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Editor's Choice paper

Peroxidase-like behavior, amperometric biosensing of hydrogen peroxide and photocatalytic activity by cadmium sulfide nanoparticles

Swarup Kumar Maji[a], Amit Kumar Dutta[a], Divesh N. Srivastava[b], Parimal Paul[b,*], Anup Mondal[a,*], Bibhutosh Adhikary[a,*]

[a] Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711 103, West Bengal, India
[b] Department of Analytical Sicences, Central Salt & Marine Chemicals Research Institute, Gijubhai, Badheka Marg, Bhavnagar 364002, Gujarat, India

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ABSTRACT

A convenient solvothermal route has been developed for the synthesis of CdS nanoparticles (NPs) using a cadmium (II) complex [Cd(ACDA)$_2$] of 2-aminocyclopentene-1-dithiocarboxylic acid (HACDA). Decomposition of the precursor complex has been carried out by ethylenediamine (EN), hexadecylamine (HDA) or dimethyl sulfoxide (DMSO). Structural analyses reveal the formation of crystalline nanoparticles with rod-like shape from EN and spherical shape from HDA or DMSO as solvents, while the optical properties suggest the quantum confinement by the nanoparticles. Superior photocatalytic activity towards the degradation of aqueous Rose Bengal (RB) solution has been achieved with the use of CdS NPs as photocatalyst under light irradiation. CdS NPs is found to possess peroxidase-like activity that can catalyze the oxidation of the peroxidase substrate 3,3′,5,5′-tetramethylbenzidine (TMB) in the presence of H_2O_2 to produce a blue color reaction. CdS NPs anchored on glassy carbon (GC) electrodes have been prepared to study the electrocatalytic reduction of H_2O_2 in phosphate buffer solution. This modified electrode has also been used as amperometric biosensor for the detection of H_2O_2.

1. Introduction

Nanostructured semiconductors are drawing increasing attention for biomedical and biosensing applications due to their unique physical and chemical properties, which depend on their structures, sizes and shapes [1]. For this reason, preparation of semiconductor nanomaterials with controlled shape and size are of great importance [2]. Considerable efforts have been made to control the nanostructures in past few decades and despite remarkable progress made, it still remains challenge task to researchers to develop simple and reliable methods for fabrication of various semiconductor nanomaterials with controlled morphologies [3].

Dyes that are widely used in textile, photography, coatings etc. are therefore, common industrial pollutants in waste water [4]. Normal aerobic waste water treatment processes not very effective for removal of these toxic chemicals from the environment. In recent years, a new technology termed as advanced oxidation processes are in use for treatment of pollutants in both water and wastewater [5]. To this end, photocatalytic oxidation using semiconductor nanomaterials has turned out to be a promising alternative method for environment water management [6]. The photo-degradation of several toxic compounds using TiO_2 as a photocatalyst has been widely studied over the past decade [7,8]. However, the photocatalytic activity of TiO_2 is limited to the UV region ($\lambda < 400$ nm) and therefore is not much effective in the visible region, which is the main component solar light and indoor illuminations [9]. Thus, there is considerable interest in developing visible light sensitive photo-catalyst [10–17].

Designing of biomimetic materials exhibiting peroxidase activities is the focus of considerable attention [18,19]. In this regard, nanomaterials-based compounds such as Prussian blue, iron oxide, iron sulfide, cupric oxide and grapheme oxide have been found to show peroxidase-like activity to catalyze oxidation of typical peroxidase substrate [20–26]. For instance, with nanostructure FeS peroxidase-like activity has been reported using 3,3′,5,5′-tetramethylbenzidine as the peroxidase substrate and detection of H_2O_2 has been made by employing it as an amperometric sensor [24]. Since, H_2O_2 it self is widely used for green chemical oxidation reactions, development of methodologies for detection and quantification of H_2O_2 are highly important. Carbon nanotubes, noble metals, macrocyclic complexes of transition metals and protein modified electrodes have been used as amperometric sensors of H_2O_2, although each of them have some disadvantages [27,28]. Very recently semiconductor nanomaterial modified electrode has been used for this purpose [24,29].

* Corresponding authors. Tel.: +91 3326684561; fax: +91 3326682916.
E-mail addresses: anupmondal2000@yahoo.in (A. Mondal), bibhutoshadhikary@yahoo.in (B. Adhikary).

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Table 1
Summary of reaction conditions and experimental results of CdS NPs.

Solvent (mL)	Temp (°C)	Time (min)	Shape	Average size (nm)		Pore diameter (nm)	Surface area ($m^2\ g^{-1}$)
				XRD	TEM		
EN (20)	120	15	Rod	4.8	$D = 5^a L = 70^b$	3.1	44.8
HDA (15) + TOP (5)	120	15	Sphere	3.4	4	4.6	81.9
DMSO (20)	120	15	Sphere	5.6	6	2.4	32.1

[a] Diameter.
[b] Length.

Cadmium sulfide is one of the most important visible-light-sensitive semiconductor with narrow band gap energy (E_g = 2.41 eV) and has been extensively investigated because its emission in the visible-light range can be tuned by changing the size and shape of the particles [30–32]. CdS nanomaterials with varying morphologies have been prepared recently from single precursor sources by solvothermal route using different solvents and capping agents [33–39]. This method has the advantage of adopting a single-pot procedure under mild condition and the product obtained in this way has fewer defects and better stoichiometry. We report here a simple solvothermal decomposition route for preparing CdS NPs by using the complex $Cd(ACDA)_2$ as the precursor. CdS nanorods and nanoparticles thus obtained have been used for the photocatalytic decomposition of RB and catalytic oxidation of TMB. These NPs have also been used for evaluating their efficiencies for detection/estimation of H_2O_2 by electrochemical methods.

2. Experimental

2.1. Chemicals and materials

The chemicals used for the preparation of the ligand 2-aminocyclopentene-1-dithiocarboxylic acid (HACDA) and the metal complex $[Cd(ACDA)_2]$ were of analytical grade. Ethylenediamine (EN), hexadecylamine (HDA), dimethyl sulfoxide (DMSO), tri-octylphosphine (TOP), Rose Bengal (RB), commercial CdS, terephthalic acid (TA), hydrogen peroxide (H_2O_2) and 3,3′,5,5′-tetramethyl benzidine (TMB) were purchased from Sigma–Aldrich. Standard titanium dioxide (Degussa-P25) was purchased from Degussa Company. Methanol, ethanol, acetic acid, diethyl ether and millipore water were used without any further purification.

2.2. Synthesis of single-source precursor

The ligand (HACDA) was prepared according to the reported method [40]. To a clear methanol solution (10 mL) of HACDA (160 mg, 1 mmol) was added dropwise with stirring to an aqueous solution (10 mL) of cadmium chloride (92 mg, 0.5 mmol). The yellow compound that precipitated was filtered after 15 min and washed first with methanol and then with diethyl ether.

Yield: 89% (191 mg), CHN analyses ($C_{12}H_{16}N_2S_4Cd$): Calc.: C, 33.59; H, 3.77; N, 6.53. Found: C, 33.53; H, 3.81; N, 6.51. Selected IR bands: νNH_2: 3289 m cm^{-1}, δNH_2: 1634s cm^{-1}, $\delta CH_2 + \nu C{=}C$: 1459s cm^{-1}, $\nu C{-}N + \nu C^{C{=}S}_{S}$: 1315 cm^{-1}, $\nu C^{C{=}S}_{S} + \nu CN$: 1282 m cm^{-1}; $\nu_{assym}CSS$: 902 cm^{-1}, $\nu_{sym}CSS$: 623 cm^{-1}. ESI-MS: $[Cd(ACDA)_2 + H]^+$ (m/z = 430.07), $[Cd(ACDA)_2 + Na]^+$ (m/z = 451.96) and $[Cd(ACDA)_2 + K]^+$ (m/z = 468.24).

2.3. Preparation of CdS NPs

CdS NPs were prepared by solvothermal decomposition of the single-source precursor using EN, HDA or DMSO as the solvents. In case of EN and DMSO, 250 mg of the precursor was dissolved in 20 mL solvent in a round bottom flask. For the preparation of CdS NPs using HDA, 250 mg of the precursor was dissolved in 5 mL hot TOP and then it was added to a 15 mL hot HDA solution in a round bottom flask. The resulting clear yellow solutions were heated at 120 °C for 15 min and then cooled to room temperature. At this stage, 20 mL methanol was added to them. Thus obtained yellow precipitates were centrifuged, followed by washing with ethanol for several times for their purification. The pure nanomaterials were collected after drying in oven at 50 °C for 30 min. The reaction conditions and results are summarized in Table 1.

2.4. Characterization

Elemental analyses (C, H and N) were performed using Perkin-Elmer 2400II analyzer. FTIR spectra were recorded on KBr disks using a JASCO FTIR-460-Plus spectrophotometer. Electron spray ionization mass spectroscopic measurements were carried out on a Micromass Qtof YA 263 mass spectrometer in dimethylformamide. X-ray diffraction (XRD) patterns were recorded on a Philips PW 1140 parallel beam X-ray diffractometer using with Bragg–Bretano focusing geometry and monochromatic CuK_α X-radiation (λ = 1.540598 Å). Transmission electron microscopy (TEM) images were collected by using JEOL JEM-2100 microscope working at 200 kV. EDX analyses were carried by using Hitachi S-3400 N (EDS, Horiba EMAX) instrument. N_2-sorption isotherms were obtained using a Quantachrome Instruments adsorption (77 K). UV–vis absorption spectra were recorded with a JASCO V-530 UV–vis spectrophotometer. Photoluminescence measurements were carried out using a Photon Technology International fluorometer. The catalytic oxidation of TMB was monitored spectrophotometrically using an Agilent 8453 diode-array spectrophotometer. Cyclic voltammetric and amperometric measurements were performed on CHI 620D electrochemical analyzer.

2.5. Measurements of photocatalytic activity

The experiments were carried out in a round bottom flask kept in a thermostated bath at 20 °C and an incandescent tungsten halogen lamp (200 W) was placed vertically on the reaction vessel at a distance of ca. 15 cm. The experiments were carried out with 40 mL aqueous solution of RB (3.6×10^{-5} M) and 15 mg of catalysts. Before irradiation, the suspension was magnetically stirred in the dark for 30 min to reach the adsorption–desorption equilibrium. After a given interval of illumination, 3 mL of the aliquot was withdrawn from the suspension and centrifuged. The absorption spectrum of the filtrate solution was then measured in the range 400–650 nm and the peak at 540 nm (λ_{max}) was monitored. To test the chemical stability of CdS NPs, it was recycled and reused for five times for the decomposition of RB under same experimental condition. After each photocatalytic test, the aqueous solution was centrifuged to collect CdS NPs, which was then dried at 60 °C and used for the next cycle.

In order to find out whether the photodegradation of RB by CdS NPs occur through the generation of hydroxyl radical or not, the commonly used terephthalic acid (TA) photoluminescence probing technique was adopted [11–13]. 40 mL aqueous solution of sodium terephthalate (2×10^{-3} M) containing 15 mg of either TiO_2 or CdS