



# Single-source precursor approach for the preparation of CdS nanoparticles and their photocatalytic and intrinsic peroxidase like activity

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## ABSTRACT

CdS nanoparticles (NPs) with different shapes and sizes (rods and spheres) have been synthesized through decomposition of a newly synthesized precursor complex  $[\text{Cd}(\text{SOCPh})_2\text{Lut}_2]$  using structure-directing solvents such as ethylenediamine (EN), dimethylsulfoxide (DMSO) and ammonia ( $\text{NH}_3$ ). In addition, CdS NPs is also prepared by thermal decomposition of the precursor complex under  $\text{N}_2$  atmosphere. The precursor complex is characterized by elemental analyses, TGA, FTIR, UV–vis spectroscopy and single crystal X-ray diffraction. The distorted tetrahedron geometry of the precursor complex has been determined by X-ray diffraction, which crystallizes in monoclinic crystal system of  $P2(1)/n$  space group with  $a = 11.0487(17)\text{Å}$ ,  $b = 16.396(3)$ ,  $c = 15.413(2)\text{Å}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 109.708(4)^\circ$ ,  $\gamma = 90.00^\circ$  and  $Z = 4$ . The CdS NPs are characterized using powder X-ray diffraction, transmission electron microscopy, BET analyses, UV–vis absorption and photoluminescence spectroscopy. The photo-catalytic activity of CdS NPs is studied by the degradation of Rose Bengal (RB) dye, indicating an excellent photocatalytic activity compared to that of commercial  $\text{TiO}_2$ . The mechanism behind photocatalytic degradation of RB in presence of CdS NPs is elucidated using terephthalic acid photoluminescence probing technique and evidence have shown that the photogenerated holes to be the predominant active species. This paper also demonstrates the intrinsic peroxidase like activity of CdS NPs toward peroxidase substrates 3,3',5,5'-tetramethyl benzidine (TMB) and hydrogen peroxide. Kinetic analysis indicates that the catalysis by CdS NPs show typical Michaelis–Menten kinetics. Moreover, our synthesized CdS NPs show higher catalytic performances with a higher binding affinity for the substrate TMB than horseradish peroxidase (HRP) and other recently reported nano-mimetics.

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## 1. Introduction

Organic dyes, phenolic compounds and their derivatives are commonly used in various and most of which are highly toxic and can remain in the environment in waste water for a long time [1]. Although a variety of physical, chemical and biological methods are used for treatment of waste water, majority of these processes are expensive and not highly effective [2]. In this regard, uses of semiconducting nanomaterials for degradation of organic pollutants have many advantages over other methods because of their environmental friendliness oxidation, mild reaction condition and low concentration usage [3].  $\text{TiO}_2$  is a well-known catalyst for photodegradation of toxic organic compounds; however, it is

catalytically active only under UV irradiation because of its wide band gap energy [4]. Consequently, there is considerable demand for materials which are active in the visible region, since visible light is the main component in solar light and indoor illuminations [5]. Hence, alternate semiconductor nanomaterials as photocatalyst have been a topic of contemporary interest [6]. To this end, there are a lot of visible-light responsive photocatalysts such as ZnS, CdS,  $\text{Bi}_2\text{S}_3$ ,  $\text{In}_2\text{S}_3$ ,  $\text{CdIn}_2\text{S}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , CuO, ZnO,  $\text{MnO}_2$ ,  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$  etc. have been reported in literatures [7–15]. In this work, we have chosen Rose Bengal (RB) dye to test the photoactivity, since it is a fluorescent dye and an important class of synthetic organic compound commonly used in textile, photographic and photochemical industries and therefore it is a common industrial pollutant. Few works have been made for the photocatalytic decomposition of RB in presence of semiconductor nanomaterials [16].

Moreover, peroxidases are the enzymes that typically catalyze the chemical reactions in a biological cell. The natural enzymes are efficient and higher specific biocatalyst under mild conditions.

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Due to their especial properties, natural enzymes also have significant applications in medicine, chemical industry, food processing and agriculture; however, it has some serious disadvantages [17]. In recent years, artificial enzymes have drawn prospective interest due to their simpler preparation, greater stability and effective efficiency over a wide range of pH and temperature. Mimetics of many natural enzymes have been developed and among them significant attention has been drawn on peroxidases, since it has potential applications in enzymatic analysis and also it is important for the waste water treatment [18]. Recently, it has been observed that different types of II–VI semiconductor nanomaterials show peroxidase-like activity [19–29]. However, how to develop a reproducible, environmental friendly and easier method to synthesize stable nanomaterials having good biological activity is still a challenge.

Cadmium sulfide, a direct band gap visible-light-sensitive II–VI group semiconductor ( $E_g = 2.41$  eV) has been extensively studied as its optical properties can be tuned easily by changing the size and shape of the material [30]. It is useful for many important potential applications, such as light emitting diodes, flat panel displays, solar cell, photocatalyst, sensors, optoelectronic devices and thin film transistors [31–35]. Many synthetic methods have been employed for the preparation of CdS nanomaterials, but recently the single-source precursor approach has attracted considerable attention. It has the advantage of adopting a single-pot procedure under mild condition and the product obtained in this way has higher surface area, fewer defects and better stoichiometry. Several sulfur containing Cd(II) complexes have been used as precursors to synthesize variable shapes and sizes of CdS NPs under different conditions. The most widely used sulfur containing precursor complexes are the dithiocarbamate, dithiophosphinato, xanthate, thiohydrocarbazide, thiourea, thiocarboxylate, dithiocarbamate and thiosemicarbazide [36–47]. Nyman et al. synthesized  $\text{Cd}(\text{SCOCR}_2)_2\text{Lut}_2$  [ $\text{R} = \text{CH}_3, \text{C}(\text{CH}_3)_3$ , Lut = 3,5-dimethylpyridine (lutidine)] as the precursor complex for the preparation of spherical CdS NPs by thermal decomposition in toluene and pyridine [36]. Later, Yan et al. reported the preparation of quantum-confined CdS nanowires by the solvothermal decomposition of a cluster precursor  $\text{Cd}_2(\text{S}_2\text{CNEt}_2)_4$  in presence of ethylenediamine as the nucleophile [47]. A  $\text{Cd}(\text{C}_2\text{H}_5\text{OCS}_2)_2$  complex was synthesized by O'Brien et al. for the preparation of tri-*n*-octylphosphine oxide capped CdS NPs by solvothermal decomposition of the precursor complex [37]. Recently, Bera et al. developed a solvothermal single-source route for the bulk synthesis of CdS nanorods using a new dimeric cadmium(II) complex of *S*-benzylthiocarbamate,  $[\text{Cd}(\text{PhCH}_2\text{SC}(=\text{S})\text{NHNH}_2)_2\text{Cl}_2]_2$  in hexamethylenediamine [46]. In majority of the cases they have used different nucleophilic solvents for the decomposition of precursors which are expensive and environmentally hazardous. In our case, we have shown that very commonly used, cheap laboratory reagents like  $\text{NH}_3$ , EN and DMSO, which are much less toxic, can be used for the preparation of CdS NPs. Additionally, we have shown that thermal decomposition of the precursor leads to the formation of CdS NPs, which has not been experimented by others.

In this work, we have tried to explore the effect of single-source molecular precursors on the morphology and size of the nanoparticles prepared from a newly synthesized Cd(II) thiocarboxylate complex. To the best of our knowledge, a simpler, greener and facial template-free method for the synthesis of CdS NPs has not been reported earlier. We demonstrate that the CdS NPs, either spherical or rod shape show remarkable photocatalytic efficiency toward the degradation of aqueous solution of RB in presence of white light and the kinetics of the decomposition process is also investigated. These CdS NPs exhibit good catalytic activity for the oxidation of TMB in presence of  $\text{H}_2\text{O}_2$ , by following the Michaelis–Menten kinetics.

## 2. Experimental

### 2.1. Materials

Reagent grade chemicals and solvents obtained from commercial sources were used as received. Standard titanium dioxide (Degussa-P25) was purchased from Degussa Company. Phosphate buffer solutions (PBS, 0.025 mol/L) with various pH were prepared by mixing standard solutions of  $\text{Na}_2\text{HPO}_4$  adjusted the pH with  $\text{H}_3\text{PO}_4$  or NaOH.

### 2.2. Synthesis of precursor complex

$\text{CdCO}_3$  (1.0 g, 3.8 mmol), 3,5-lutidine (0.82 g, 7.6 mmol) and 20 mL toluene were mixed in a round-bottom flask. Thiobenzoic acid (1.05 g, 7.6 mmol) mixed in 10 mL toluene was then added dropwise to the previous solution, with stirring. Within 30 min, a yellow suspension was obtained and the solvent was removed under reduced pressure after 2 h. The resulting yellow residue was re-dissolved in toluene and filtered. Filtrate was kept for slow evaporation in air for overnight. A good yellowish orange crystalline solid was collected by filtration.

Yield: 2.64 g (76%).  $\text{C}_{28}\text{H}_{28}\text{CdN}_2\text{O}_2\text{S}_2$ , Calcd: C, 55.89; H, 4.69; N, 4.66. Found: C, 55.84; H, 4.66; N, 4.63. FTIR ( $\text{cm}^{-1}$ ): 3436 br, 3055 w, 2921 w, 1592 s, 1552 s, 1448 m, 1382 m, 1387 m, 1205 s, 11677 s, 1034 w, 934 s, 863 w, 776 m, 695 s, 660 m, 545 w. UV/Vis [Chloroform,  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ): 275 (32000). Crystal data: monoclinic, space group  $\text{P}2(1)/n$ ;  $a = 11.0487(17)$  Å,  $b = 16.396(3)$  Å,  $c = 15.413(2)$  Å,  $\alpha = 90.00^\circ$ ,  $\beta = 109.708(4)^\circ$ ,  $\gamma = 90.00^\circ$ ;  $V = 2628.7(7)$  Å<sup>3</sup>;  $\rho = 1.519$  g/cm<sup>3</sup>;  $R1^a = 0.0190$ ;  $wR2^b = 0.0422$  [ $I > 2\sigma(I)$ ] for 428 parameters and 5763 data.

### 2.3. Preparation of CdS NPs

#### 2.3.1. Decomposition by heat treatment *c.a.* HT

1.0 g of  $\text{Cd}(\text{SOCPh})_2\text{Lut}_2$  was taken in a quartz boat and heated at 400 °C for 1 h in  $\text{N}_2$  atmosphere, using a quartz tube furnace. The product was taken out after the furnace cooled down to room temperature. The color of the product changed to yellow after the thermal treatment.

#### 2.3.2. Decomposition in EN

1.0 g of  $\text{Cd}(\text{SOCPh})_2\text{Lut}_2$  was dissolved in 20 mL EN in a round-bottom flask and then heated to reflux at 120 °C for 15 min. It was then cooled to room temperature and 20 mL methanol was added to it. The yellow suspension was centrifuged, followed by washing with methanol for several times for purification and then dried in air.

#### 2.3.3. Decomposition in DMSO

1.0 g of  $\text{Cd}(\text{SOCPh})_2\text{Lut}_2$  was dissolved in 20 mL DMSO in a round-bottom flask and then heated at 120 °C for 15 min. The pure nanomaterial was then collected as mentioned in the earlier section.

#### 2.3.4. Decomposition in $\text{NH}_3$

1.0 g of  $\text{Cd}(\text{SOCPh})_2\text{Lut}_2$  was dissolved in 50 mL of  $\text{NH}_3$  in a conical flask and kept undisturbed at room temperature (300 K) for 12 h. A yellowish product was then collected following the above mentioned procedure.

### 2.4. Physical measurements

Elemental analyses (C, H and N) were carried out by a Perkin-Elmer 2400II instrument. Mass spectroscopic measurement was carried out on an Agilent Quadrupol LC–MS 6120 series mass

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