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Phthalate precursor mediated synthesis of cadmium oxide nanoparticles and their photocatalytic application

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Cadmium oxide samples have been prepared by thermal decomposition of their precursors [Cd(pht)(H_2O)] (**1**), [Cd(pht)(Im)(H_2O)$_{0.5}$] (**2**), [Cd(pht)(MeIm)] (**3**) and [Cd(pht)(bpy)(H_2O)$_2$] (**4**) respectively (pht = phthalate, Im = imidazole, MeIm = 2-methylimidazole, bpy = 2,2′-bipyridine). Precursor **1** has been synthesized by a reaction of *in situ* generated disodium phthalate with cadmium acetate, while **2-4** were prepared by adding Im, MeIm and bpy respectively, to the solution of **1**. All compounds are characterized by elemental analysis, infrared spectroscopy and thermal techniques (TG/DTA). The particle size of CdO nanoparticles ranges from 53–62 nm as evident by PXRD, SEM/ TEM studies. The band gap values for CdO samples lie in the range 1.95–1.98 eV. The photolytic degradation rates of methylene blue by CdO are inversely proportional to the crystallite sizes of CdO samples.

Keywords: Nanoparticles, Oxides, Cadmium oxide, Photocatalytic degradation, Dye degradation, Methylene blue, Thermogravimetry, Phthalate precursors

The synthesis and characterization of nanomaterial oxides of transition metals is a rapidly growing area of research in the world of nanotechnology. The nanosized metal oxides have been prepared by different synthetic routes and known for their wide applications. The precursor method has been frequently used as one of the methods for production of various metal oxide (as well as mixed metal oxide) nanoparticles[1-4]. The right choice of synthetic route often decides morphology, shape, size, phase distribution and other structural parameters of the nano sized oxides. In recent years, the cadmium oxides with different particle size have been extensively explored by material scientists[5-10]. CdO behaves as an *n*-type semiconductor with direct band gap between 2.2 - 2.5 eV and an indirect band of 1.36 - 1.98 eV[11]. Although the precursor method is quite popular, several other methods such as hydrothermal[12], solvothermal method[13], pyrolytic[14], sonochemical[15], mechanochemical[16], precipitation[10,17], sol-gel[18] and microwave synthesis[6,19,20] for the preparation of CdO nanoparticles are also reported.

The increasing growth of production of chemicals and their release into the environment as waste products has contributed largely to the environmental pollution. Water pollution caused due to the discharge of coloring dyes and pigments by the textile, food and dyeing industries is a major global concern[12]. Methylene blue (MB), an organic dye used as a decontaminant for removing other dyes and organic contaminants is an equally potential and hazardous pollutant[21]. Several conventional methods involving the use of charcoal filtration, coagulation, ozonization, incineration, biodegradation, etc., are often used for the removal of methylene blue. However, these procedures have various drawbacks such as high disposal waste, residues of low molar mass dye fragments, high-cost treatment, conversion of pollutants from one phase to another, which have let to their limited use[14,22].

Metal oxides play significant roles as photocatalysts in the treatment of effluent waste waters released by the industries. A small amount of photocatalytically active oxide is sufficient to degrade the harmful and water soluble dyes under the readily available sunlight[22]. The photodegradation of MB using graphene-SnO_2 composites[21], $BaTiO_3$ in combination with UV/H_2O_2[22] ZnO[23], TiO_2 nanoparticles[24] titanomagnetite[25], manganese oxide with H_2O_2[26] have been reported. Here we report the synthesis of CdO nanoparticles from the well-characterized Cd-phthalate precursors and their photolytic activity in the biodegradation of methylene blue.

Materials and Methods

All chemicals were procured commercially and used without further purification. Deionized water was used for the preparations of all the aqueous solutions. The infrared spectra were recorded in the region between 4000 and 400 cm^{-1} on a Shimadzu FT-IR spectrometer (IR-Prestige-21). Elemental analysis (C, H, and N) was carried out using Elementar Variomicro Cube CHNS Analyzer. The cadmium content of precursors **1-4** was estimated by complexometric titration[27]. The thermogravimetric (TG) and differential thermal analysis (DTA) was carried out on a NETZSCH STA 409PC Luxx thermal analyzer with a heating rate of 10 °C min^{-1} in the temperature range of 30–700 °C. The spectral changes for the degradation of MB were monitored at ~665 nm using an Agilent diode array 8453 UV-vis spectrophotometer. The PXRD patterns were recorded (2θ (deg.): 20–80) on a Rigaku Miniflex diffractometer with Cu-Kα radiation at CSIR-National Institute of Oceanography, Goa. The diffused reflectance spectra of CdO samples were recorded in the range of 200-800 nm using a Shimadzu UV 2450, UV-vis spectrophotometer with $BaSO_4$ as standard. The morphologies of CdO nanoparticles were investigated by scanning electron microscopy using a Zeiss EVO 18 instrument equipped with EDX (Ametek Inc USA) facility as well as by transmission electron microscopy (TEM). For recording the TEM images, the samples were well dispersed in isopropanol and drop coated on a carbon coated Cu grid (200 mesh). Subsequently, the sample coated grid was dried in vacuum and used for recording the images. on a FEI, TECNAI G2 F20 instrument (accelerated voltage: 200 kV; Cs: 0.6 mm: resolution = 0.17 nm).

Synthesis of CdO precursors

Synthesis of [Cd(pht)(H_2O)] (**1**) was carried out as follows: To a hot solution of phthalic acid (1.7 g, 0.01 mol) (20 mL H_2O), $NaHCO_3$ (1.7 g, 0.02 mol) was added slowly with continuous stirring. Once the solution was clear and no brisk effervescence of CO_2 was observed, $Cd(CH_3COO)_2.2H_2O$ (2.7 g, 0.01 mol) was added to this hot solution. On cooling, the polycrystalline white solid was obtained by filtration. The compound was air dried. Yield (**1**): 2.7 g. Anal. (%): Calc. for $CdC_8H_6O_5$: C, 32.62; H, 2.05; Cd, 38.16. Found: C, 32.35; H, 2.03, Cd 37.78. IR (KBr, cm^{-1}): 3346 *ν*(OH); 1555 $\nu_{asym}(COO^-)$; 1412 $\nu_{sym}(COO^-)$.

[Cd(pht)(Im)$(H_2O)_{0.5}$] (**2**) was obtained as follows: $Cd(CH_3COO)_2.2H_2O$ (2.7 g, 0.01 mol) was added to a hot stirring solution of phthalic acid (1.7 g, 0.01 mol) and $NaHCO_3$ (1.7 g, 0.02 mol), followed by addition of imidazole (0.7 g, 0.01mol). The crystalline compound obtained after two days was filtered and air dried. Yield (**2**): 1.9 g. Anal. (%): Calc. for $CdC_{11}N_2H_9O_{4.5}$: C, 37.36; H, 2.57, N, 7.92; Cd, 31.78. Found: C, 37.82; H, 2.74; N, 8.42, Cd, 32.28. IR (KBr, cm^{-1}): 3338 ν(OH), 1558 $\nu_{asym}(COO^-)$, 1404 $\nu_{sym}(COO^-)$.

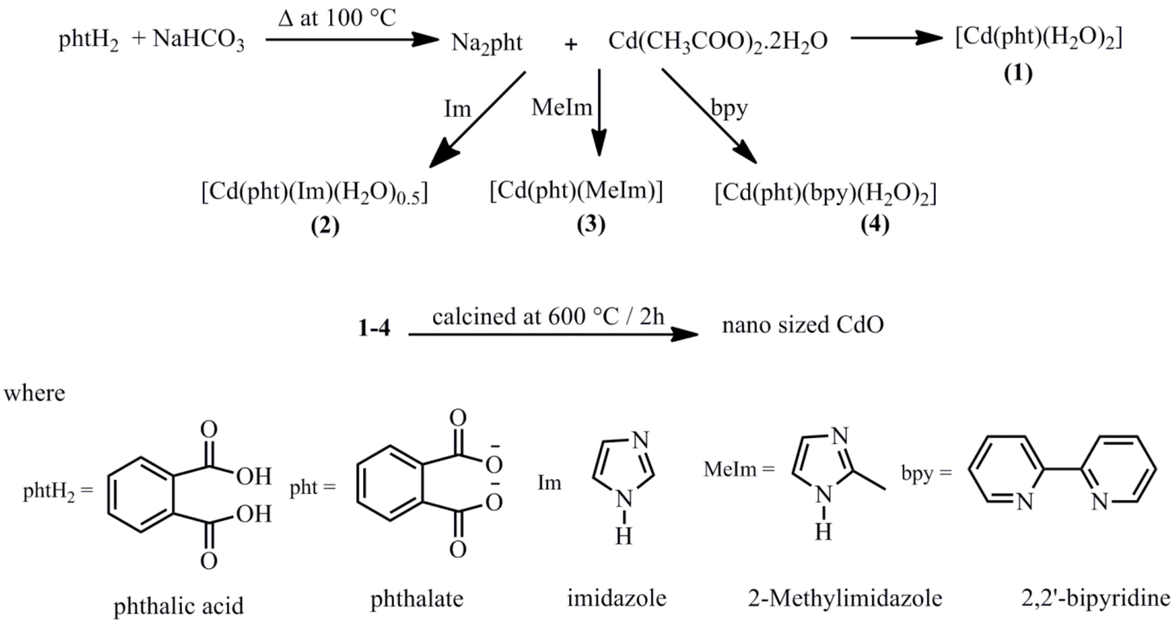
Compounds **3** and **4** were prepared similarly using 2-methylimidazole (0.8 g, 0.01mmol) for **3** and 2,2′-bipyridine (1.6 g,0.01 mmol) for **4**. Yield (**3**): 3.5 g. Anal. (%): Calc. for $CdC_{12}H_{10}N_2O_4$: C, 40.19; H, 2.81, N, 7.81; Cd, 31.34. Found: C, 39.56; H, 2.72; N, 7.70; Cd, 30.71. IR (KBr, cm^{-1}): 3234 ν(NH), 1550 $\nu_{asym}(COO^-)$, 1407 $\nu_{sym}(COO^-)$. Yield (**4**): 2.7 g. Anal. (%): Calc. for $CdC_{18}H_{16}N_2O_6$: C, 46.12; H, 3.44; N, 5.98; Cd, 23.98. Found: C, 45.60; H, 3.31; N, 5.96; Cd, 24.42. IR (KBr, cm^{-1}): 3389 *ν*(OH), 1565 $\nu_{asym}(COO^-)$, 1409 $\nu_{sym}(COO^-)$.

Synthesis of CdO nanoparticles

The samples of CdO were prepared by thermal decomposition of their precursors [Cd(pht)(H_2O)] **1**, [Cd(pht)(Im)$(H_2O)_{0.5}$] **2**, [Cd(pht)(MeIm)] **3** and [Cd(pht)(bpy)$(H_2O)_2$] **4**. The residue from **1** is labelled as **1a** and **2a**, **3a** and **4a** for those obtained from **2**, **3** and **4** respectively. For a representative synthesis of CdO, 2.5 g of the powdered precursor sample was taken in a previously weighed silica crucible and sintered at 600 °C for 2 h in a furnace. The final residue left in the crucible was 1.12 g for precursor **1** which corresponded to CdO (calc. 1.09 g). Other oxides were prepared similarly. The precursors **1-4** were subjected to TG-DTA analysis, where the weighed samples of **1-4** were taken in an alumina crucible and heated at 700 ^{o}C in TG furnace (*vide infra*). The corresponding weight loss in TG plot suggested the formation of CdO residue.

Photolytic degradation of methylene blue

Four Erlenmeyer flasks (50 mL) containing aqueous methylene blue solution (6×10^{-5} *M*, 25 mL H_2O) and 0.1 g of finely ground samples of CdO (**1a-4a**) were exposed to sunlight for 3 h between 10:00 a.m. and 1:00 p.m. After every 10 minutes, 3 mL of the sunlight-exposed methylene blue solution was taken in a test tube and centrifuged to separate the fine powder of CdO at the bottom. The changes in the absorbance at 665 nm in the UV-vis spectrum of methylene blue were noted after every 10 min for each sample. After the measurement of absorbance, the solutions were transferred back to the parent flasks for further degradation process.



Synthetic route to obtain cadmium precursor complexes and CdO nanoparticles

Scheme 1

Results and Discussion

Synthesis of precursors and CdO samples

A simple method for the preparation of the precursors **1-4** has been adopted in this investigation. The *in situ* generated sodium phthalate (by the reaction of phthalic acid and NaHCO$_3$) was treated with Cd(CH$_3$COO)$_2$.2H$_2$O to afford precursor **1**. To an aqueous solution of **1**, the N-donor ligands imidazole, 2-methylimidazole and 2,2′-bipyridine were added to obtain the precursors **2-4**. A general synthetic strategy followed for the preparation of precursors **1-4** is shown in Scheme 1. The coordination polymer [Cd(pht)(H$_2$O)] **1** was earlier reported by a reaction of Cd(NO$_3$)$_2$.4H$_2$O and phthalic acid under an alkaline medium[28] as well as using a hydrothermal method[29]. The imidazole coordinated Cd(II)-phthalate with polymeric composition [Cd$_2$(pht)$_2$(Im)$_4$]·(H$_2$O) has been earlier synthesized by hydrothermal method[30]. The cadmium(II) complexes containing the ligand Im and other carboxylic acids are also known[31]. Interestingly, following the above preparation method, we obtained a new Cd(II)-phthalate complex of imidazole which has been formulated as [Cd(pht)(Im)(H$_2$O)$_{0.5}$] (**2**) based on C,H,N analysis (Supplementary Data, Table S1), isothermal weight loss studies, and thermal data (TG) corroborated with IR spectroscopy (vide infra). Similarly, compounds **3** and **4** containing 2-methylimidazole and 2,2′-bipyridine were formulated as [Cd(pht)(MeIm)] and [Cd(pht)(bpy)(H$_2$O)$_2$] respectively. The bpy incorporated cadmium(II) phthalate with a formula [Cd(pht)(bpy)(H$_2$O)$_2$] has been earlier reported[32]. Thermal decomposition of compounds **1-4** was carried out in an electric furnace at 600 °C to obtain CdO nanoparticles.

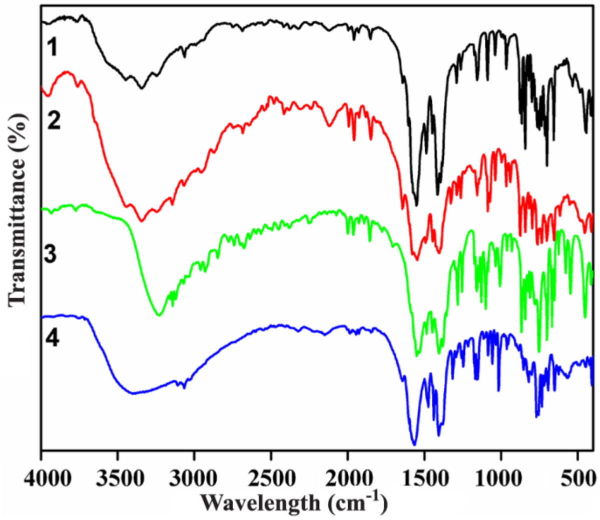


Fig. 1 – Infrared spectra of the precursors, [Cd(pht)(H$_2$O)] **1**, [Cd(pht)(Im) (H$_2$O)$_{0.5}$] **2**, [Cd(pht)(MeIm)] **3**, and, [Cd(pht)(bpy)(H$_2$O)$_2$] **4**.

Infrared spectral characterization of precursors 1-4

The infrared spectra of compounds **1-4** were recorded to investigate the bonding modes of carboxylate as well as N-donor ligands with cadmium(II) ion (Fig. 1). The broad absorption peaks at ~3346, ~3338 and 3389 cm^{-1} in precursors **1**, **2** and **4** respectively are attributed to the O-H stretching vibrations of the coordinated H_2O molecule(s). The O-H vibration stretching is not observed in the IR spectrum of **3,** indicating the absence of coordinated water. Similar bands were also reported for carboxylate complexes of zinc(II) and copper(II) ions with imidazole and 2-methylimidazole[33,34]. The N-H stretching vibration[33-35] in the IR spectrum of **3** appears at ~3234 cm^{-1} which are not clearly seen in the IR of **2** due to the overlap of O-H stretching band. The presence of the peak due to protonated carboxylic group[36] in cadmium hydrogen phthalate at ~1719 cm^{-1} and the absence of this band in **1-4**, indicate that the phthalic acid moiety is completely deprotonated[29,36]. The strong absorption bands in the region of 1550-1565 cm^{-1} and 1404-1412 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the coordinated phthalate ligand respectively[29,33,34,37,38]. The IR spectra of cadmium oxide residues were free of any bands due of organic moieties.

TG-DTA analysis

All the four precursors showed different thermal decomposition profiles with well resolved exo- and endothermic peaks in their DTA patterns (Fig. 2 for **1**, Supplementary Data, Fig. S1 for **2**, **3**, **4**). TG graph showed an initial weight loss of 6.8% between the temperatures 135-185 °C for **1**, 2.7% from 75-107 °C for **2** and 7.8% from 85-145 °C for **4** associated with the corresponding endothermic peaks in the DTA profiles which were assigned to the mass loss of one, half and two water molecules in compounds **1**, **2** and **4** respectively. The isothermal mass loss studies of **1**, **2** and **4** also showed loss of one, half and two water molecules respectively when compounds were heated in the oven up to 200 °C. For compound **3**, no mass loss in the TG and absence of exo/ endo peaks in DTA were observed till 200 °C. Thus this result along with IR data (vide supra) unambiguously suggests the absence of water in compound **3**. The major weight losses were observed between 230-450 °C in TG accompanied by exothermic DTA peak at ~410 °C for all four compounds. This major weight loss at high temperature has been attributed to the oxidative decarboxylation of the phthalate ligand as well as simultaneous decomposition of imidazole/ bpy moieties. In addition to above, the compounds **2-4** showed an endothermic peak at ~300 °C corresponding to the loss of Im/ MeIm/ bpy amines. The decomposition was almost over at ~450 °C to give CdO for all precursors.

Characterization of cadmium oxide nanoparticles

The synthesized CdO nanoparticles were characterized by PXRD, SEM-EDAX, TEM and UV-DRS techniques. The overlaid X-ray powder patterns of the CdO samples, **1a-4a**, are displayed in Fig. 3. The diffracted peaks were matched with the standard JCPDS data (file no. 03-065-29081049) which confirmed face centered cubic (FCC) phase of CdO in all the cases[19,20]. The average crystallite sizes of **1a-4a** were calculated using Scherrer's equation, D = Kλ/β cos θ where D = average size of the crystallite grain, K = constant (0.9), λ = 1.5418 Å (Cu-Kα radiation), β = full width at half maxima, θ = diffraction angle. The crystallite sizes of **1a-4a** were 52.65, 58.21, 59.52 and 62.02 nm respectively.

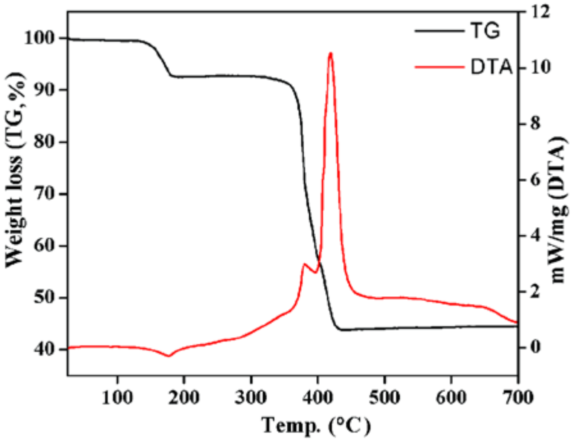


Fig. 2 – TG/DTA of precursor complex [Cd(pht)(H_2O)] (**1**).

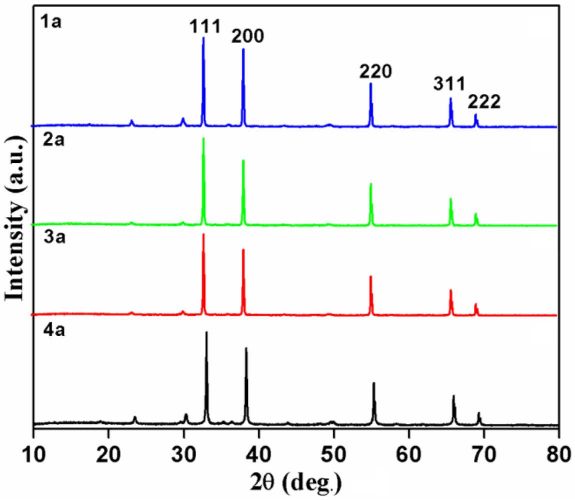


Fig. 3 – XRD powder patterns of CdO nanoparticles (**1a-4a**) obtained from precursors **1-4**.

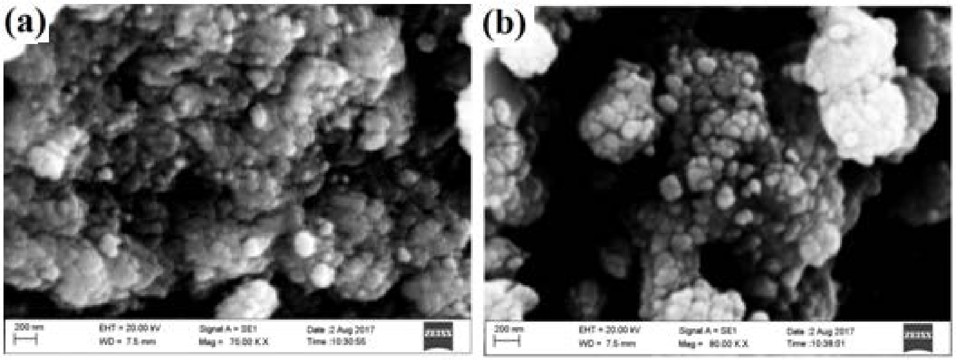


Fig. 4 – SEM images of CdO nanoparticles obtained from precursors **1** and **2**. [(a) **1a**; (b) **2a**].

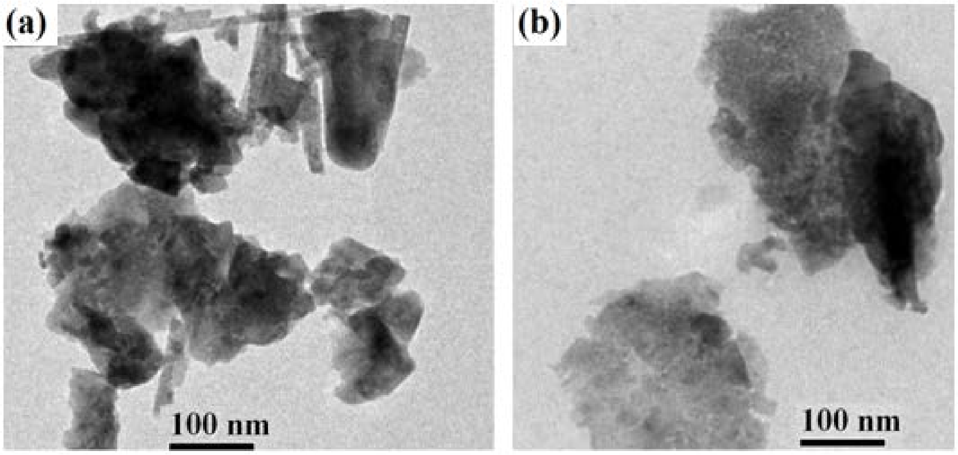


Fig. 5 – TEM images of CdO nanoparticles obtained from precursors **1** and **2**. [(a) **1a**; (b) **2a**].

The SEM images of CdO samples exhibit the agglomeration of granular nanoparticles with particle size ranging from 50–70 nm (Fig. 4, Supplementary Data, Fig. S2). These are in good agreement with the values obtained by PXRD (vide supra). EDAX data revealed the absence of impurity peaks like carbon and nitrogen elements in the synthesized CdO (Supplementary Data, Fig. S3). The particle sizes obtained from PXRD and SEM are further supported by TEM. TEM images revealed the particle size of agglomerated grains with average grain size of ~50 nm (Fig. 5).

The diffuse reflectance spectra (DRS) of **1a-4a** were obtained from Tauc plots[39] (Fig. 6, Supplementary Data, Fig. S4). The band gap energies of **1a-4a** lie between 1.95 eV and 1.98 eV and are less than the band gap energy of commercial CdO[40] (Eg = 2.34 eV) (Supplementary Data, Fig. S4).

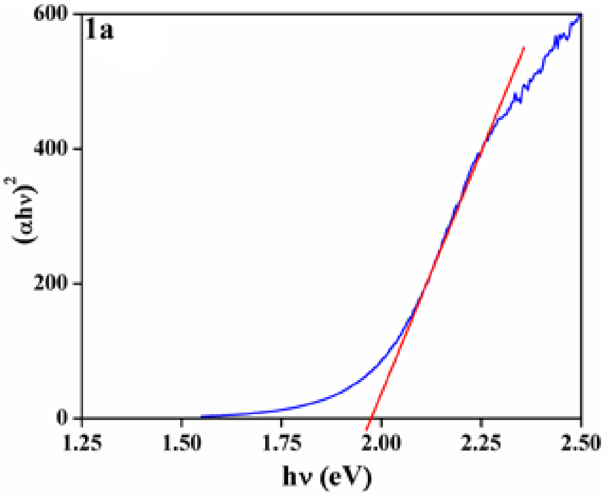


Fig. 6 – Tauc plots for determination of band gap of CdO (**1a**).

Photolytic degradation of methylene blue by CdO nanoparticles

The application of CdO nanoparticles in the photolytic degradation of methylene blue (MB) was investigated. In this experiment, the powdered oxides **1a-4a** were added to the MB solutions of known concentration and these solutions were exposed to sunlight during 10:00 a.m. to 1:00 p.m. At fixed time intervals of 10 min, the light-exposed MB extracts were centrifuged and the changes in the absorbance at

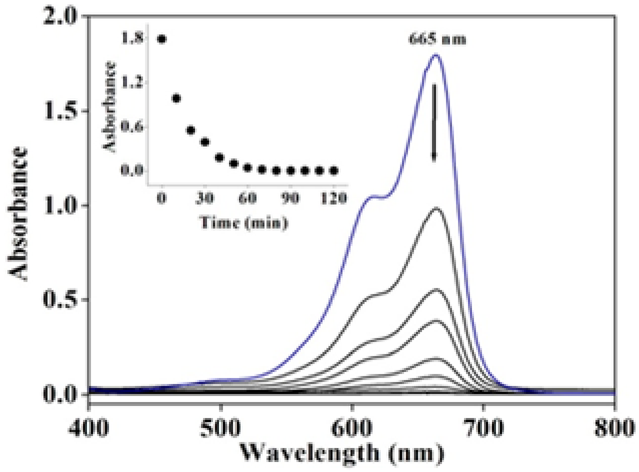


Fig. 7 – UV-visible spectral changes for the photodegradation of methylene blue dye solution (6×10^{-5} *M*) containing nanoparticles of CdO (**1a**). [The inset shows the pseudo-first order time trace at 665 nm].

λ_{max} = 665 nm were monitored (Fig. 7 for **1a**) (see also Figs S5-S7 for **2a-4a,** Supplementary Data). On comparing the time dependant decay of peak at 665 nm, we observed that **1a** effectively degraded the MB dye and the degradation reaction was completed in 60 min (Supplementary Data, Fig. S8). Further, the rates of photolytic degradation of MB were found to be inversely proportional to the crystallite sizes of **1a-4a**. Thus, sample **1a** with a crystallite size of 52.65 nm was able to degrade MB in less time compared to the time taken by **4a** (150 min), which has a crystallite size of 62.02 nm, while **2a** and **3a** took 90 and 110 min respectively. The commercial CdO showed no photolytic degradation of MB under identical conditions. The fast rate of degradation by **1a** was also correlated with the composition of the precursors **1-4**. Precursors **2-4** contain N-donor Im, MeIm, bpy and phthalate, while **1** contains only the phthalate ligand.

After the first cycle of degradation, **1a-4a** were recovered and used in the second cycle after reactivating them by heating at 200 °C for one h. The recycled samples were then characterized by PXRD, SEM/EDAX and TEM (Supplementary Data, Figs S9-S11). The degradation rates of the oxide samples in the second and third cycles remained almost constant and followed the same order: **1a** > **2a** > **3a** > **4a**. At the end of each cycle, quantitative amounts of oxides were recovered. In the mechanism of photolytic degradation of MB by CdO, the semiconducting CdO on exposure to sunlight (hυ) excites an electron (e^-) from the valence band (VB) to a conduction band (CB) leaving a positive hole (h^+) in the VB.[41,42] An electron from the CB then combines with the adsorbed molecular O_2 which subsequently leads to the formation of highly reactive hydroxyl radical ($OH^{\cdot}$) which reacts with MB and completes the degradation.

Conclusions

CdO nanoparticles were synthesized from cadmium phthalate precursors with or without N-donor ligands. Thermal decomposition of the precursors **1**, **2** and **4** showed an initial loss of water molecules followed by decomposition of nitrogen donor organic moieties and subsequent oxidative decarboxylation of phthalates to give CdO nanoparticles. PXRD patterns of the CdO nanomaterials suggest a face centered cubic structure. The crystallite sizes of CdO nanoparticles obtained by PXRD were further authenticated by SEM and TEM data. The CdO nanomaterials were effectively used as photocatalysts in the degradation of MB. The rates of degradation were inversely proportional to the crystallite sizes of **1a-4a**.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/1014-1020_SupplData.pdf.

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