Materials Science & Engineering B 225 (2017) 33–44

Contents lists available at ScienceDirect

Materials Science & Engineering B

journal homepage: www.elsevier.com/locate/mseb

One-pot green synthesis, characterization, photocatalytic, sensing and antimicrobial studies of *Calotropis gigantea* leaf extract capped CdS NPs

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ARTICLE INFO

Keywords:
CdS nanoparticles
Calotropis gigantea leaf extract
Photocatalysis
Sensing
Antimicrobial activity

ABSTRACT

Here, we report for the synthesis of *C. gigantea* leaf extract capped CdS NPs by a simple sonochemical method via a green approach. The obtained materials were thoroughly characterized by various physicochemical techniques such as UV–vis DRS, PL, XRD, ATR-FTIR, SEM, TEM, Raman, zeta potential and DLS. The TEM image shows the average particle size of CdS NPs as 20 nm. The photocatalytic performance of CdS NPs on the degradation of MB and EY under sunlight irradiation is investigated. The synthesized CdS NPs attain an efficient degradation efficiency of MB and EY dyes under 60 min of sunlight irradiation. To investigate the selectivity of metal ions, Pb^{2+}, Sn^{2+} and Hg^{2+} were studied for their sensing property in a nanomolar concentration by spectrofluorometrically. The antimicrobial property of CdS NPs was also investigated. Our work suggests that prepared CdS NPs could be a potential photocatalyst, a sensor, and an active antimicrobial agent.

1. Introduction

The concept of green chemistry and engineering has provided a new pathway for the environmentally benign synthesis, not harmful to the environment and human health [1]. In the past few years, bio-templates from natural sources like microorganisms and plant extracts have been a source of inspiration for designing complex nanomaterials with high surface area and potential applications in commercial products, biosensors, catalysis, photocatalysis, antimicrobial, antioxidant, as well as environmental technologies [2–5]. The biological approach is an alternative to the chemical methods, being greener, energy saving and cost effective. Regarding the stability, the nanoparticles are innoxious due to the coating of biological molecules and hence, they are more biocompatible than the nanoparticles prepared by chemical methods [6]. The biomolecules present in the extract of plants act as stabilizing agents in the formation of nanoparticles [7–8]. Very few literature reports are available on the biosynthesis of CdS NPs using plant extracts [9–11]. In view of this and importance of plant extract, we have selected *C. gigantea* leaf extract for the synthesis of CdS NPs. An attempt was made to investigate the green synthesis, characterization of structural and morphological features, microbial activity and preventing the use of toxic chemicals which are harmful to the environment. *C. gigantea* is a common and traditional medicinal plant in the Indian subcontinent, having purgative, anthelmintic, anti-convulsant, sedative and anti-pyretic effects [12–13] and is used to cure a viral infection, bacterial infection, toothache, anti-inflammation and also as an antioxidant. Several phytoconstituents have been isolated and identified from different parts of the *C. gigantea* plant extracts contain various phytochemicals such as terpenoids, flavonoids, tannin, phenol derivatives, plant enzymes, protein and reducing sugars [14]. Importantly, green synthesis of nanoparticles has an upsurge as a new nanobiotechnology method to produce eco-friendly and cost effective synthetic process for highly stable nanoparticles which emerged as safer and best alternative to conventional methods.

Calotropis gigantea (Asclepiadaceae) is a perennial herb with a long history of use in traditional medicines. Recently, the parts of leaves, roots, latex, stem bark and flowers of the *C. gigantea* plant, are widely used as the stabilization and reducing agents in the synthesis of nanoparticles [15–17]. Previous studies report the presence of a wide range of phytochemicals as major constituents in the *C. gigantea* plant material including Leaves, such as cardiac glycosides, flavonoids, terpenoids, alkaloids, steroids, tannins, saponins, mudarine, phenols, reducing sugars and resins; Root: cardiac glycosides, seven oxypregnane-oligo glycosides, and calotroposides; Root bark: β-amyrin, two isomeric crystalline alcohols, giganteol, isogiganteol, stigmasterol, and cardenolides; Latex: akundarin, 0.45% uscharin, 0.15% calotoxin, 0.15% calactin, α-calatropeol, β-calotropeol, β-amyrin, calcium oxalate, traces of glutathione and a proteoclstic enzyme similar to papain; Stem bark: β-calotropeol, β-amyrin, and giganteol; and Flower: nα-calatropeol, β-calotropeol, amyrin, cardio active glycosides, mudarine, asclepin, bitter resins akundarin, and calotropin, which have been isolated from this plant [18–22]. These phytochemicals act as both reducing as well as

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http://dx.doi.org/10.1016/j.mseb.2017.08.008
Received 19 May 2017; Received in revised form 19 July 2017; Accepted 7 August 2017
Available online 15 September 2017

capping agent required for the synthesis and stabilization of metal sulfide or metal oxide or metal nanoparticles with high surface area to degrade dyes.

Previously, dye-polluted water was treated using various methods, such as adsorption, coagulation/flocculation, photocatalysis, chemical oxidation, and microbiological or enzymatic degradation [23]. Photocatalysis, a promising strategy to combat worldwide energy consumption and associated environmental pollution, can utilize the clean and renewable solar energy by converting solar energy into environmental friendly hydrogen and decomposing toxic organic dyes. Organic dyes are among the largest group of harmful pollutants discharged into wastewater streams from industries and these are the most important classes of the pollutants due to their toxic, mutagenic, carcinogenic, and non-biodegradable features [24]. So, the degradation of organic dyes finds extensive application in environmental safety. Currently, degradation of the toxic dyes using photocatalysts is gaining more importance due to their less toxic nature and low cost. Among various photocatalysts, CdS NPs are considered as an alternative source of degradation of atmospheric pollutants since CdS has high absorption ability of UV light and its property of generating hydrogen peroxides. These photocatalysts, naturally available and cost effective plant extracts have been considered as a good source to degrade the organic dyes. Additionally, it was observed that green synthesized nanoparticles were found to increase in the different fields such as environment, synthetic chemistry, biotechnology and environmental sciences.

II–VI group semiconductor compounds have attracted intensive attention due to their electrochemical properties, various photo-induced applications: decomposition of organic pollutants, generation of hydrogen gas by splitting water, conversion of CO_2, and production of coatings, gas sensors, catalysts, solar cells, laser diodes, photo detectors, and nano-generators [25–29]. Recently, the photocatalytic degradation of various dyes by narrow band gap semiconductors under solar light response has been developed. Among all these semiconductor materials such as CuS [30], Ag_2S [31], ZnS [32] CdS [33], CdSe [34], PbS [35], Bi_2S_3 [36], MoS_2 [37–38], SnS_2 [39], CdS is emerging one of the most extensively investigated material. CdS, a typical metal chalcogenide semiconductor with a direct band gap (~2.40 eV) at room temperature [40], has become one of the most significant materials in research communities due to its diverse promising applications in the field of solar cells, photoelectronic devices, photophysical and photocatalysis [41]. Therefore, CdS NPs as a photocatalyst is being employed to mineralize and thereby decontaminate dyes in wastewater due to their low cost, non-toxicity, and stability. Many methods have been utilized for the synthesis of CdS nanostructures such as co-precipitation [42], polyol [43], microwave-solvothermal [44], hydrothermal [45], non-aqueous chemical [46], and chemical bath deposition [47]. There are different methods used for the synthesis of CdS NPs: but the biological method of the synthesis of CdS NPs is gaining importance due to its simplicity, eco-friendliness and extended antimicrobial activity [48]. According to Mahanty et al. [49], the use of eco-friendly bio-synthesized nanoparticles as an alternative to the chemically synthesized ones would help to control chemical toxicity in the environment.

In this present work, the importance of the synthesis of nanoparticles as a green method to produce eco-friendly, cost effective, highly stable nanoparticles is presented, which emerges as safer and better alternative to conventional methods. The biologically synthesized CdS NPs using an aqueous leaf extract of *C. gigantea* were found to have antimicrobial and antifungal activities against various bacterial and fungal strains. The developed *C. gigantea* leaf extract capped CdS NPs is a viable approach in a suitable size range for the selective Pb^{2+}, Sn^{2+}, and Hg^{2+} metal ions detection. The photocatalytic activity of these CdS NPs against MB and EY dyes were extensively studied under sunlight irradiation. The structural and optical properties of these nanoparticles were investigated using UV–vis DRS, PL, ATR-FTIR, SEM, TEM, XRD, Raman, zeta potential and DLS techniques. These results indicated that the obtained CdS NPs showed remarkable photocatalytic, sensing and antimicrobial activity. More importantly, we believe that this route can be extended to the synthesis of other transition metal sulfide which may act as photocatalysts.

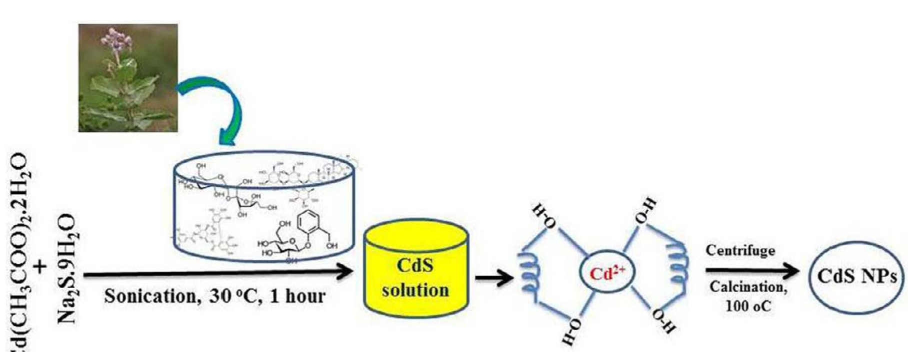
2. Materials and methods

2.1. Collection of leaves of C. gigantea and preparation of leaf extract

Fresh leaves of *C. gigantea* were cropped in the rainy season from the Osmania University campus, Hyderabad, India. The collected leaves were surface washed with tap water followed by Milli-Q water to remove the impurities and dried at room temperature for 2 days in the dark to remove moisture completely. The dried leaves were powdered in an electric blender and final sieved powder (5 g) is added to 100 ml of Milli-Q water and boiled at 60 °C for 15 min. Then, *C. gigantea* leaf extract was filtered through Whatman No.1 filter paper and the resulting filtrate was stored at 4 °C for the synthesis of CdS NPs.

2.2. One pot synthesis of CdS nanoparticles

In a typical procedure for the green synthesis of CdS NPs using *C. gigantea* leaf extract solution by the sonochemical method at room temperature, about 20 mL of *C. gigantea* leaf extract (0.05 g/L) was dissolved in double distilled water. The extract solution was mixed with 40 mL of 1 mM of cadmium acetate and 40 mL of 1 mM of sodium sulphide to synthesize CdS NPs. The 100 mL of the total reaction mixture was kept in the sonochemical bath for ultrasound irradiation for 1 h at room temperature. The yellow colored colloidal solution of CdS was formed. After the formation of CdS NPs, the mixture was centrifuged and kept in a furnace at 100 °C for 3 h. A similar procedure was adopted to synthesize uncapped CdS NPs. The probable reaction mechanism of formation of CdS NPs using C. gigantea leaf extract by the sonochemical method is shown in Scheme 1. When cadmium acetate is mixed with *C. gigantea* leaf extract, the Cd^{2+} ions dispense consistently and form a complex with active sites of hydroxyl groups of polyphenols. The polyphenolic molecules interact with divalent Cd^{2+}, forming a



Scheme 1. The schematic diagram of *C. gigantea* leaf extract capped CdS NPs under sonochemical method.