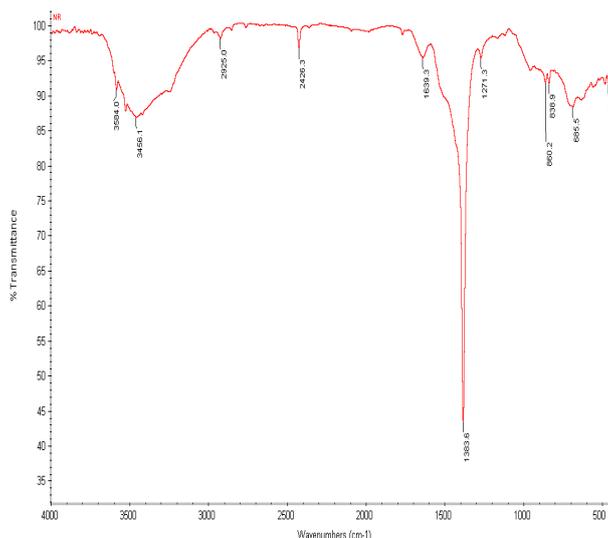


Fig. 4. FT-IR spectrum of CdO nanoparticles.

3.4. Particle Size Analysis

The nanoparticle clusters were measured at 25 °C with a refractive index of 1.3328, a cP viscosity of 0.8878, and a scattering intensity of 31397 cps using a Nano plus Particle Size Analyzer with Dilution Method. The particle size diameter of CdO nanoparticles suspended in liquids at concentrations ranging from 0.0001% to 40% [10] might be determined using this technique. Using an index polydispersity value of 0.239, Fig. 5 shows that the average size of the nanoparticles developed in this study was 159.2 nm. Most of the time, CdO nanoparticles are made in the shape of spheres with a diameter equal to their nanometer scale.

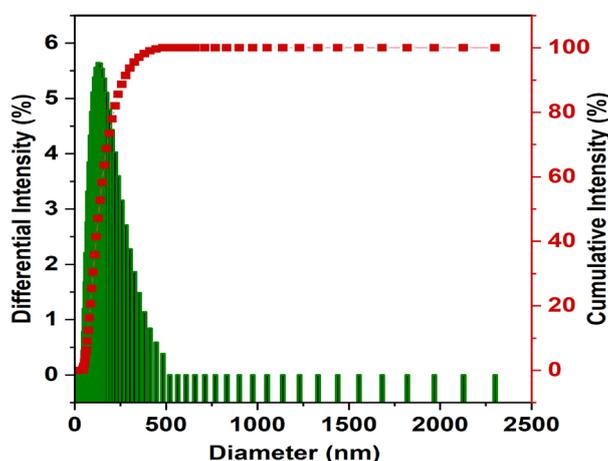


Fig. 5. Diameter vs. Intensity Distribution.

3.5. UV-Vis Analysis

Absorption spectrum of cadmium oxide nanoparticles measured using a UV-Vis spectrophotometer across the wavelength range of 200–800 nm are shown in Fig. 6.

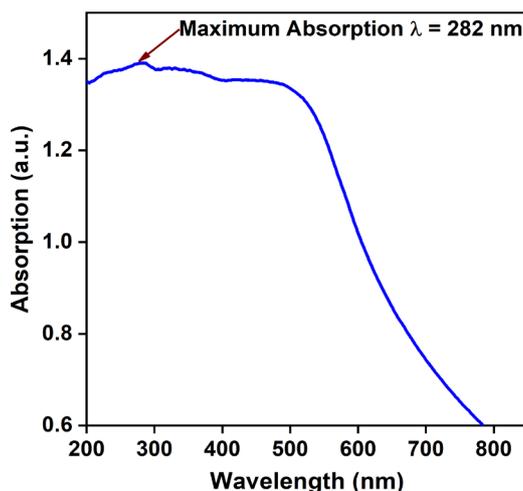


Fig. 6. UV-Vis spectrum of CdO nanoparticles.

With the maximum absorption happening at 282 nm [9], In other words, this quantifies the current absorption spectrum by establishing a cut-off wavelength. From the beginning of the UV region to its conclusion, absorption diminishes steadily over the visible spectrum. As a result, these nanoparticles would have improved transmittance and could be used in opto-electrics. The nanoparticle size affects the optical transition between the conduction band and the valence band levels. The band gap, which is calculable using Tauc's relation, is mostly determined using absorption spectroscopy. It can be shown that the absorption coefficient for a direct band gap may be calculated using Tauc's relation;

$$\alpha = A (h\nu - E_g)^n / h\nu \quad (3)$$

For direct band gap semiconducting materials, $n = 1/2$, where A is a constant, is the absorption coefficient of the semiconductor, E_g is the energy band gap, and h is the incoming photon energy. The relationship between $(h\nu)^2$ and $(h\nu)$ for CdO nanoparticles is seen in Fig. 7. This is because the E_g of CdO nanoparticles is 2.7eV [9], which is higher than the E_g of Cadmium Oxide in its more common bulk form.

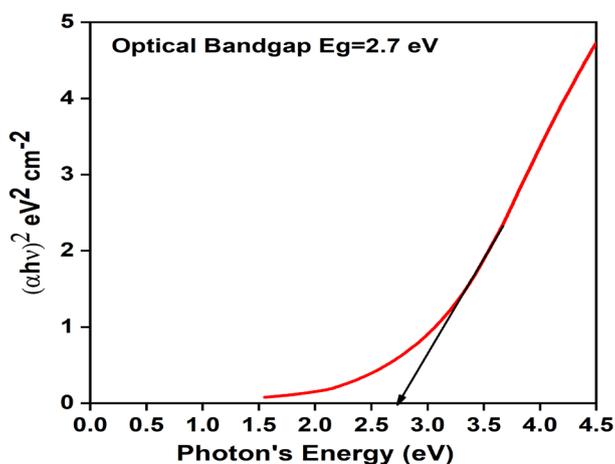


Fig. 7. Optical band gap of CdO nanoparticles.

3.6. Fluorescence Spectral Analysis

Analysis of Fluorescence Spectrum at room temperature, a fluorescence spectrophotometer is used to collect the Cadmium Oxide fluorescence spectrum. Nanoscale of CdO particles and their associated spectrum are shown in Fig. 8. A significant spectral emission peak was seen at 566 nm, within a broad 200-800 nm emission spectrum. The nanoparticles of cadmium oxide (CdO) are guided by an excitation in the ultraviolet region of 282 nm. Furthermore, it is a helpful tool for analysing the stability of a synthetic material in a semiconductor by precisely determining its band edge emission. The emission peaks are now lower in wavelength due to the quantum confinement effect. The transition from the valence band to the conduction band is responsible for the yellowish emission at 566 nm. CdO nanoparticles have intrinsic flaws that cause them to emit light at extremely low energies. The observations are in agreement with those of earlier studies.

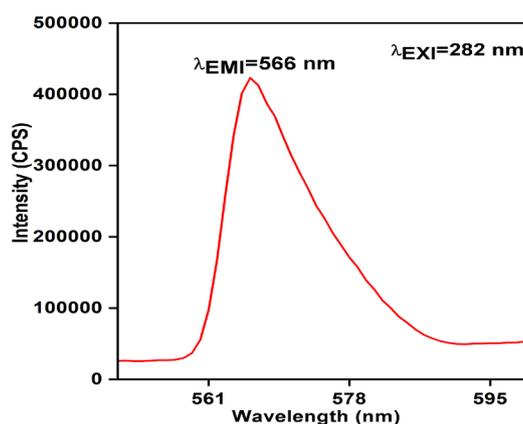


Fig. 8. Emission spectrum of CdO nanoparticles.

3.7. Electro chemical Analysis

The method of electrochemical measurement known as cyclic voltammetry has been clarified. Fig. 9 displays the electrochemical activity of the synthesized CdO nanoparticles. As seen in Fig. 9, CdO nanoparticles have a scan rate of 10 mV/s throughout a potential range of 2 V to 2 V. Due to its high conductivity, CdO facilitates charge transfer and reaction conduction. Indeed, the shape of the CdO nanoparticles in CV was a narrow rectangle, and their electrochemical activity and capacitance were all readily apparent [11, 12]. In Fig. 10, in the high frequency domain, we see the charge transfer resistance of redox reactions (R_{ct}) caused by the diffusion of electrolyte with CdO nanoparticles. The R_{ct} value of 0.72[9] is deduced from the Nyquist plot. CdO might be employed as an electrode in a high-efficiency energy storage super capacitor due to its excellent electronic properties.

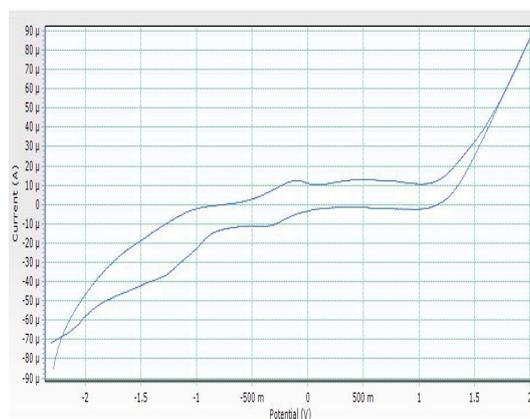


Fig. 9. Voltage vs. Current.

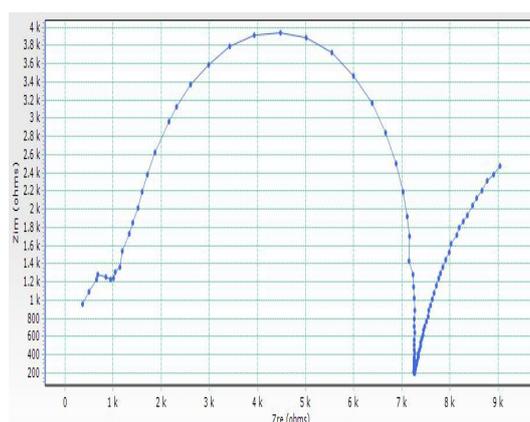


Fig. 10. Z_{im} vs. Z_{re} .

3.8. Magnetic characterization

The magnetic activity of CdO nanoparticles has not been much investigated so far. Vibrating sample magnetometer was used to study the magnetic properties of CdO nanocrystals at different growth temperatures[13]. Figure 11 shows the hysteresis loops for as prepared and annealed CdO nanocrystals. The annealed formulations reveal typical paramagnetic behavior. The paramagnetism of the products is clearly shown that magnetization versus magnetic field. The saturation magnetization is the maximum induced magnetic field moment that can be obtained in a magnetic field, beyond this field no further increase in magnetization occurs. Coercivity is the reverse magnetic field required to reduce the net magnetization to zero. For magnetic materials, it is necessary to reduce the coercivity as a way to control the energy losses.

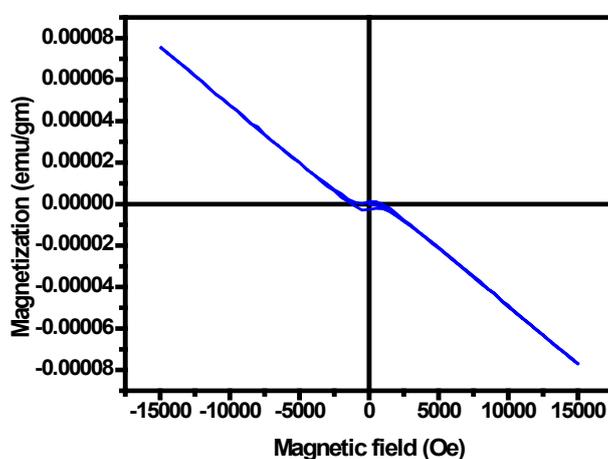


Fig. 11. Magnetic hysteresis loop of the Cadmium Oxide Nanoparticles 0.8M concentration and Vibrating Sample magnetometer a reaction temperature of room.

4. Conclusion

Cadmium Oxide nanoparticles have been successfully synthesized using co-precipitation technique. The cubic crystal structure with the space group $Fm\bar{3}m$ was verified by an X-ray powder diffraction investigation. SEM photos magnified to a high enough level reveal the Nano rod form. The title nanoparticles revealed using Fourier transform infrared spectroscopy, belongs to cadmium and hydroxyl functional groups in CdO nanoparticles integrated at various peaks. The average diameter of CdO particles was calculated to be 159.2 nm using the particle size analysis

technique. The UV-visible analysis's cutoff wavelength of 282 nm shows that absorptions go off with increasing wavelength. The optical energy in the band gap was calculated to be 2.7 eV. The fluorescence emission peaked strongly at 566 nm, where it was excited due to the excitation wavelength of 310 nm. CdO nanoparticles' Rct values of 0.72 in the Nyquist plot confirmed the evidence of an electrochemical investigation proving their super capacitance. These features of CdO nanoparticles were included in the electrodes of storage capacitors. The CdO nanocrystals annealed the coercivity of magnetization suggesting potential usage in data storage.

References

- [1] Maged S. Al-Fakeh, Roaa O. Alsaedi, Nesrine Amiri, Gadah A. Allazzam, *Coatings* 12, 215 (2022); <https://doi.org/10.3390/coatings12020215>
- [2] K. Karthik, S. Dhanuskodi, C. Gobinath, S. Prabukumar, S. Sivaramakrishnan, *Mat. Res. Inno.* (2018); <https://doi.org/10.1080/14328917.2018.1475443>
- [3] K. Karthik, S. Dhanuskodi, C. Gobinath, S. Prabukumar, S. Sivaramakrishnan, *J Mater Sci: Mater Electron* 28, 11420-11429 (2017); <https://doi.org/10.1007/s10854-017-6937-z>
- [4] Heidari A, Brown C, *Jour. Nanomed. Res.* 2 (5), 141-154 (2015); <https://doi.org/10.15406/jnmr.2015.02.00042>
- [5] Ahmed Atta, Nehal Ali, Mohamed Taman, Emad Etman, *Const. Inno.*, 18 (2), 134-151 (2018); <https://doi.org/10.1108/CI-01-2017-0011>
- [6] K. Manickathai, S.K. Viswanathan, M. Alagar, *Ind. Jour. of Pure and App. Physics*, 46 (8), (2008),
- [7] Ch. Venkata Reddy, B. Babu, Jaesool Shim, *Jour. of Phy. and Chem. of Solids*, 112, 20-28 (2018); <https://doi.org/10.1016/j.jpcs.2017.09.003>
- [8] Gopi Somasundaram, Jayaprakash Rajan, P. Sangaiya, R. Dilip, *Res. in Mat.*, 4, 100044 (2019); <https://doi.org/10.1016/j.rinma.2019.100044>
- [9] M. Iniya Pratheepa, M. Lawrence, *Vacuum* 162 208-213 (2019); <https://doi.org/10.1016/j.vacuum.2019.01.042>
- [10] Deasy Pertiwi, Ronny Martien, Sismindari, Hilda Ismail, *Pak. J. Pharm. Sci.*, 31, 2, 379-384 (2018).
- [11] W.H. Shi, J.X. Zhu, D.H. Sim, Y.Y. Tay, Z.Y. Lu, X.J. Zhang, Y. Sharma, M. Srinivasan, H. Zhang, H.H. Hng, Q.Y. Yan, *J. Mater. Chem.*, 21, 3422 (2011); <https://doi.org/10.1039/c0jm03175e>
- [12] B.J. Lokhande, R.C. Ambare, R.S. Mane, S.R. Bharadwaj, *Mater. Res. Bull.*, 48, 2978-2983 (2013); <https://doi.org/10.1016/j.materresbull.2013.03.028>
- [13] R. Ranjithkumar, A. Albert Irudayaraj, G. Jayakumar, A. Dhayal Raj, S. Karthick, R. Vinayagamoorthy, *Materials Today: Proceedings* 3, 1378-1382 (2016); <https://doi.org/10.1016/j.matpr.2016.04.018>
- [14] Nadana Shanmugam, Balan Saravanan, Rajaram Reagan, Natesan Kannadasan, Kannadasan Sathishkumar and Shanmugam Cholan, *Mod Chem Appl* vol 2- 000124-000129 (2014); <https://doi.org/10.4172/2329-6798.1000124>