Experimental Investigation of the Inhibitory Behavior of CDO Nanoparticleson Co-Precipitation Method

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Abstract: The undoped CdO nanoparticles were synthesized by chemical co-precipitation method at room temperature. The prepared sampled have been characterized by X-ray powder diffraction (XRD) analysis, scanning electron microscopy (SEM), ultraviolet (UV)- visiblespectroscopy, photoluminescence (PL)spectroscopy and Fourier transform infrared(FTIR) spectroscopy. The cubic structures of the CdOproducts were confirmed by XRD analysis. The influence of particle size on structural parameters such as lattice constant, dislocation density, microstrain, stacking fault and texture co-efficient were also determined. The effect of temperatures on shifting the bands in the samples was observed by UV-Visible spectroscopy and also their optical band gap energies were calculated. The emission spectra and energy band diagram of the powders were derived from PL spectroscopy. The structural bond vibrations of CdO nanoparticles were investigated by FTIR spectroscopy.

Keywords: CdO nanoparticles; precipitation method; Cubic structure; Structural parameters; Optical band gap; Emission spectra.

1. Introduction

Nanotechnology is a new and fast-emerging field that involves the manufacture, processing and application of structures, devices, and systems by controlling shape and size at the nanometer scale [1]. Nanomaterials possess unique and specific physicochemical and surface properties related with their size, i.e., mechanical resistance, electronic properties, thermal conductivity and chemical reactivity [2]. In the recent past, semiconducting nanoparticles have attracted much attention because of their unique properties observed only at nanosized dimensions in comparison with that bulk in terms of their electronic, optical, and catalytic properties [3]. As a metal oxide structure, muchattention has been given to pure cadmium oxide (CdO) due to its physical properties that allow it to be used in a wide range of device applications such as solar cells, optical communications, photo-transistors, gas sensors, low emissive windows, antifungal activity and catalytic applications[4].Cadmium oxide (CdO) is a well-known II–VI n-type semiconductor with a cubic (fcc) crystal structure and possesses a direct band gap of 2.2 eV[5] with non-stoichiometric composition due to the presence of either interstitial cadmium or oxygen vacancies, which act as doubly charged donors[6]. In the present study, CdO has been chosen because it has potential importance applications, low cost, chemical stability and wide spread availability.

Various methods were used to prepareCdO nanocrystals such as, solgel [7], solvothermal [8], micro emulsion method [9], precipitation method [10] and sonochemical method [11]. Among all of these methods, Co-precipitation method is a simple technique to grow thin films that are uniform and free from pinholes. On the other hand, low cost, easy processing and suitable for large area deposition are also its advantages.The surfactants play an essential role in controlling morphology of nanostructure because of their softtemplate effect, their ability to modify the chemical kinetics and simple maneuverability. However the ability to understand and foretell the final structure/morphology is still limited [12]. Therefore, the aim of the present study is to synthesize the pure CdO nanoparticles via co- precipitation method and to investigate the effect of temperature on the band gap of CdO. Further, the crystallinity,morphology, functional groups and band gaps of the composites were studied by different techniques like XRD, SEM with EDX, FT-IR, UV–Vis and PL,respectively.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of Pure CdO nanoparticles

The Cadmium oxide nanoparticles were synthesized by using cadmium acetate as precursor. 2.37g of cadmium acetate was dissolved in 50ml of deionized water and then stirred by magnetic stirring apparatus at room temperature. 20ml of aqueous ammonia solution was gradually added drop wise in the solution. The resultant solution was continuously stirred for 24h. Finally, the gray color precipitate appeared. The resulting precipitate was filtered, and washed several times in deionizer water and ethanol. The gray precipitate was dried at 100°C for 4 h in hot air oven. The samples were annealed at 350°C for 1 h to get the phase pureCdO nanoparticles. Similar procedure has been repeated for different calcination temperatures400°C, 450°C, 500°C and 550°C. The synthesis process of CdO nanoparticles was depicted in Figure.1.
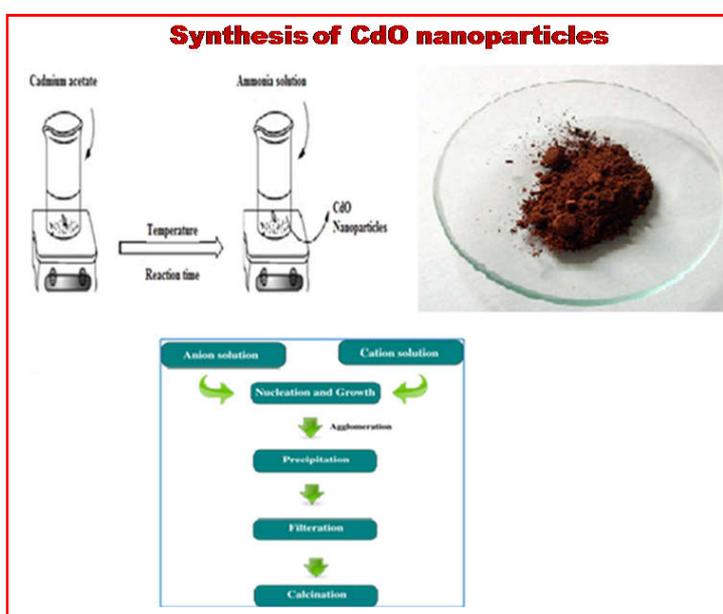

Figure 1. Synthesis process of CdO nanoparticles

2.2. Characterizations

The crystal structure and phase of CdO nanoparticles were characterized by X-ray diffractometer SHIMADZU-XRD 6000. The morphology of the CdO nanoparticles was analyzed by scanning electron microscope Hitachi S-4500 SEM Machine.The chemical structure was investigated by SHIMADZU Fourier Transform Infraredspectrophotometer in which the IR spectrum was recorded by diluting the milled powder in KBr.

And, in the wavelength between 4000 and 400 cm^{-1} was used to assess the presence of functional groups in CdO.The absorption spectra were measured using UV-Vis spectrophotometer SHIMADZU-UV 1800. PL study was carried out at room temperature using a VARIAN spectrophotometer equipped with a 450 W Xenon lamp as the excitation source.

3. RESULTS AND DISCUSSION

3.1. Structural analysis

The phase characteristics of the products were examined by powder X-ray diffraction patterns. It can be seen from Figure.2 that all of the peaks can be indexed to the face centered cubic CdO crystal (JCPDS Card No: 05-0640). The XRD curve of the CdO nanoparticles reveals that the relatively strong diffraction peaks are (111) and (200) with low intensity reflections corresponding to (220), (311) and (222) planes. The sharp peaks of the XRD patterns indicate that the fabricated CdO nanostructures possess good crystallinity.

The average crystallite sizes of the synthesized samples were calculated using the Debye–Scherer formula[13],

$$D = \frac{K\lambda}{\beta \cos\theta} \text{----------------------------- (1)}$$

where λ is the wavelength for the Kα component of the employed copper radiation (1.5406 Å), β is the corrected full width at half maximum (FWHM) and θ is the Bragg's angle. The calculated crystallite size and lattice constant was increases with increasing temperature up to 450°C, and then decreases for higher temperature (500-550°C). The decrease in FWHM of the peak obtained at 450°C indicates the increase of crystalline nature. It is also evident from Table 1 that the crystallite size increases with increasingtemperature. When the reaction is carried out at higher temperature of 450°C, remarkable changes in the XRD pattern is observed.
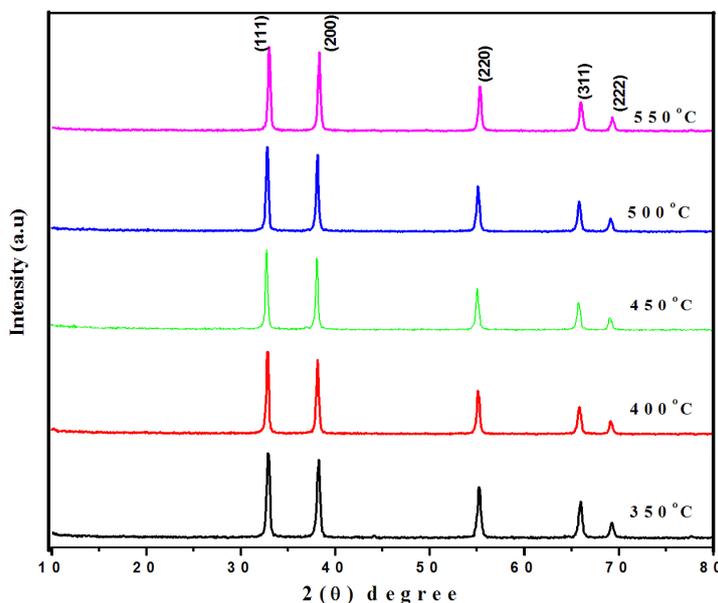

Figure 2. XRD spectra of CdO nanoparticles at different temperatures

The lattice constants a=b=c was calculated using the following formula used for cubic (fcc) systems [14]:

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \text{---------------------- (2)}$$

wheredis the lattice spacing,a, b and care the lattice constants,h, k, and l are the miller indices, θ is the angle of corresponding peak and λ is the wavelength of X-ray used (1.5406 Å). The unit cell volume of the products is given by the formula V = a^3[15].

The structural parameters are calculated from the following equations [16],

Microstrain, $\quad \varepsilon = \dfrac{\beta cos\theta}{4}$ ------------------- (3)

Dislocation density, $\qquad\qquad \delta = \dfrac{1}{D^2}$ -------------------- (4)

Stacking fault, $SF = \left[\dfrac{2\pi^2}{45(3tan\theta)^{\frac{1}{2}}}\right]\beta$ ----------- (5)

The structural parameters including dislocation density (δ), microstrain (ε) and stacking fault (SF) of cubic CdO nanoparticles are summarized in Table 2. The lattice defects like δ, ε and SF showed a decreasing trend with increasing temperature from 350-550°C, which may be due to the improvement of crystallinity as well as the high orientation along (111) direction (Figure.2). This type of change in δ and ε might be due to the recrystallization process in the polycrystalline nature[17].

Table 1. Structural parameters: 2θ, FWHM, D, lattice constant and d spacing

Temperature	2θ	FWHM	Crystal size(nm)	Lattice constant a (=b=c)	d spacing
350°C	32.8870	0.39370	21.9424	4.7132	5.4438
400°C	32.8291	0.28920	29.5510	4.7213	5.4534
450°C	32.7705	0.28520	30.1897	4.7295	5.4631
500°C	32.8405	0.30980	27.9592	4.7196	5.4515
550°C	32.9704	0.29630	29.0437	4.7016	5.4303

Table 2. Structural parameters: δ, Ɛ, SF, TC and Volume

Temperature	Dislocation density δ (10^{18})	Micro strain Ɛ (10^{-3})	Stacking fault	Texture coefficient	Volume V=a³
350°C	0.207694	1.6544	3.2156	1.1975	104.7002
400°C	0.114513	1.2229	2.3776	1.3020	105.2409
450°C	0.109719	1.1992	2.3329	1.2721	105.7902
500°C	0.127923	1.2949	2.5161	1.2721	105.1273
550°C	0.118548	1.2465	2.5835	1.2475	103.9290

3.2. Texture co-efficient

XRD patterns also revealed that the increase of temperature induces a variation of the crystal growth texture. The texture of a particular plane can be represented by the texture coefficient TC(hkl), which can be calculated from X-ray data using the formula[18]

$$TC = \dfrac{I(hkl)/I_0(hkl)}{\frac{1}{N}\Sigma_N \frac{I(hkl)}{I_0(hkl)}}$$ ------------------- (6)

WhereI(hkl) is the measured relative intensity of the plane (hkl), I_0(hkl) is the standard intensity of the plane (hkl)takenfromthe JCPDS data, andNis the number of reflections. Any deviation of the calculated TC value from unity implies preferred growth. The texture coefficient values of CdO NPs calculated for the diffraction peak (111) are compiled inTable 2.Itcan be seen from the table that, the value of TC(111) initially decreases with increase of temperature up to 450°C and then it increases linearly with increasing temperature in the crystals.

3.3. Functional group analysis

The existence of strong cadmium oxide molecules are confirmed by the FTIR spectrum in the wavelength region of 4000–400 cm⁻¹ for the synthesized CdO nanoparticle is presented in Figure.3. FTIR spectrum shows three characteristic absorption peaks at 437, 511 and 651 cm⁻¹. A peak observed at around 470cm⁻¹ is assigned to Cd–O of CdO which confirms the formation of pure CdOnanoparticles[19]. The band at 651 cm⁻¹ indicates the vibrations of Cd-OH groups. A strong absorption band at 615cm⁻¹ is due to metal–oxygen (M–O) bond[20].
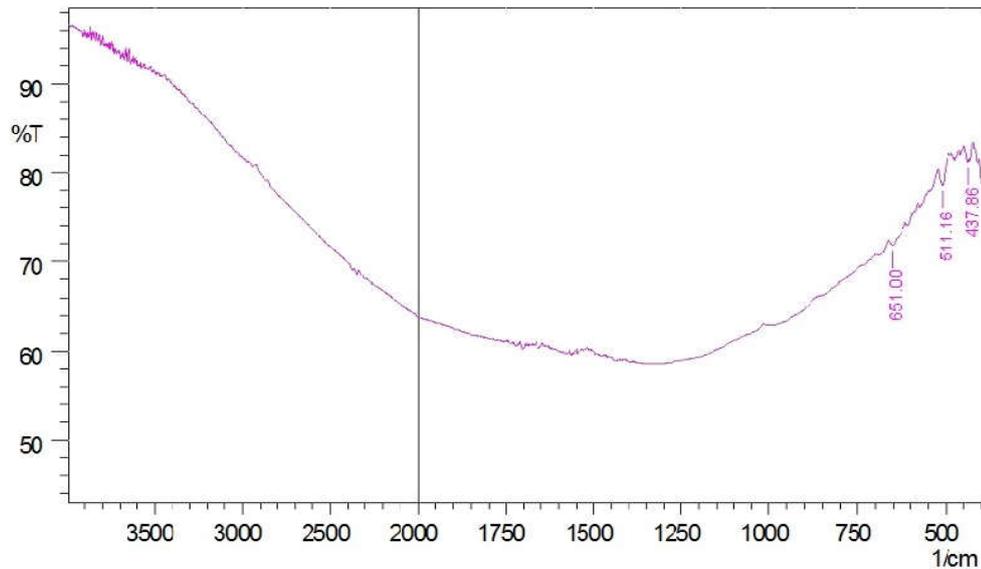
Figure 3. FT-IR spectra of CdO nanoparticle prepared at 450°C

3.4.Surface morphology

The morphology and microstructure of prepared pure cadmium oxide nanoparticles were elucidated by SEM measurements. From the Figure.4(a-b), it is observed that all the particles show spherical morphology with degree of agglomeration.Figure.4(c-d) depicts the

Figure 4. (a&b) SEM images of CdO nanoparticles at different magnifications
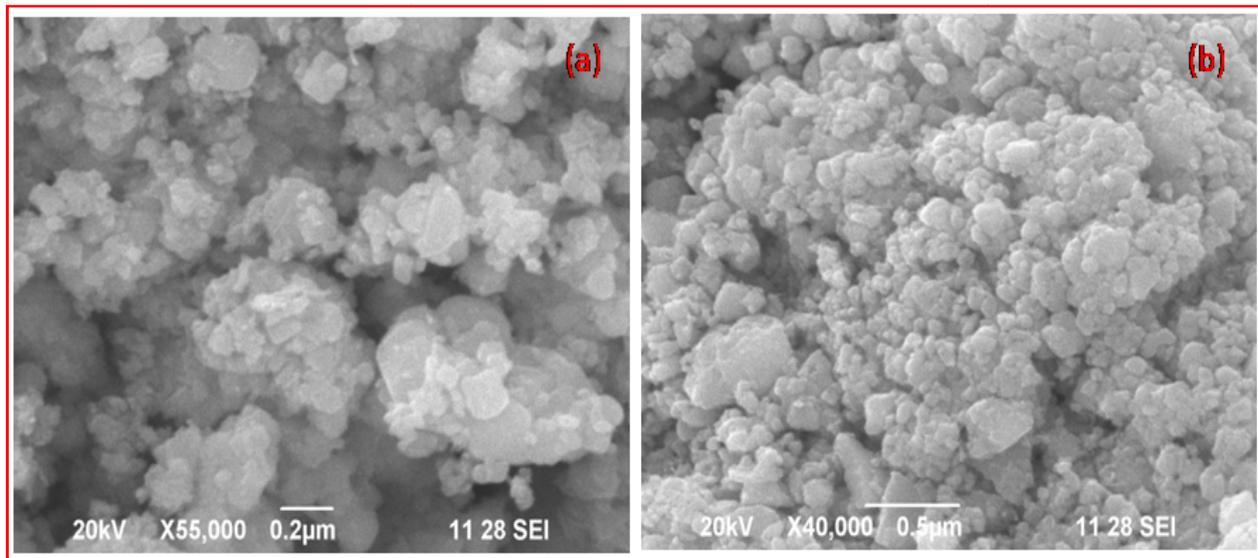
surface occupancy plot (SOP) for pure CdO nanoparticles.The EDX analysis was carried out for the pure CdO and the results are shown in Figure.5. From this figure, it can be demonstrated that the synthesized CdO spheres consisted of cadmium and oxygen, which is in agreement with nearly staichiometric ratio without any impurity.
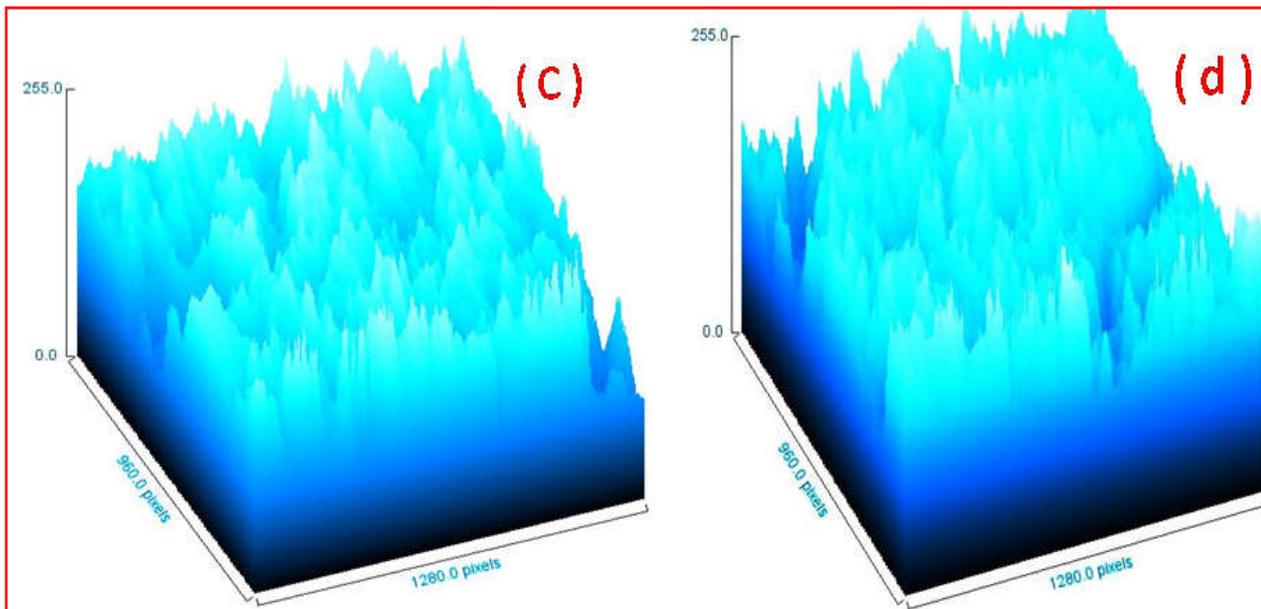
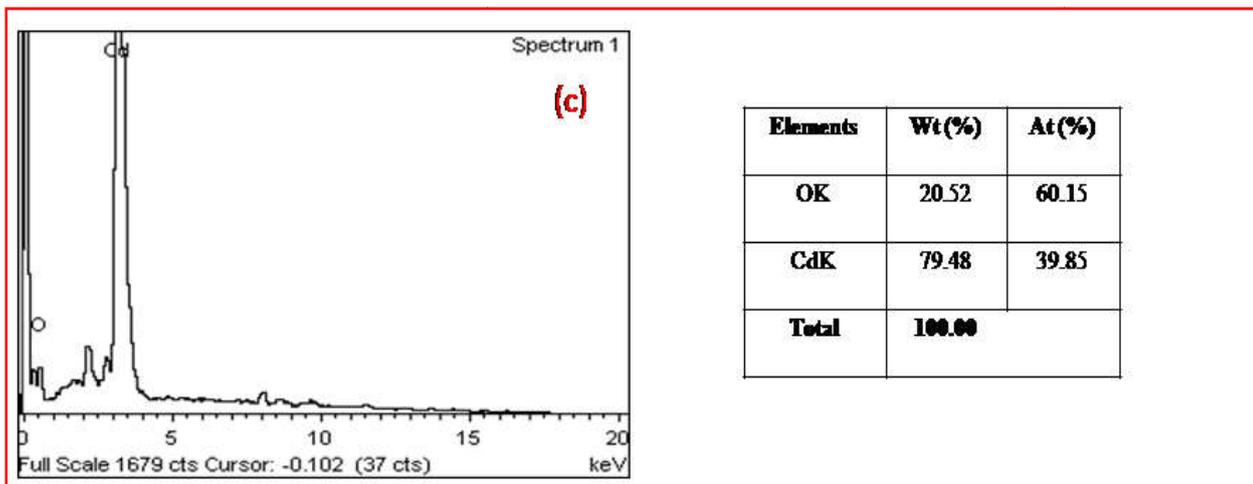**Figure 4. (c&d) Surface Occupancy Plot of CdO nanoparticles**

Elements	Wt(%)	At(%)
OK	20.52	60.15
CdK	79.48	39.85
Total	100.00	

Figure 5. EDX spectrum of CdO nanoparticles (represented sample)

3.5. Optical study
3.5.1. Evaluation of band gap energy

The absorption spectra of prepared CdO nanoparticles were illustrated in Figure.6. The absorption edge is observed at around 383 nm, which is due to the phase of cadmium oxide. The absorption co-efficient is calculated using the formula,

$$\alpha = \frac{2.303A}{l}$$

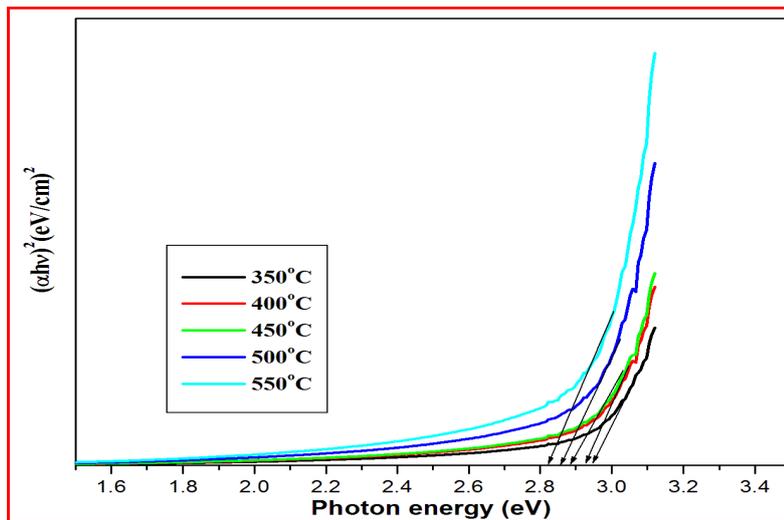where, A is the absorbance and l is the path length.

Figure 6. Absorption spectra of pure CdO nanoparticles

The value of optical band gap is determined from the absorption spectra using the Tauc relation[21],

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

where, α is the absorption co-efficient, A is the constant having separate value for different transitions, $h\nu$ is the photon energy and E_g is the band gap energy. The value of n depends upon the nature of transition. The values of n for allowed direct, allowed indirect, forbidden direct and forbidden indirect transition are 1/2, 2, 3/2 and 3, respectively. The band gap energies are found to be a negative number for n = 2, 3/2 and 3, and hence the relationship fitting to the CdO is n =1/2, which confirms the allowed direct transition. Figure.7 shows the curves of $(\alpha h\nu)^2$ versus $h\nu$ for pure CdO nanoparticles prepared at different temperatures. The E_g values are obtained by extrapolating the straight line portions of the graph to the X-axis. The measured energy band gaps from these plots are represented in Table 3. From this table, it can be observed that the E_g values varied from 2.95 to 2.82eV for Pure CdO nanoparticles prepared at different temperatures.The energy bandgap of semiconductors tends to decrease as the temperature is increased. An increased inters atomic spacing decreases the potential by the electrons in the material, which in turn reduces the size of the energybandgap
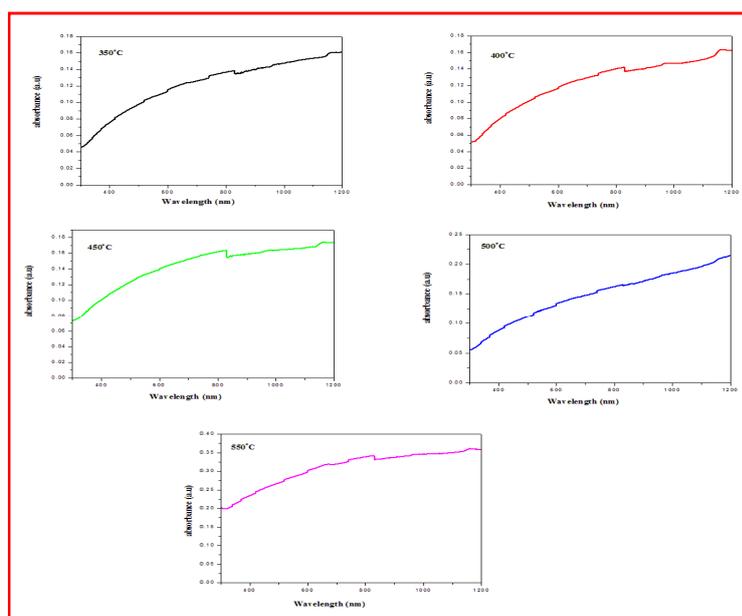

Figure 7. The plot of $(\alpha h\nu)^2$ versus $h\nu$ for Pure CdO nanoparticles

3.6. Photoluminescence spectroscopy

Figure.8 shows the PL spectra of CdO nanoparticles recorded in the wavelength range between 350 and 650nm, prepared at different calcinations temperatures (350–550°C). The PL peak intensities decreased with increasingcalcinations temperatures.
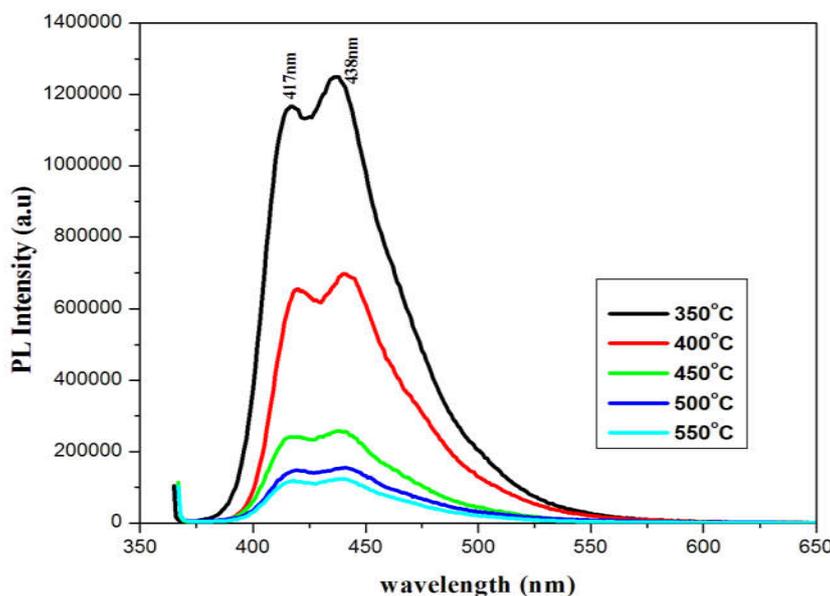

Figure 8. PL spectra of Pure CdO NPs prepared at different calcination temperatures

As the temperature increases, the quantum confinement effect is higher and the PL peak intensity is decreased. On increasing the calcinations temperature, the full width at half maximum of the photoluminescence emission peak is increased. This suggests that due to enough thermal energy supplied by increase of growth temperature atoms move to stable sites and that impurities moved to grain boundary. From the Figure.8, two emission shoulder peaks were observed for CdO nanoparticles centered at 417 (2.95 eV) and 438 (2.81eV) nm. The emission spectra exhibited that a strong violet-blue emission band at around 417–438 nm for all temperatures. This blue peak could be attributed to the O, Cd and/or Cd/O vacancies centers.

4. CONCLUSIONS

To conclude, well crystalline CdOnanoparticles prepared by simple Co-precipitation method. X-ray diffraction results show that the prepared particles are in the CdOcubic (FCC) crystalline structure without any other secondary phases and with an average size of about 27.68 nm. Meanwhile, Surface morphology observations reveal clearly that the particles are spherical in shape. The optical energy band-gap also decreases from 2.95 eV to 2.82 eV as the temperature increases. The PL emission showed the decrease of defects in the prepared particles which were decreased with the increase of temperature.This type of behavior can be definitely associated to the morphology changes induced by a photocatalytic reactions commonly carried out on cadmium oxide supports. Hence, the prepared CdO nanoparticles are promising candidate for photocatalytic dye degradation under sunlight illumination.

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