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Structural Characterization of Cadmium Oxide Nanoparticles by Means of X-ray Line Profile Analysis

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Abstract—*Cadmium Oxide nanoparticles (CdO-NPs) were prepared by simple precipitation method using Cadmium acetate and ammonia solution. The CdO-NPs were synthesized at calcinations temperatures of 350^{o}C for 3 h. The synthesized CdO-NPs were characterized by X-ray diffraction analysis (XRD). The XRD results revealed that the sample product was crystalline with a cubic phase. From X-Ray Diffraction (XRD) spectrum the particle size, d-spacing value and structure of the nanoparticles were analysed. The crystalline development in the CdO-NPs was investigated by X-ray peak broadening. The Williamson Hall (W-H) analysis methods were used to study the individual contributions of crystallite sizes and lattice strain on the peak broadening of the CdO-NPs. The physical parameters such as strain, stress and energy density values were calculated more precisely for all the reflection peaks of XRD corresponding to the cubic phase of CdO lying in the range of 20^o to 100^o from the modified form of the W-H plot assuming a uniform deformation model (UDM), uniform stress deformation model (USDM), and uniform deformation energy density model (UDEDM).. Size of the nanoparticles and the elemental composition were detected by using Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray Analysis (EDX).*

Keywords*: Nanoparticles; Cadmium Oxide; Williamson–Hall plot; X-ray diffraction (XRD),Scanning Electron Microscope (SEM)*

1. INTRODUCTION

Nanoparticles have attracted great interest recently due to their unique physical and chemical properties, which are different from those of either the bulk materials or single atoms. Over the past few decades, nanomaterials, including metal oxide nanoparticles, have received enormous scientific attention because of their interesting novel and improved physico-chemical and biological properties as a result of size reduction to the nano-regime .Their unique physical properties that are size and shape-dependent , render them applicable in many fields such as optics, magnetism, catalysis, electricity, energy production and storage, environmental remediation, antimicrobial agents and drug delivery. Among the different metal oxide nanoparticles, CdO is an important n-type semiconductor with a cubic structure, which belongs to the II–VI group, with a direct band gap of 2.2 to2.5 eV and an indirect band gap of 1.36 to 1.98 eV. Some reports have presented that the band gap of this material can change in the range of 1.1 to 3.3 eV Such diversity can be assigned to lattice's defects due to the Burstein-Moss effect [1]. Meanwhile, it can be originated from the nanosized structure, i.e., the preparation of the material in nanoscale can impress the optical and electrical characteristics. Because of the appropriate optical and electrical properties, cadmium oxide nanostructures are used in solar cells, gas sensors, transparent electrodes, photodiodes, catalysts, and optoelectronic devices. Up to now, various methods have been employed to prepare the cadmium oxide nanostructures such as micro emulsion [2], chemical co-precipitation method [3], chemical/hydrothermal technique [4], solvo thermal process [5], and also mechano chemical process [6]. A perfect crystal would extend infinitely in all directions; therefore, no crystals are perfect due to their finite size. This deviation from perfect crystallinity leads to a broadening of the diffraction peaks. The two main properties extracted from peak width analysis are the crystallite size and lattice strain. Crystallite size is a measure of the size of coherently diffracting domains. The crystallite size of the particles is not generally the same as the particle size due to the formation of polcrystalline aggregates. Lattice strain is a measure of the distribution of lattice constants arising from crystal imperfections, such as lattice dislocations. Other sources of strain include the grain boundary triple junction, contact or sinter stresses, stacking faults and coherency stresses.

Crystallite size and lattice strain affect the Bragg peak in different ways. Both these effects increase the peak width and intensity and shift the 2θ peak position accordingly. The peak width derived from crystallite size varies as 1/cosθ , whereas strain varies as tanθ. This difference in behavior as a function of 2θ enables one to discriminate between the size and strain effects on peak broadening. The Bragg width contribution from crystallite size is inversely proportional to the crystallite size [7]. W-H analysis is a simplified integral breadth method where size-induced and strain-induced broadening is de-convoluted by considering the peak width as a function of 2θ [8]. Although X-ray profile analysis is an averaging method, apart from TEM imaging, it still holds a dominant position in grain-size determination.

In this study, a chemical precipitation method was used to prepare CdO-NPs. In addition, a comparative evaluation of the mean particle size of the CdO-NPs obtained from Debye Scherrer equation and from W-H procedures is reported. The strain due to lattice deformation associated with the CdO-NPs calcined at 350^{o}C was estimated by a modified form of W-H, namely uniform deformation model (UDM). The other modified models, such as uniform stress deformation model (USDM) and uniform deformation energy-density model (UDEDM).

2. MATERIALS AND METHODS

0.1M of cadmium acetate was dissolved separately in 100ml distilled water and solution is stirred at room temperature. After stirring process, ammonium hydroxide solution was added to above solution drop wise until pH value of about 9 was reached with constant stirring. The white precipitate was formed and it was allowed to settle for overnight. Then filtered with whatman filter and washed 3-4 times with distilled water. The particles were collected in a petty dish and dried at 100^{o}C for 1hour, keeping material in a hot air oven for 1hour and then grinded using mortal piestel. The resulting powder was calcined at 350°C for 3 hours in a muffle furnace. The Brownish CdO-NPs are collected, grained and preserved in an air tight container. The chemical reactions are given as

$(CH_3COO)\ _2Cd.2H_2O+2NH_4OH \rightarrow Cd\ (OH)\ _2 + 2H_2O + 2CH_3COONH_4$

During calcinations at 350^{0}C , as prepared powder loses H_2O which is as follows:

$Cd\ (OH)_2 \rightarrow\ CdO + H_2O$

3. RESULTS AND DISCUSSION

1. X-Ray Diffraction Structural Analysis:

The XRD pattern of CdO obtained is shown in Fig. ure 1. The sharp and well defined peaks indicate the crystalline nature of CdO. The interplanar spacing (d)(calculated from the Bragg equation (1)) and lattice constant (a) (calculated from equation (2) for cubic phase structure) of CdO-NPs samples with different molarities of cadmium acetate were determined which is very close to the reported values (JCPDS, No. 05-0640.). The values of lattice constant ‘a’ and ‘d’ spacing at different molarities of cadmium acetate are given in Table 1.

$$\lambda=2d\sin\theta \rightarrow \qquad (1)$$

$$\&\ d = \frac{a}{\sqrt{h^2+k^2+l^2}} \rightarrow \qquad (2)$$

4. PARTICLE SIZE AND STRAIN

Scherrer method

XRD can be utilized to evaluate peak broadening with crystallite size and lattice strain due to dislocation .The particle size of the CdO-NPs was determined by the X-ray line broadening method using the Scherrer equation: $D=k\lambda/\beta cos\theta$ where D is the particle size in nanometers, λ is the wavelength of the radiation (1.54056 Å for CuK_{α} radiations), k is a constant equal to 0.94, β is the peak width at half-maximum intensity and θ is the peak position. The breadth of the Bragg peak is a combination of both instrument- and sample dependent effects. To decouple these contributions, it is necessary to collect a diffraction pattern from the line broadening of a standard material such as silicon to determine the instrumental broadening. The instrument-corrected broadening β corresponding to the diffraction peak of CdO was estimated using the relation:

$$\beta^2 = (\ \beta^2)_{measured} - (\beta^2)_{instrumental} \text{------------} \qquad \text{- (3)}$$

$$D = \frac{k\lambda}{\beta \cos\theta} - - - -(4) \Rightarrow cos\theta = \left(\frac{1}{\beta}\right)\left(\frac{k\lambda}{D}\right) \text{----}\ (5)$$

Plots were drawn with *1/β* on the x-axis and *cosθ* along the y-axis for the CdO-NPs prepared at different molarities such that the preferred orientation peaks of CdO with the cubic phase appeared between 2θ= 20^{o} and 100^{o}. By fitting the data, the crystallite size D was extracted from the slope of the fit line; Fig. 2

5. WILLIAMSON HALL METHODS

The strain induced in powders due to crystal imperfection and distortion was calculated using the formula:

$$\epsilon = \frac{\beta}{4tan\theta} - - - -(6)$$

From Equations (4) and (6), it was confirmed that the peak width from crystallite size varies as 1/cosθ, strain varies as tanθ. Assuming that the particle size and strain contributions to line broadening are independent to each other and both have a Cauchy-like profile, the observed line breadth is simply the sum of Equations 4 and 6. i.e.

$$\beta = \frac{k\lambda}{Dcos\theta} + 4\epsilon tan\theta \text{ -----} \qquad \text{- (7)}$$

By rearranging the above equation, we get

$$\beta cos\theta = \frac{k\lambda}{D} + 4\epsilon sin\theta \text{ -----} \qquad \text{- (8)}$$

The above equations are W-H equations. A plot is drawn with 4sinθ along the x-axis and βcosθ along the y-axis for prepared CdO-NPs as shown in Fig. 3.

From the linear fit to the data, the crystalline size was estimated from the y-intercept, and the strain ε, from the slope of the fit. Equation(8) represents the UDM, where the strain was assumed to be uniform in all crystallographic directions, thus considering the isotropic nature of the crystal, where the material properties are independent of the direction along which they are measured. In the Uniform Stress Deformation Model, USDM, a generalized Hooke's law refers to the strain, keeping only the linear proportionality between the stress and strain as given by $\sigma = Y\varepsilon$, where σ is the stress of the crystal and Y is the modulus of elasticity or Young's modulus. This equation is valid for a significantly small strain. Assuming a small strain to be present in CdO-NPs, Hooke's law can be used here. With a further increase in the strain, the particles deviate from this linear proportionality.

Applying the Hooke's law approximation to the above equation (8), we get

$$\beta cos\theta = \frac{k\lambda}{D} + \frac{4\sigma sin\theta}{Y} - - - - (9)$$

Again, the modulus of elasticity or Young's modulus Y for cubic crystal is given by the relation

$$\frac{1}{Y} = S_{11} - 2\left(S_{11} - S_{12} - \frac{1}{2}S_{44}\right)\frac{(hk)^2 + (hl)^2 + (kl)^2}{(h^2 + k^2 + l^2)^2} - - - - - (10)$$

Where S_{11}, S_{12}, S_{44} are the elastic compliances of CdO [9]. The relations which provide the connection between the elastic compliances and the stiffness cij are as follows [10]:

$$S_{11} = \frac{C_{11} + C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})} - - - - (11)$$

$$S_{12} = -\frac{C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})} - - - (12)$$

and

$S_{44} = \frac{1}{C_{44}} - - - - (13)$ Using the values of C_{11} , C_{12} and C_{44} [9] as 207.8GPa, 106.3 GPa and 54.9 GPa respectively, we can calculate elastic compliances S_{11}, S_{12}, S_{44} which are given as 7.36 x 10^{-12},-2.49 x 10^{-12} and 18.21 x 10^{-12} m^2/N respectively. Young's modulus Y has been calculated and resulted to be 145.7 GPa for (111) lattice plane followed by Y=135.9 GPa for (200), Y=143.1 GPa for (220) , Y=140.3 GPa for(311), Y=145.69 GPa for(222) and Y=135.9 GPa for (400) lattice planes respectively. Using equation (10), Young's modulus (Y*)*, for cubic CdO-NPs was calculated as ~ 141 GPa [11]. Plots were drawn with $\frac{4sin\theta}{Y}$ on the x-axis and βcosθ on the y-axis for the CdO-nanoparticles. The USDM plots for CdO-NPs calcinations at 350°C are shown in Fig. 4.The stress is calculated from the slope of the fitted line.

There is another model that can be used to determine the energy density of a crystal called the Uniform Deformation Energy Density Model, UDEDM. In Equation (9), the crystals are assumed to have a homogeneous, isotropic nature. However, in many cases, the assumption of homogeneity and isotropy is not justified. Moreover, the constants of proportionality associated with the stress -strain relation are no longer independent when the strain energy density u is considered. According to Hooke's law, the energy density u (energy per unit volume) as a function of strain is $u = \frac{\epsilon^2 Y}{2}$. Therefore, Equation (9) can be modified to the form $\beta cos\theta = \frac{k\lambda}{D} + 4sin\theta\left(\frac{2u}{Y}\right)^{\frac{1}{2}} - - - - - (14)$.

The uniform deformation energy density (UDEDM) can be calculated from the slope of the line plotted between βcosθ and $4sin\theta\left(\frac{2u}{Y}\right)^{1/2}$

The lattice strain can be calculated by knowing the Y values of the sample. W-H equations modified assuming UDEDM and the corresponding plot is shown in Fig. 5

From Equations (9) and (14), the energy density and the stress can be related with UDSM and UDEDM, but approaches are different, based on the assumption of uniform deformation stress, according to Equation (9). The assumption of uniform deformation energy is as per Equation (14), even though both models consider the anisotropic nature of the crystallites. From Equations (9) and (14), the deformation stress and deformation energy density are related as $u = \frac{\sigma^2}{Y}$. It may be noted that though both Equations (9) and (14) are taken into account in the anisotropic nature of the elastic constant, they are essentially different. This is because in Equation (6), it is assumed that the deformation stress has the same value in all crystallographic directions allowing u to be anisotropic, while Equation (14) is developed assuming the deformation energy to be uniform in all crystallographic directions treating the deformation stress σ to be anisotropic. Thus, it is clear that from Williamson-Hall plots using Equations (9) and (14), a given sample may result in different values for lattice strain and crystallite size.

Table 1: Structural parameters of CdO nanoparticles

Sample No	**hkl**	**d (Å) observed values**	**FWHM β (degree)**	**2θ (degree)**	**Grain size(nm)**	**a_{cal} (Å)**	**Texture Coeff.**
CdO1 (0.1M)	111	2.71	0.265	33.05	32.08	4.688	1.05
	200	2.34	0.285	38.34	30.26	4.686	1.03
	220	1.66	0.328	55.33	28.05	4.686	1.03
	311	1.41	0.386	65.95	25.20	4.689	0.98
	222	1.35	0.393	69.29	25.20	4.690	0.99
	400	1.17	0.436	82.01	24.75	4.690	0.96

Table 2 summarizes the geometrical parameters of CdO-NPs of different molarities obtained from Scherrer's method and various methods of W-H analysis. The average value of crystallite size, internal strain and stress obtained from the various models of modified W-H analysis are different, thus indicating that the inclusion of strains in various form of W-H analysis have an impact on the average crystallite size of CdO-NPs. However, there is a variation between the crystallite size obtained from Debye-Scherrer's equation and the modified W-H analysis. This difference might be due to the strain contribution to the peak broadening in CdO-NPs.

6. TEXTURE COEFFICIENT

The texture coefficient (*TC*) represents the texture of the particular plane, in which greater than unity values imply that there are numerous of grains in that particular direction. The different texture coefficient *TC* (*h k l*) has been calculated from the X–ray data using the well–known formula

$$T_c(hkl) = \frac{I(hkl)/I_0(hkl))}{N^{-1}\sum_n I(hkl/I_0(hkl)} \text{----------} \qquad \text{-- (15)}$$

where I(*hkl*) is the measured intensity, $I_o(hkl)$ taken from the JCPDS data, (N) is the reflection number and (*hkl*) is Miller indices. The texture coefficient is calculated for different crystal planes .The values of texture coefficient which were greater than 1 indicate the abundance of grains in that direction. All these results are shown in table (1) which shows that the (111) plane is the preferred orientation with highest (*TC)* value 1.05.

7. SEM &EDX STUDY

The Scanning Electron Microscope (SEM) micrographs of the samples are shown in Fig. 6 calcinations at 350°C. It is clear that the prepared CdO-NPs have nearly spherical shape with an average size of 43 nm. The composition of obtained CdO-NPs was then analyzed by means of energy dispersive X-ray analysis (EDX).As shown in Fig. 7, the EDX result showed the presence of CdO by the appearance of Cd and O peaks in these spectra. However, the presence of carbon as impurity (CdO1) as small amount is also evidenced (which may be due to sample holder) from the EDX spectrum. No other impurity was detected. Table 3 indicates the amount of Cadmium and Oxide present in the CdO-NPs.

8. CONCLUSIONS

The CdO-NPs with cubic structure have been synthesized by simple cost competitive precipitation method after annealing the precursor at 350°C. The prepared CdO-NPs were characterized by XRD, SEM, and EDX. The line broadening of CdO-NPs due to the small crystallite size and strain was analysed by Scherrer's formula. The size and strain contributions to line broadening were analyzed by the method of Williamson and Hall using uniform deformation, uniform deformation stress, and uniform deformation energy density models. The three modified forms of W-H analysis were helpful in determining the strain, stress, and energy density value with a certain approximation, and hence, these models are highly preferable to define the crystal perfection.

9. ACKNOWLEDGMENTS

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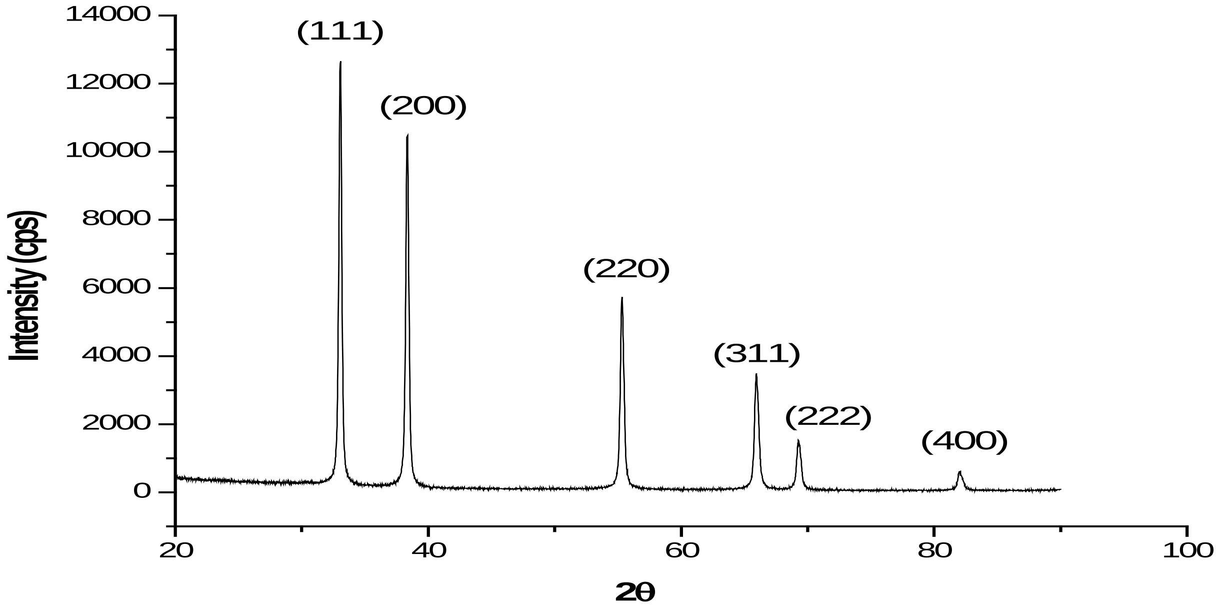

Fig. 1: XRD of synthesized CdO-NPs

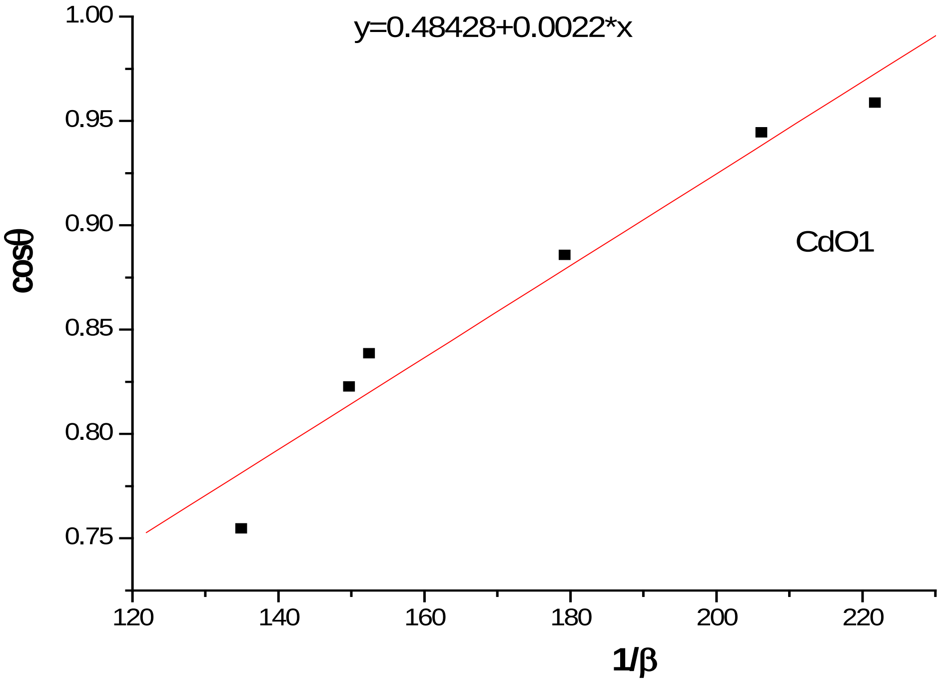

Fig. 2: Sherrer plot of CdO-NPs

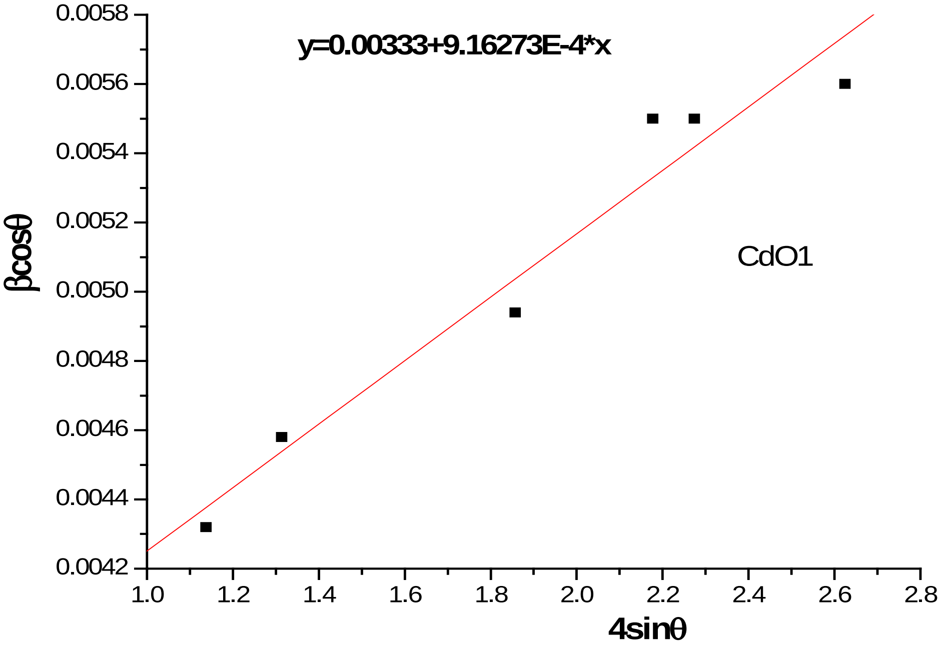

Fig. 3: plot of βcosθ vs.4sinθ

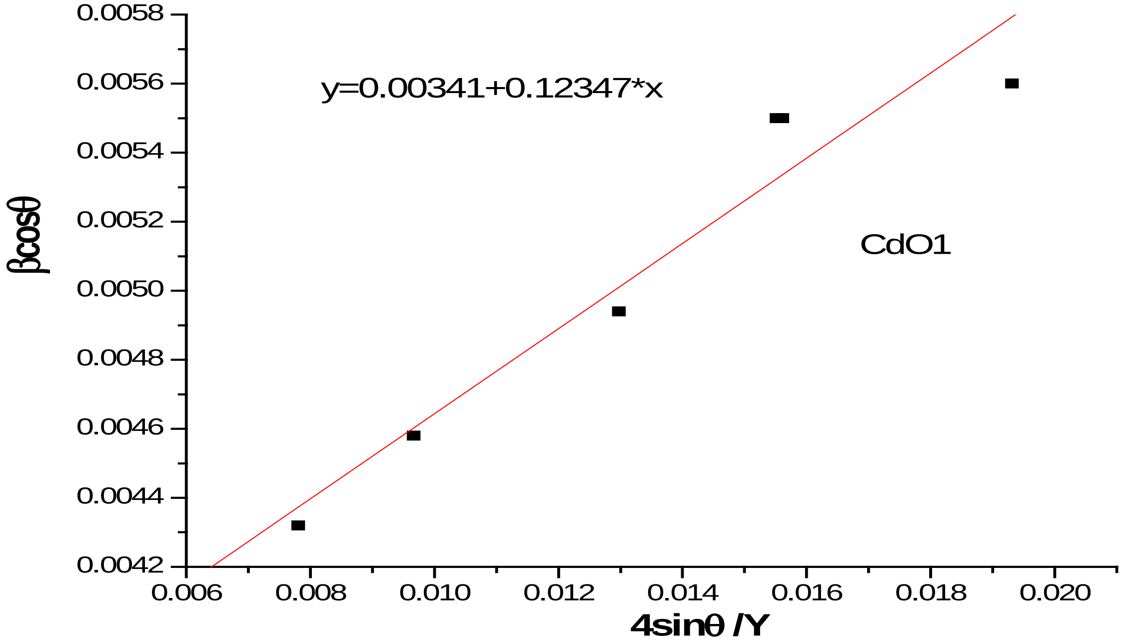

Fig. 4: Plot of βcosθ vs.4sinθ/Y for CdO-NPs

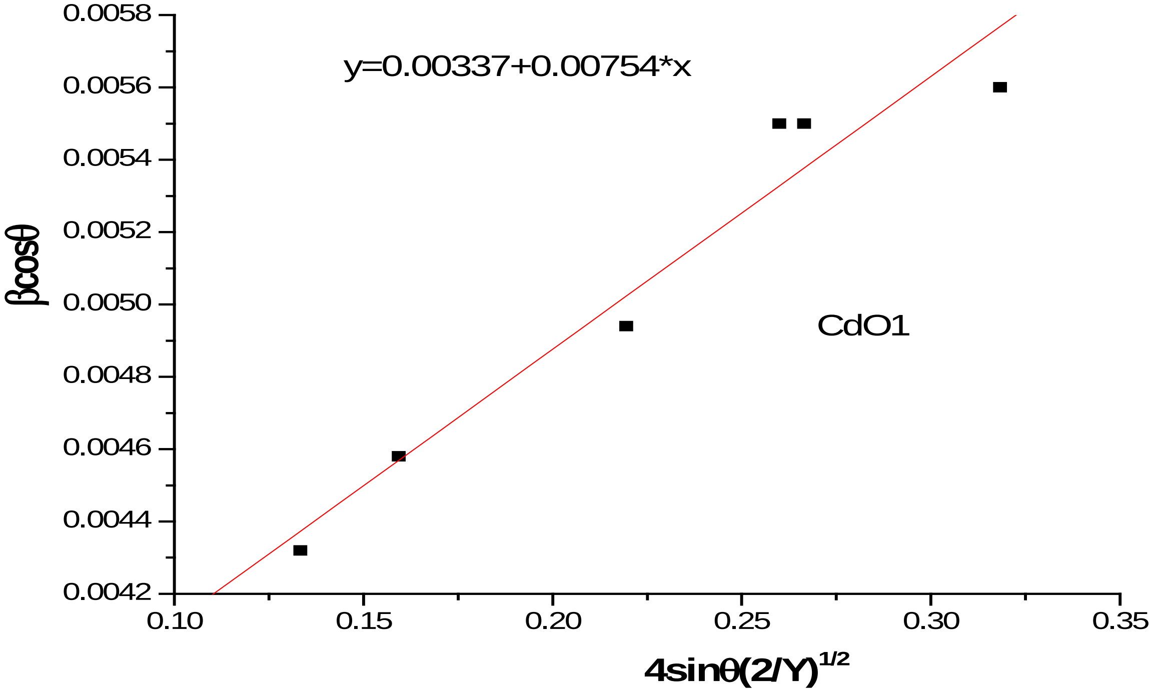

Fig. 5: Plot of βcosθ vs.4sinθ $(2/Y)^{1/2}$ for CdO-NPs

Table 2: The geometric parameters of prepared CdO-NPs

Sample	Scherrer Method	Williamson Method								
		UDM		UDSM			UDEDM			
	(D nm)	D (nm)	strain ϵ x10^{-3}	D (nm)	Strain ϵ x10^{-3}	Stress σ(MPa)	D (nm)	Strain ϵ x10^{-3}	Stress σ(MPa)	u KJ/m^3
CdO1 (0.1 M)	63	41.6	0.92	40.64	0.876	123.47	40.95	0.634	89.530	56.85

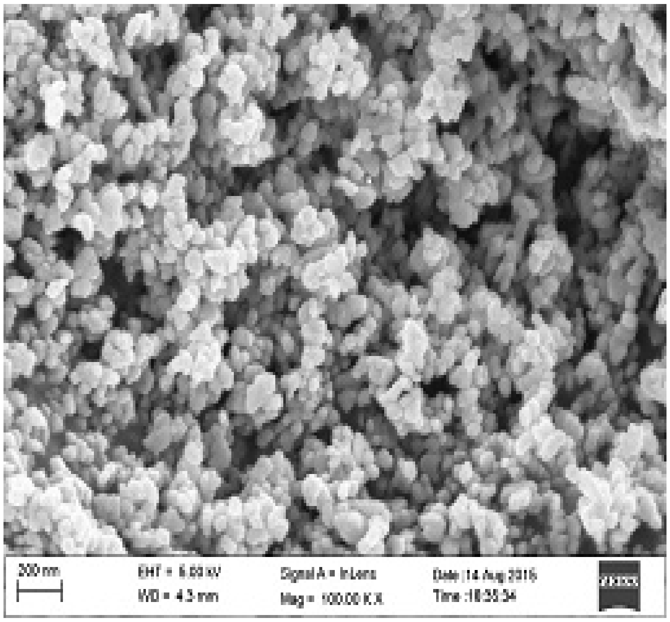

Fig. 6: SEM image of CdO nanostructures

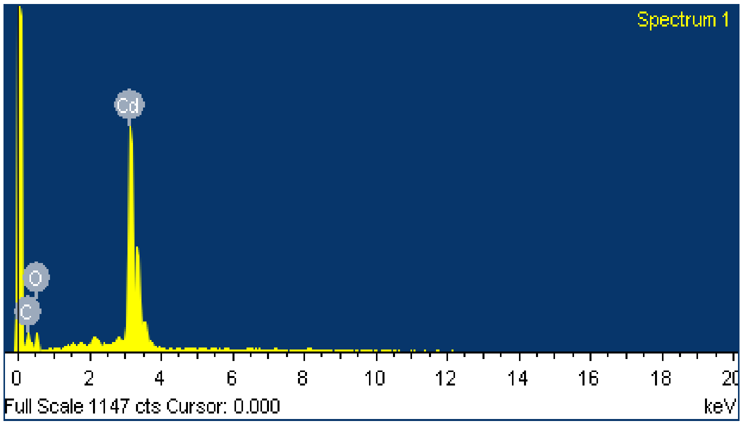

Fig. 7: EDX spectrum of CdO nanostructures

Table 3: EDX Result of CdO-NPs

Sample	Element	Weight%	Atomic%
CdO1	C K	5.65	19.53
	O K	20.48	53.17
	Cd L	73.87	27.29
	Total	100	100

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