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Highly-sensitive and selective detection of hydrazine at gold electrode modified with PEG-coated CdS nanoparticles

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ABSTRACT

PEG-coated CdS nanoparticles (P-CdS NPs) modified gold (CdS/Au) electrode has been used as an efficient electron mediator for the fabrication of highly sensitive chemical sensor for detection of hydrazine, which is a well known neurotoxin and carcinogen. P-CdS NPs of mean diameter 15 nm and hexagonal crystallites have been synthesized using microwave irradiation method and characterized by various techniques. The prepared CdS/Au electrode has been used for detection of hydrazine which yields a high sensitivity of 89 μA/cm^2 μM and detection limit of 0.061 μM. The response time of sensor is <4 s and sensor responded linearly for concentration range of 100–1000 nM. The sensor has also been found to be selective for hydrazine even in presence of common interferents. Moreover, the sensor has been tested for analysis of real world samples, which makes it useful in practical area of environment applications.

1. Introduction

II–VI semiconductor nanoparticles are of great interest for their diverse applications such as such as biological sensors, solar cells, field-effect transistors, hydrogen evolution, electricity generation and light-emitting diodes [1–5]. Cadmium sulphide (CdS) is an important II–VI semiconductor with a direct band gap of 2.4 eV and has wide range of electrical and optical properties. Numerous reports [6–8] are available in the literature for the synthesis of CdS NPs. In the present study, PEG-coated CdS (P-CdS) NPs of mean diameter of 15 nm and hexagonal crystallites have been synthesized using microwave irradiation method and characterized by various techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), UV–vis spectroscopy and photoluminescence (PL) spectroscopy. An attempt has also been made to fabricate sensitive as well as more selective electrochemical sensor for hydrazine using P-CdS NPs. Hydrazine has been employed in both chemical and pharmaceutical industries, as rocket fuel, emulsifiers, catalysts, weapons for mass destruction, corrosion inhibitors, insecticides, plant growth regulators, etc. [9]. However, it can intimidate people's health from inhalation of vapours, injection, or skin contact. It has been classified as human carcinogen by Environmental Protection Agency (EPA). The neurotoxin and carcinogenic nature of hydrazine as well as its high solubility in water raises concern for ground water contamination and generates interest among researchers for developing simple, economic and sensitive methods for its detection. The reported methods for detection of hydrazine include chemiluminescence, spectrophotometry, coulometric titration, flow injection analysis, spectroscopic methods, electrochemical detection [10–12]. The main problem with electrochemical detection of hydrazine at bare electrode is its large oxidation overpotential. However, the use of chemically modified electrodes has solved this problem to a large extent. The use of NPs for modifying electrode has gained a lot interest these days. Although metals such as Pd, Au and Ag are very active in the anodic oxidation of hydrazine [13–15], however, they are too expensive for the practical applications. In this context, less expensive semiconductor NPs are expected to provide a better solution. However, most of the reported [13–16] sensors for hydrazine either deal with high values of detection limit, lack of specificity and low sensitivities or the sensors have not been examined for analysis of real world samples. All these disadvantages prompt the need of a simple, accurate, cost-effective, less time consuming, highly sensitive method which can detect very low concentrations of hydrazine and also should be practically applicable to real world samples. Recently, we have reported [16] the use of ZnS NPs for detection

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of hydrazine with a sensitivity of ~89.3 μA/cm^2 μM and detection limit up to 1.07 μM. In comparison, the fabricated sensor based on modification of gold electrode with P-CdS NPs shows a sensitivity of 89 μA/cm^2 μM and detection limit of 0.061 μM. Although the sensitivity obtained is nearly same as in case of ZnS NPs, but detection limit achieved is lower in the present case.

2. Materials and methods

2.1. Materials

Cadmium acetate ($Cd(CH_3COO)_2{\cdot}2H_2O$; CdOAc) was purchased from BDH, India. Thioacetamide (CH_3CSNH_2) (TA) was obtained from CDH, India. Hydrazine monohydrate and PEG-2000 were received from Sigma–Aldrich. All the chemicals were used as received without further purification. Deionized water (DW) was used for all the experiments.

2.2. Synthesis of P-CdS NPs

P-CdS NPs were prepared by a facile microwave process by using cadmium acetate (CdOAc), thioacetamide (TA; CH_3CSNH_2) and PEG-2000. In a typical reaction process, 10 mM of PEG was dissolved in 10 ml DW. Consequently, 0.005 M CdOAc solution made in 10 ml DW and 0.005 M TA solution prepared in 10 ml DW were added in the prepared PEG solution. The final solution was then placed in a domestic microwave (MW; IFB-20PG2S of consumption power 1200 W) oven at optimized reaction conditions, i.e. 60% power for 20 s. After completing the reaction, the MW was cooled to room-temperature and obtained products were examined by various analytical tools. Moreover, the prepared CdS products were used as efficient electron mediators to fabricate hydrazine amperometric chemical sensor.

2.3. Characterizations of P-CdS NPs

The structural analysis of synthesized NPs was done by X-ray diffractometer (XRD; PANalytical X'Pert PRO) measured with Cu-Kα radiations (λ = 1.54178 Å) in the range of 10–70°. The size and morphologies were investigated by transmission electron microscopy (TEM) at 80 kV (Hitachi H-7500). The UV–vis spectrum was recorded at room temperature using thermo Fisher Scientific Evolution 160 UV–vis spectrophotometer. Photoluminescence (PL) spectrum was recorded using a Perkin Elmer-L55 fluorescence spectrophotometer.

2.4. Preparation of hydrazine electrochemical sensor based on P-CdS NPs

The electrochemical experiments were conducted using μAutolab III cyclic voltammeter and a three electrode configuration. The electrocatalytic activity of CdS/Au electrode towards

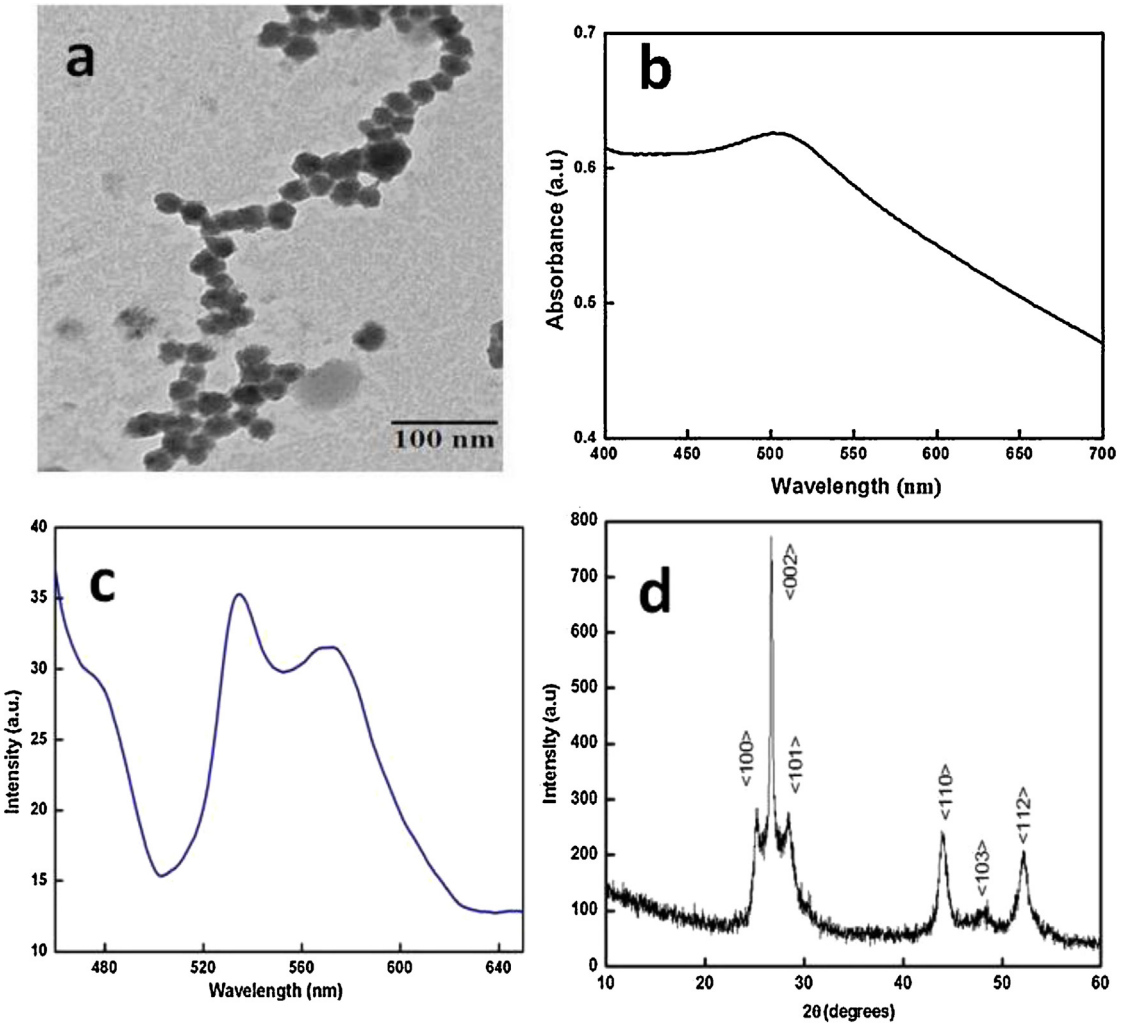

Fig. 1. (a) TEM images, (b) UV–vis spectrum, (c) PL spectrum and (d) XRD pattern of as synthesized P-CdS NPs.