



## Green synthesis of Monteponite CdO nanoparticles by *Agathosma betulina* natural extract



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### ABSTRACT

This contribution reports on the synthesis and the main physical properties of CdO nanoparticles synthesized for the first time by a completely green process using *Agathosma betulina* plant extract as an effective bio-oxidizing/bio-reducing agent. The surface/interface and volume room temperature properties by HRSEM, EDS, XRF, XRD, ATR-FTIR, Raman, XPS and Photoluminescence are reported.

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### 1. Introduction

Nano-scaled Cadmium oxide (CdO) have attracted special interest due to their unique optical transparency combined with a significant electronic conductivity, a property which was known as back as 1907 [1]. More precisely, CdO is a III–IV n-type semiconductor with a direct large and a narrow indirect band gaps ranging within 2.2–2.5 eV and 1.36–1.98 eV respectively [2,3]. The n-type conduction is attributed to its native oxygen vacancies and cadmium interstitials. Its average electron mobility is of the order  $531 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with a significant linear refractive index of about 2.49, conjugated to a high optical transparency in the visible spectral solar range [4–7]. Consequentially, it is considered as one of the most attractive Transparent Conducting Oxides (TCOs) as the ZnO family. It is an ideal candidate for several optoelectronics applications including solar cells, phototransistors, photodiodes, and transparent electrodes for gas sensors and flat panel displays based devices [8–15]. As-grown CdO n-type films exhibit a large electron

concentration higher than  $10^{19}/\text{cm}^3$  [16]. This type of conductivity refers to rare cases where native defects, localized impurities and surface states can be donors in n-type or acceptors in p-type materials [17–19]. This is believed to be due to the location of defect level at  $\sim 1.15 \text{ eV}$  above the conduction band (CB) in CdO. As a result, the Fermi energy at the free CdO surface is always pinned at this level [20]. This is similar to the situation observed in the well-known narrow bandgap InN based materials [21]. The high free electron concentration of CdO materials also results in a blue shift in the optical absorption edge due to the Burstein–Moss effect [22,23]. In recent years, many researchers have focused on CdO based nanomaterial due to their versatile applications in optoelectronics and TCOs sector. Reduction in the dimensionality of such materials from the 3-D bulk phases to the 0-D nanoparticles can lead to enhanced properties favored by quantum size effects and additional mesoscopic effects.

Yet, it is associated to a certain degree of toxicity in relation to cadmium content itself, extensive physical and chemical techniques have been used to prepare nanostructured CdO. In this regard, epitaxial CdO thin films, and highly crystalline micro-whiskers, nano-needles, nano-belts, nano-cubes, nano-clusters, nano-wires, nano-rods, and nanoparticles have been synthesized [24–36]. Hitherto, these physical/chemical methods are very

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effective; they are complex, and environmentally not friendly in view of the required energy balance and/or generated waste. To the best of our knowledge, green synthesis of nano-scaled CdO was never reported so far. However, it was demonstrated that such an attractive approach is successful in the synthesis of noble metallic nanoparticles, Au and Ag mainly as well as some limited oxides [37,38].

This contribution reports for the first time on the synthesis and the main physical properties of highly crystalline Monteponite CdO nanoparticles by a green chemistry process using *Agathosma betulina* natural extract as an effective oxidizing/reducing agent. The physical characteristics of such CdO nanoparticles engineered without any additional standard bases/acids, are investigated by high resolution scanning electron microscopy, energy dispersive X-Ray spectroscopy, X-rays fluorescence, X-rays diffraction, attenuated total reflection-Fourier transform infrared, Raman and X-rays photon spectroscopies in addition to room temperature photoluminescence to confirm their Monteponite CdO nature.

## 2. Synthesis: green process via *Agathosma betulina* natural extract

As it is mentioned above, the originality of this contribution resides in demonstrating for the first time the possibility to synthesize CdO nanoparticles by green chemistry process. More explicitly, natural extract from the *Agathosma betulina* was used to bio-oxidize/bio-reduce several cadmium based salts including CdNO<sub>3</sub>, CdCl<sub>2</sub>, CdSO<sub>4</sub>, and Cd-Ammonium hydrate. This communication reports on the green reduction of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O as a proof of the concept of synthesis of pure Monteponite CdO nanoparticles.

*Agathosma betulina*, as is scientifically labeled, is a plant commonly known as Buchu, Bucco, iBuchu, Boegoe, or round leaf of Buch in vernacular names [39]. This plant is a sprouting shrub to 1.5 m height with about 20 mm long leaves in average, with broad but less than twice as long as wide (widest in the upper half). Rounded apex which curves backwards [40]. The flowers have five white or pale purple petals, solitary and star shaped. This plant is restricted to the Cederberg Mountains of the Western Cape Province of South Africa and Tulbagh in the South to Citrusdel and Clanwilliam in the North [40,41]. *Agathosma betulina* chemical composition is shown in Table 1 as reported below.

Dry leaves of *Agathosma betulina* were supplied from the Western Cape Province-South Africa. The identity of *Agathosma betulina* plant was confirmed by the taxonomy experts in the herbarium of the Department of Life Sciences at the University of Western Cape. The 15 g of *Agathosma betulina* leaves were weighed and washed with distilled water at room temperature. The leaves were then immersed in the de-ionized water to extract the green dye and heated at about ~100 °C for an hour. The dye extract solution was filtered twice to eliminate residual solids if there were any. The hydrated cadmium nitrate Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O was considered

as cadmium precursor. This Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O was of analytical grade reagent and was used without any further purification in view of its relatively high solubility. In a typical procedure, the required amount of cadmium nitrate (6.0 g) was homogeneously mixed with 100 ml of *Agathosma betulina* solution. This mixture was then heated at temperature of 100 °C for two hours while tightly closed. The cadmium nitrate dissolved and resulted into a fine precipitate. The as prepared deposit was washed with deionized water repeatedly, centrifuged using a Lasec Sigma 2–6 unit at 1000 rps for 10 min. The mixture was dried in an oven at 100 °C and then annealed in an open furnace at 500 °C for 2 h.

## 3. Results & discussion

### 3.1. Morphology & microscopy observations

Fig. 1 reports a typical High Resolution Scanning Electron Microscopy (HRSEM) of the annealed CdO nanoparticles at 500 °C for 2 h. The powdered sample consists of agglomerated clusters of various sizes up to 100 nm in spatial extension. More accurate analysis, yet within the limits of resolution of the HRSEM unit, one could still notice that the clusters are formed by smaller agglomerated quasi-spherical nanoparticles with diameters as small as 8 nm.

### 3.2. Elemental analysis

Fig. 2 reports a typical Energy Dispersive X-Ray Spectroscopy (EDS) spectrum collected with an Oxford instruments X-Max solid state silicon drift detector operating at 20 keV of the annealed CdO nanoparticles at 500 °C for 2 h. In addition to the expected Cd (3.15 and 3.45 eV) and O (0.52 eV) peaks, one can distinguish several additional peaks related to Au, Pd, Si, and Carbon. Excluding the Carbon (0.27 eV), these later ones correspond to the Au–Pd surface coating used to minimize the charge effects on the surface of the pelletized sample and the Si substrate respectively. The presence of carbon can be assigned to residue formed during the Cd nitrate green reaction with the *Agathosma betulina* natural extract. To confirm the CdO nature of the nanoparticles, X-Ray Fluorescence

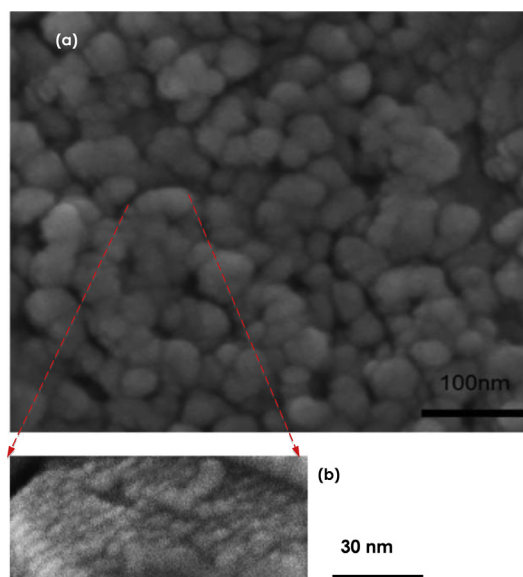


Fig. 1. (a) Typical High resolution Scanning Electron Microscopy of the annealed CdO nanoparticles at 500 °C for 2 h. (b) Zoom on a single nanoparticle showing the internal morphology consisting of several nano-grains.

Table 1  
Major bioactive compounds in the *Agathosma betulina* natural extract.

Flavonoids:	Pelargonidin-3,5-diglucoside(I), Cyanidin-3,5-diglucoside(II), Kaempferol(III);
Monoterpenoids:	β-pinene(IV) 1,8-cineol;
Tannins:	Pyrogallol(V) Catechol(VI);
Triterpenoids:	Betulinic acid(VII), α-amyrin(VIII) Oleanolic acid(IX) β-sitosterol(X)

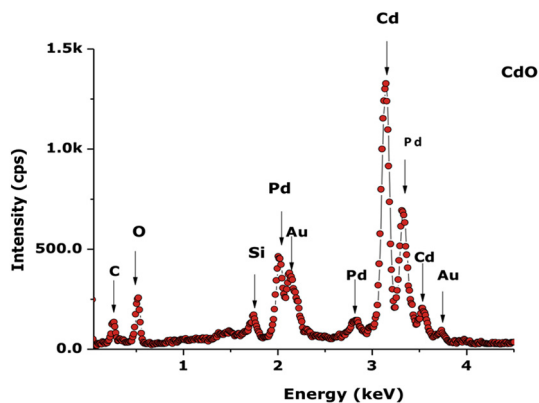


Fig. 2. Typical Energy Dispersive X-Ray Spectroscopy (EDS) spectrum of the annealed CdO nanoparticles at 500 °C for 2 h.

(XRF) investigations were carried out at various spots of the pellet. Fig. 3 shows a typical energy-dispersion XRF spectrum of the annealed CdO nanoparticles at 500 °C for 2 h. The spectrum exhibits the double Cd L-band located within 3.133–3.528 keV without any additional element [42], this reaffirms the pure chemical form of the CdO nanoparticles.

### 3.3. Structural & crystallographic analysis

The standard conditions stable phase of CdO is a cubic phase within the space group Fm 3m and a unit-cell parameter  $a = 4.694 \text{ \AA}$ . Fig. 4 reports a typical XRD profile of the CdO synthesized particles. Such a powder X-ray diffractometry was carried out using computer controlled X'pert PRO PANalytical diffractometer with a monochromatic  $\text{CuK}\alpha_1$  radiation (wavelength  $1.5406 \text{ \AA}$ ), operating at a voltage of 40 KV and a current of 35 mA, in the angular range  $2\theta$  of 20–75 deg. Five Bragg peaks are observed (Table 2) only highlighting on the high degree of symmetry of the investigated crystallites so far. More accurately, the diffraction peaks can be indexed as a cubic CdO structure (JCPD card no 05–0640) with an average lattice parameter  $\langle a \rangle = 4.701 \text{ \AA}$ . No peak from pure Cd or other Cd–O phases can be found in the XRD spectrum. This sustains the single phase of the prepared product i.e. pure CdO. The 3 peaks positioned before the (111) CdO intense Bragg diffraction are assigned to Carbon which could have originated from the synthesis process itself as highlighted in the

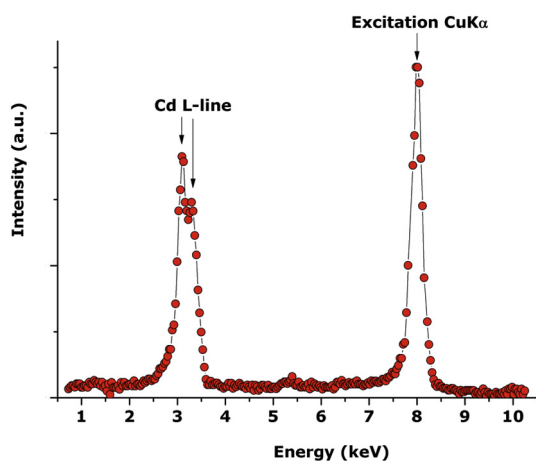


Fig. 3. Typical X-Ray Fluorescence spectrum of the annealed CdO nanoparticles at 500 °C for 2 h using  $\text{CuK}\alpha$  radiation as an excitation source.

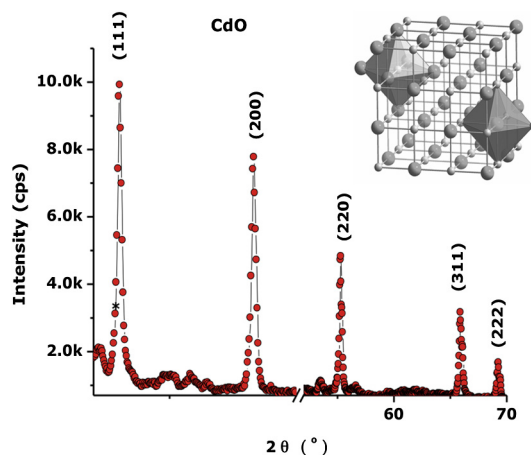


Fig. 4. Room temperature X-Rays Diffraction profile of the CdO synthesized nanoparticles at 500 °C for 2 h ( $\text{CuK}\alpha_1$  radiation =  $1.5406 \text{ \AA}$ ).

previous section. The Debye-Scherrer approximation  $\langle \phi_{\text{Particles}} \rangle \sim 0.9 \lambda / \Delta\theta_{1/2} \cos\theta_B$  allows to estimate the average diameter of the CdO nanocrystals  $\langle \phi_{\text{Particles}} \rangle$  which was found to be ranging from 25 to  $\sim 50 \text{ nm}$  in a good agreement with the previous HRSEM observations. Likewise, Table 2 shows that the ratio  $(d_{\text{hkl}}^{\text{EXP}} - d_{\text{hkl}}^{\text{BULK}}) / d_{\text{hkl}}^{\text{BULK}}$  is less than 0.03% for all hkl reticular plans except for the (111) direction. For this orientation specifically, the ratio is about  $\sim +7.5\%$  indicating that (111) reticular plans are under elongation conditions.

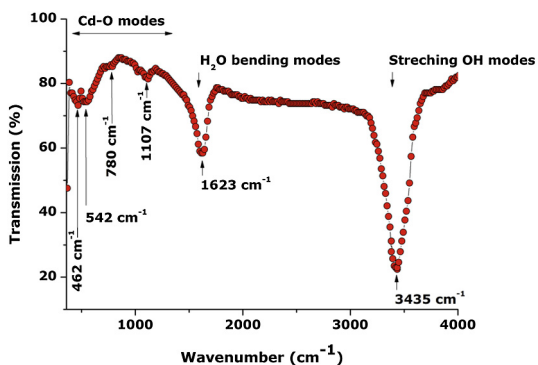
### 3.4. Vibrational properties

To validate once more the Montepelite nature of the synthesized CdO particles and their purity, Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR) studies were performed at room temperature. Fig. 5 reports the typical ATR-FTIR spectrum of the pressed powder in the spectral range of  $400\text{--}4000 \text{ cm}^{-1}$ . The IR transmission is plotted versus the wavenumber so to single out the major absorptions observed at lower wavenumbers. As one can observe, we distinguish mainly 2 relatively intense absorptions centered at approximately  $3435$  and  $1623 \text{ cm}^{-1}$ . They are associated to standard OH stretching and  $\text{H}_2\text{O}$  bending modes respectively. These OH/ $\text{H}_2\text{O}$  functional groups content could be related to surface adsorbed water or atmospheric water vapor. The ATR-FTIR spectrum shows no residual organic compounds such as  $\text{NO}_3^-$  after filtration and centrifugation. The less intense peaks located at  $462, 542, 780,$  and  $1107 \text{ cm}^{-1}$  are all associated to the stretching Cd–O modes [43–47]. The presence of these four characteristic Cd–O stretching modes supports the phase purity of the Montepelite CdO nature of the nanoparticles.

From Raman view point, bulk CdO is the only  $\text{II}_b\text{-VI}$  compound with a cubic structure of the NaCl type. This crystal structure has  $O_h$  space group symmetry [48,49]. The corresponding CdO major transverse and longitudinal optical modes are located within the Raman spectral range of  $291\text{--}1000 \text{ cm}^{-1}$  [50,51]. Fig. 6 reports the room temperature Raman spectrum using the  $532 \text{ nm}$  excitation laser line with an average excitation power of  $2.48 \text{ mW}$  in the spectral range of  $200\text{--}1000 \text{ cm}^{-1}$ . One can distinguish 3 major peaks centered at  $\sim 259.3, \sim 390.4$  and  $\sim 937.5 \text{ cm}^{-1}$ . An additional peak at about  $\sim 329.9 \text{ cm}^{-1}$  located as a shoulder of the most intense  $\sim 390.4 \text{ cm}^{-1}$  peak. Based on the experimental and theoretical results of Bilz et al., Popovic et al., Ashrati et al. as well as Cusco et al., the 4 modes are assigned to the transverse and longitudinal modes of cubic CdO with a possible internal compressive stress which might be surface effect induced.

**Table 2**  
Major XRD characteristics of the various Bragg diffraction peaks.

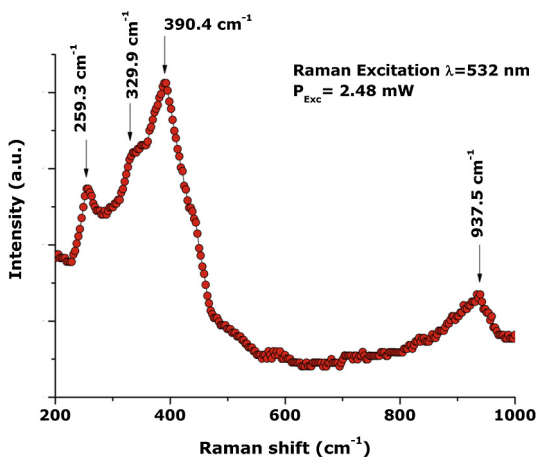
Miller indexation ( <i>hkl</i> )	$\theta_{\text{bulk}}$ (rad)	$d_{\text{bulk}}$ (Å)	$d_{\text{exp}}$ (Å)	$d_{\text{exp}} - d_{\text{bulk}}/d_{\text{bulk}}$	$\Delta\Theta_{1/2}$ FWHM ( $10^{-2}$ rad)	$\langle\phi_{\text{Particles}}\rangle$ (nm)	$a$ (nm)
(111)	0.288	2.7118	2.762	0.7561	0.378	38.2	4.676
(200)	0.334	2.3488	2.348	-0.0003	0.394	37.3	4.696
(220)	0.482	1.6603	1.660	-0.0001	0.501	31.3	4.695
(311)	0.575	1.4159	1.412	-0.0031	0.604	27.4	4.682
(222)	0.605	1.3549	1.355	-0.0000	0.635	26.6	4.693



**Fig. 5.** Typical ATR-FTIR spectrum of the pressed powder consisting of CdO synthesized nanoparticles at 500 °C for 2 h in the spectral range of 400–4000  $\text{cm}^{-1}$ .

### 3.5. Surface properties

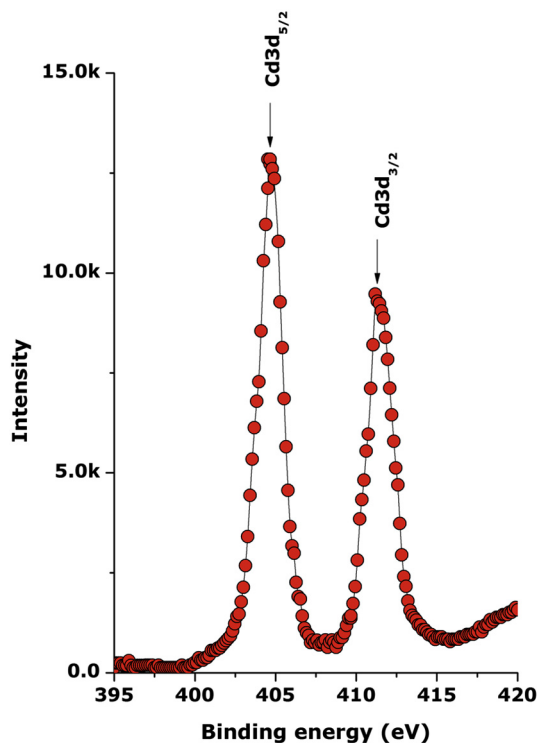
As a preliminary conclusion, and from the combined HRSEM, EDS, XRF, XRD, ATR-FTIR and Raman results, one could conclude on the phase purity of the synthesized CdO nanoparticles. To gain information on their surface chemistry, X-rays Photoemission Spectroscopy (XPS) investigations were therefore, carried out. Indeed, the species covering the surface of the nanoparticles can be detected by the kinetic-energy analysis of both valence-band and inner-shell photoelectrons. To obtain information on the surface properties of the CdO nanoparticles, the binding energies of Cd (3d) and O (1s) electrons were measured by analyzing the XPS spectra. These investigations were acquired using a constant 50 eV pass energy mode, in 0.1 eV increments at 50 ms dwell time with the signal averaged for at hundreds of regular scans. The XPS system was equipped with a dual Mg  $K\alpha$ –Al  $K\alpha$  anode for photo excitation.



**Fig. 6.** Typical room temperature Raman spectrum using the 532 nm excitation laser line with an average excitation power of 2.48 mW in the spectral range of 200–1000  $\text{cm}^{-1}$ .

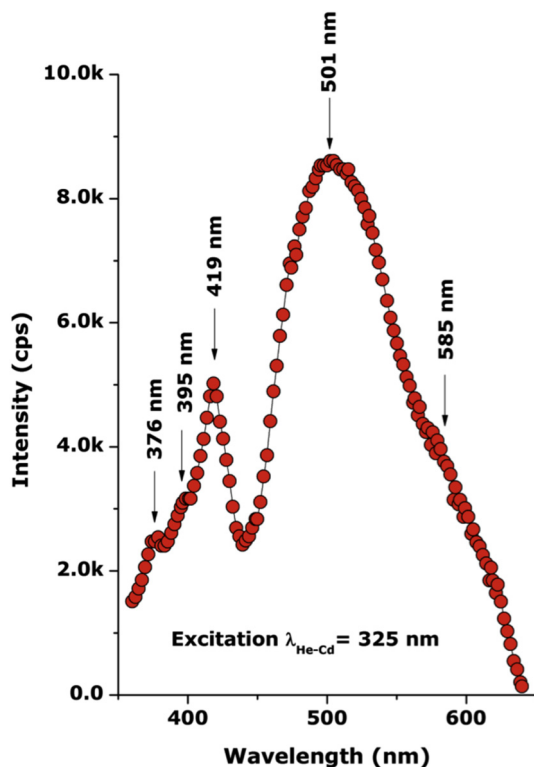
**Fig. 7** reports a typical core level spectra of the Cd (3d) that consists of the Cd  $3d_{5/2}$  and Cd  $3d_{3/2}$  spin orbit components that are located at binding energy of 405.0 and 411.7 eV, respectively which are in agreement with those reported by Gulino et al., and Gujar et al. [52,53]. Such a binding energy of the Cd (3d) is attributed to the  $\text{Cd}^{2+}$  bonding state and hence the CdO single phase of the synthesized samples.

As a follow up of the EDS, XRF, XRD, ATR-FTIR, Raman and XPS investigations, room temperature photoluminescence (PL) studies were conducted to estimate the nature and the density of the defects and ion deficiencies if any. Indeed the photoluminescence phenomenon is directly related to electronic structure and transitions. Differences in the electronic behavior between bulk semiconductor and their nano-scaled counterpart arise due to the difference in the electronic density of states. An excitation wavelength  $\lambda_{\text{exc}} = 325$  nm from a He–Cd laser source was used to conduct the room temperature PL measurements. **Fig. 8** reports the PL spectrum of the annealed CdO nanoparticles at 500 °C for 2 h. One can distinguish a broad VIS emission centered at about ~ 501 nm with a shoulder at ~ 585 nm in addition to a relatively sharp UV emission at ~ 409 nm and 2 additional less intense peaks at about ~ 376 nm and ~ 395 nm respectively. The UV emission peak at 409 nm is well known to be related to the exciton emission. The mechanism of VIS emission centered at 501 nm within the spectral



**Fig. 7.** Typical core level spectra of the Cd (3d) that consists of the Cd  $3d_{5/2}$  and Cd  $3d_{3/2}$  spin orbit components.





**Fig. 8.** Room temperature photoluminescence spectrum of the annealed CdO nanoparticles at 500 °C for 2 h. The excitation wavelength  $\lambda_{\text{exc}} = 325 \text{ nm}$  from a He–Cd laser source was used.

range of 450–600 nm, is suggested as mainly due to the presence of various point defects, either extrinsic or intrinsic, which can easily form recombination centres [54–57]. The emissions centered at ~376 nm and ~395 nm are attributed to deep level emissions usually appearing due to surface effects [58–66].

#### 4. Conclusions

The synthesis of single phase highly crystalline CdO nanoparticles by green novel and environmental friendly pathway using the natural extract of *Agathosma betulina*'s extract as an effective oxidizing/reducing chemical agent was demonstrated. A thermal annealing of ~500 °C during ~2 h under normal air conditions allows to obtain highly crystallized single phase CdO nanoparticles as substantiated by the HRSEM, EDS, XRF, XRD, ATR-FTIR, Raman, XPS, and PL investigations. The follow up study will consist of identifying the physical/chemical mechanisms and the dynamic formation of the CdO nanoparticles during the interaction of the Cadmium salt precursor and the *Agathosma betulina*'s natural extract compounds. More specifically, the bioactive compound (s) would be identified. In addition, the synthesis of less stable oxides such as CdO<sub>2</sub> nanoparticles is being investigated.

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