Inorganic Chemistry Communications 72 (2016) 33–41

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Feature article

CdS nanocapsules and nanospheres as efficient solar light-driven photocatalysts for degradation of Congo red dye

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ARTICLE INFO

Article history:
Received 30 June 2016
Received in revised form 21 July 2016
Accepted 4 August 2016
Available online 09 August 2016

Keywords:
Growth mechanism
CdS
Nanocapsules
Nanospheres
Photocatalysis
Congo red

ABSTRACT

CdS-1 (nanosphers) and CdS-2 (nanocapsule), were synthesized via green synthetic route without using any toxic surfactants by thermolysis of *bis*(4-benzhydrylpiperazine-1-carbodithioate-κ^2 S, S′)cadmium(II) (**1**) and *bis* (4-benzylpipera-zine-1-carbodithioate-κ^2 S, S′)cadmium(II) (**2**), respectively in the presence of ethylenediamine as a solvent. The nanoparticles were characterized by TEM, XRD, SEM, FT-IR UV–Visible and Fluorescence spectroscopy. The TEM results showed the formation of nanospheres (CdS-1) and nanocapsules (CdS-2) from complexes **1** and **2**, respectively. Both CdS nanoparticles (NPs) have hexagonal crystal phase and a band gap value in the visible region as confirmed by the XRD and UV–Visible spectra, respectively. The photoluminescence (PL) data revealed that CdS-2 has longer recombination time of photo-injected electron hole pairs than CdS-1. The similar FT-IR spectra for both CdS NPs, and different HOMO-LUMO gap values for complexes {4.8187 eV (**1**) and CdS-2 4.7504 eV (**2**)} as predicted by DFT calculations suggest that stability of complexes play a key role in controlling morphology. Furthermore, the visible light driven photocatalytic degradation of Congo red dye was observed higher for nanocapsules than nanospheres due to a longer recombination time of photo-injected electron hole pairs.

Contents

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http://dx.doi.org/10.1016/j.inoche.2016.08.001
1387-7003/

1. Introduction

Water pollution is a noteworthy environmental problem caused by the release of toxic textile dyes [1]. These colored compounds upset aquatic biological processes either by blocking light penetration or direct destruction of aquatic communities due to associated noxiousness [2]. To find an effective and long lasting solution for the exclusion of these aquatically harmful compounds a range of technologies have been tested which include biodegradation, adsorption and photocatalytic oxidation [3–5]. The photocatalytic oxidation of these toxic pollutants seems to be more appropriate strategy using group II-VI chalcogenides as photocatalyst [6]. Among these nanoparticles, TiO_2 has been certainly regarded as the most efficient catalyst for degradation of organic pollutants under UV radiation during the last two decades, but its poor response to visible light due to wide band gap hinders its application as photocatalyst [7]. In recent years, tremendous efforts have been witnessed for maximum utilization of clean, safe and abundant solar energy through the development of visible light driven photocatalyst [8]. Cadmium sulfide is an important chalcogenide and has been the focus of considerable interest due to direct band gap (2.42 eV) and nonlinear optical properties [9], possessing potential applications in many fields such as sensors [10], in fluorescence probe [11] solar battery [12], laser light-emitting diodes [13], field effect transistors (FEDs) [14] and light emitting diodes (LEDs) [15]. The direct and narrow band gap, excellent transportation and high electronic mobility of cadmium sulfide make it a promising photocatalyst in the visible region [16,17], but the rapid recombination of photo generated electrons and holes reduces its photocatalytic efficiency. However, it is believed that synthesis of cadmium sulfide nanoparticles with controlled morphology and high crystallinity can enhance its photocatalytic efficiency [7]. The literature contains a number of techniques reported for the synthesis of cadmium sulfide nanoparticles, which include sol gel template [18], solvothermal [19], chemical precipitation method [20], reversed micelle [21] and ultrasonic irradiation in an aqueous solution [22]. Nevertheless, the use of single source precursors (SP) for the aforesaid purpose has paid more attention due to associated advantages, including ambient conditions, the presence of all constituent elements in single molecule in a requisite atomic ratio and their conversion to metal chalcogenides under safe and mild conditions [23]. Interestingly, size and morphology can be tuned by varying the solvent/surfactant system and the attached ligand as reported by Trinanjana Mandal et al. [24]. Another research group established the effect of thermolizing solvents {ethylene glycol (EG) and ethylenediamine (en)} on the solvothermal decomposition of cadmium(II)-*S*-benzyldithiocarbazate, and obtained spheres (EG) and rods (en) [25]. Ajibade et al. observed that a slight modification in metal(II) dithiocarbamate's side chain from methyl to ethyl has a pronounced impact on the morphology of the offspring metal sulfide NPs, though, with no obvious explanation [26]. Linda et al. rationalized that temperature variation (180–270 °C) in thermolysis of SP stemmed in diverse shapes from nanorods (rods, bipods, tripods and tetrapods) to nanocubes. Furthermore, a correlation between the capping agent chain length and size of nanorods was noticed [27].

Herein, we report a simple, safe and green route for the synthesis of CdS NPs of unlike morphology by the thermolysis of two new cadmium(II) dithiocarbamates using en as a solvent devoid of any toxic capping agent/surfactant. The possible growth mechanism of NPs, and their potential as photocatalyst for the degradation of Congo red (CR) dye under direct sunlight is argued.

2. Experimental

2.1. Materials

1-(Diphenylmethyl)piprazine, 1-benzylpiperazine and CS_2 were purchased from Fluka. Methanol, en, solvents and metal salts were purchased from Sigma Aldrich, and Congo red from Merck.

2.2. Synthesis of complex 1

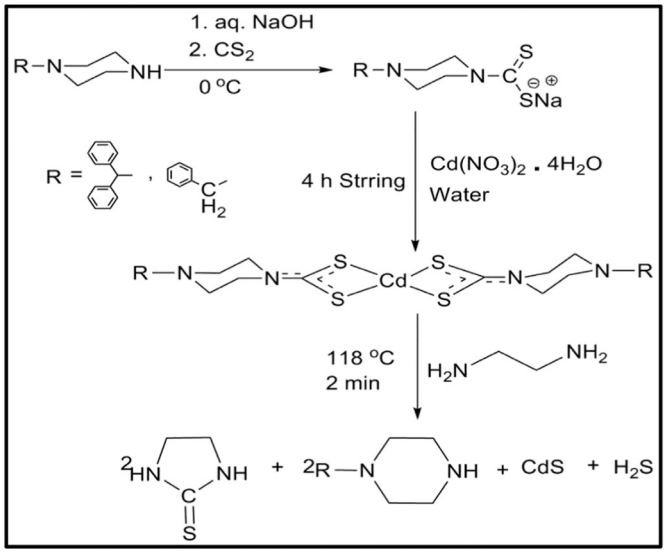
Sodium 4-benzhydrylpiperazine-1-carbodithioate was synthesized by our previously reported method [28]. To an aqueous solution of sodium 4-benzhydrylpiperazine-1-carbodithioate (0.7 g, 2 mmol), was added aqueous $Cd(NO_3)_2 \cdot 4H_2O$ (0.3 g, 1 mmol) with constant stirring. White milky product precipitated down readily; however, the stirring was continued for further 3 h. The precipitates thus obtained, were washed with distilled water and methanol, filtered off and dried (Scheme 1). Yield: (0.60 g, 78%); White Solid; m.p.: 290–292 °C; IR (neat, cm^{-1}): 1434 ($\nu_{C\text{-}N}$), 1014 (ν_{CSS}), 358 ($\nu_{Cd\text{-}S}$). ^1H NMR ($CDCl_3$, δ (ppm), 300 MHz): 7.20–7.44 (20H, m, phenyl), 4.30 (2H, s, C—H), 4.21 (8H, t, $J = 5.2$ Hz, piperazinyl), 2.54 (8H, t, $J = 5.1$ Hz, piperazinyl). ^{13}C NMR ($CDCl_3$, δ (ppm), 75 MHz): 203.2 (SCS), 127.3, 127.8, 128.7, 142.1 (phenyl), 76.7 (CH_2), 53.0, 51.4 (piperazinyl).

2.3. Synthesis of complex 2

An aforesaid procedure was adopted for the synthesis of complex **2** using 0.55 g (2 mmol) and 0.3 g (1 mmol) of sodium 4-benzylpiperazine-1-carbodithioate and $Cd(NO_3)_2 \cdot 4H_2O$, respectively. Yield: (0.46 g, 76%); white solid; m.p.: 320–321 °C; IR (neat, cm^{-1}): 1485 ($\nu_{C\text{-}N}$), 996 (ν_{SCS}), 361 ($\nu_{Cd\text{-}S}$). ^1H NMR (DMSO, δ (ppm), 300 MHz): 7.28–7.38 (10H, m, phenyl), 3.57 (4H, s, CH_2), 4.16 (8H, t, $J = 5.1$ Hz, piperazinyl), 2.56 (8H, t, $J = 5.1$ Hz, piperazinyl). ^{13}C NMR (DMSO, δ (ppm), 75 MHz): 201.2 (SCS), 127.8, 128.4129.2, 142.7 (phenyl), 62.7 (CH_2), 52.3, 51.2 (piperazinyl).

2.4. Synthesis of CdS NPs

Both complexes were converted into CdS NPs by the previously reported procedure [29] and named as CdS-1 from **1** and CdS-2 from **2**. Typically 0.4 g of the synthesized cadmium complexes were dissolved in 8 mL of en in 50 mL flask connected to a condenser, then heated slowly to the boiling point of en (118 °C) on a hot plate with constant stirring, and was refluxed for 2 min. The progress of the reaction was noted by the formation of white PdS suspension when the evolved H_2S gas from flask was allowed to bubble into the lead nitrate solution. Yellow precipitates of CdS thus obtained by the thermolytic decomposition were separated by centrifugation, repeatedly washed with methanol and dried in a furnace at 50 °C for 2 h (Scheme 1).



Scheme 1. Synthesis of SPs and cadmium sulfide NPs.