Size and shape controlled synthesis of CdS and ZnS nanoparticles and their applications in photodegradation of organic dyes

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Research Article

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Abstract

Different size and shapes of CdS and ZnS nanoparticles have been synthesized, characterized and studied for photodegradation of organic dyes. In this study, effect of alkyl chain of dithiocarbamates was investigated for the size and shaped controlled CdS and ZnS nanoparticles. A thorough structural characterization of nanoparticles has been carried out by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM) images, EDS, XRD, and UV/vis spectroscopy. Results showed that the alkyl chain in dithiocarbamate complexes of zinc and cadmium systems plays a significant role in the final morphology of the CdS and ZnS nanoparticles. A photocatalytic degradation of UV-irradiated Methylene Blue solutions in the presence of ZnS and CdS nanoparticles was studied in order to examine the nanoparticles influence on photodegradation rates.

1. Introduction

Fluorescent nanomaterials have attracted increasing attention due to their applications in visualizing biological processes, thermotherapy agents for the diagnosis of many diseases, drug delivery, and catalysts in organic transformations [1–5]. Amongst the various fluorescent nanomaterials, CdS and ZnS nanoparticles are the first discovered fluorescent nanoparticles that extensively studied due to their unique electronic and optical properties which make them useful in optoelectronic applications [6–11]. Recent studies have demonstrated that due to high surface free energy of the CdS and ZnS nanoparticles, the particles are easily aggregated [12]. On the other hand, the optical properties of the CdS and ZnS nanoparticles can be controlled by changing their size and distribution [13]. Therefore, control of the particles sizes and their stability is an important challenge for the scientists.

Amongst the various reported methods for size and shaped controlled synthesis of CdS and ZnS nanoparticles, the use of single source precursors, such as metal complexes, containing both the sulfide and the metal source has proven to be an effective method to high quality CdS and ZnS nanoparticles [14]. Cadmium or zinc dithiocarbamate complexes (dithiocarbamate anion is readily available by the reaction of amines with carbon disulfide ligand) have been used as a single precursors for the synthesis of CdS and ZnS nanoparticles [15]. Revaprasadu and co-workers studied the effect of piperidine and tetrahydroquinoline dithiocarbamate for the synthesis of CdS nanoparticles [16].

To the best our knowledge, there is no any report in the literature for the systematic studies on the effect of various alkyl chains of dithiocarbamates in their cadmium and zinc complexes as a single precursors on the size and shape of synthesized CdS and ZnS nanoparticles. In this report, effect of alkyl chain of dithiocarbamates was investigated for the size and shaped controlled CdS and ZnS nanoparticles. Different size and shapes of CdS and ZnS nanoparticles have been synthesized, characterized and studied for photodegradation of organic dyes.

2. Experimental
2.1 Materials: All chemicals were purchased from Merck, Fluka and Aldrich chemical companies and used without further purification. All yields refer to isolated products. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (SILG/UV 254, Merck) using UV light as the visualizing agent. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra were recorded on a Bruker spectrophotometer. The NMR spectra were recorded on a Bruker AVANCE DMAX400 spectrometer, operating at 400 MHz ($^1$H NMR) and 100 MHz ($^{13}$C NMR).

2.1.1 Preparation of zinc and cadmium dithiocarbamate (2). The complexes of zinc and cadmium dialkyl dithiocarbamates were prepared according to the literature [16 and 17] with slight modification. Carbon disulfide (0.01 mol, 0.6 mL) was added in small portions to an equimolar solution mixture of the corresponding amine (0.02 mol) in water (3 mL) cooled in an ice bath at 0°C. After 15 min, a precipitate formed was collected which was then dried in air and recrystallized in a mixture of acetone/$n$-hexane.

Cadmium sulfate (5.0 mmol, 1.7 g) or zinc sulfate (5 mmol, 1.4 g) was dissolved in distilled water (25.0 mL) and added drop-wise to the corresponding solution of the dithiocarbamate ligand (10.0 mmol in 25 mL water) and the mixture was stirred for 1 h and the precipitate formed was filtered, washed with excess distilled water and dried overnight in an oven at 70°C.

2.1.2 Preparation of ZnS and CdS nanoparticles. ZnS and CdS nanoparticles were prepared by hydrothermal method. Deionized water was poured into the autoclave and then various dialkyl dithiocarbamate complexes were added. The autoclave was then placed in an oil bath at 120 °C and for 4 hrs. The synthesized CdS and ZnS nanoparticles were collected by centrifugation, washed thoroughly and dried before further characterization.

2.1.3 Photodegradation of Methylene Blue in the presence of ZnS or CdS nanoparticles: In a 100 ml flask, ZnS or CdS nanoparticles (25 mg) were suspended in a solution (50 mL) of 10 mg/L methylene blue (MB) in water. Prior to the light irradiation, the suspensions were magnetically stirred in the dark for 1 h to reach the absorption-desorption equilibrium of the dye on the surface of photocatalyst. Then, the solution was irradiated with a three-watt blue LED lamp. The first sample was taken out at the end of the dark adsorption period, in order to determine the MB concentration in solution. The required oxygen was supplied by leaving the balloon lid open and by the normal flow of room air. During the light reaction, the temperature of the reaction vessel was between 25–30 °C. The methylene blue decolorization process was performed by controlling the adsorption of methylene blue at wavelength of 665 nm, which is the main characteristic of this compound. The clean solution samples (after separation of any suspended solid by centrifuge) were analyzed by using a UV-vis spectrophotometer.

3. Results And Discussion

3.1 Preparation and Characterization of Controlled Sizes of CdS and ZnS Nanoparticles

The stable ammonium salts of the dithiocarbamates 2 were obtained by the reaction of the secondary amines 1 with carbon disulfide in aqueous medium at low temperature. The zinc and cadmium complexes M-3 were obtained in high yield at room temperature by the reaction of compounds 2 and the respective metal salts in water (Scheme 1).
The complexes of zinc and cadmium M-3 were used for the synthesis of ZnS-3 and CdS-3 nanoparticles by hydrothermal method at 120°C and for 4 hrs. SEM and TEM analysis showed that the alkyl chain in dithiocarbamate complexes of zinc and cadmium systems M-3 plays a significant role in the final size and morphology of the CdS-3 and ZnS-3 nanoparticles. The morphologies of nanoparticles were studied by SEM. Observations of the SEM images of CdS-3 and ZnS-3 nanoparticles reveals that variation of the alkyl groups on the complexes of M-3 gave particles with various size and morphologies (see supporting information). When Cd-3c complex was used for the synthesis CdS nanoparticles, the CdS nanoparticles (CdS-3c) exhibit pyramid-like morphology with the hexagonal base, and the particles are fused to form aggregates (Fig. 1a). The ZnS nanoparticles (ZnS-3b) prepared by hydrothermal method of complex Zn-3b (ethyl group) exhibit cubic-like aggregate morphology (Fig. 1b). TEM analysis of nanoparticles of CdS-3c and ZnS-3b were also used to obtain direct information about the structure and morphology of nanoparticles (Fig. 1c and 1d). TEM showed that the mean diameter of CdS-3c and ZnS-3b nanoparticles is about 60 and 24 nm respectively with a good uniform size distribution. Other CdS and ZnS nanoparticles were easy agglomerated and particles morphologies were unclear (see supporting information).

The EDS analysis for the CdS-3c and ZnS-3b are shown in Figs. 2a and 2b. The elemental analysis (EDS) confirmed the presence of Cd, Zn, and S in the nanoparticles (Fig. 2).

The powder X-ray diffraction patterns for the CdS-3c and ZnS-3b are shown in Figs. 3a and 3b. CdS-3c nanoparticles show the predominant planes of hexagonal phase on their XRD pattern. ZnS-3b nanoparticles show the peaks indexed to 1 1 1, 2 2 0, and 3 1 1 on their XRD pattern. The peaks are appearing due to reflection from the (1 1 1), (2 2 0) and (3 1 1) planes of the cubic phase of the zinc blended type patterns of ZnS.

The sizes and shapes of nanoparticles influence their optical band gaps. The optical band gaps of CdS-3c and ZnS-3b nanoparticles are calculated and found 4.15 and 2.36 eV respectively (see supporting information). The obtained values of the band gap of ZnS-3b nanoparticles are higher than CdS-3c (2.36 eV). The obtained values of the band gap of other type of CdS and ZnS nanoparticles were shown in supporting information.

3.2 Photocatalytic degradation of Methylene Blue in the presence of CdS-3c and ZnS-3b

Metal sulfide nanoparticles have been used widely in photodegradation of dyes. In order to consider the photoactivity of the prepared CdS and ZnS nanoparticles, photodegradation of methylene blue (MB) in water was examined under blue LED (see experimental section). The decreasing concentration of MB in the presence of nanoparticles was studied to evaluate the activity of the CdS-3c and ZnS-3b nanoparticles. To detect the concentration of MB in the solution the absorption peak of MB at 665 nm was chosen as the monitored parameter. Figures 4a and 4b show the absorption peak significantly decreases in intensity during the reaction between MB and CdS-3c and ZnS-3b nanoparticles under LED lamp. Results showed that the MB degradation rate in the presence CdS-3c is higher than ZnS-3b.
nanoparticles (The MB degradation rate results of other type of CdS and ZnS nanoparticles were shown in supporting information).

4. Conclusions

Herein we reported synthesis two different size and shapes of CdS and ZnS nanoparticles. In this study, effect of alkyl chain of dithiocarbamates was investigated for the size and shaped controlled CdS and ZnS nanoparticles. The complexes of zinc and cadmium were used for the synthesis of ZnS and CdS nanoparticles by hydrothermal method at 120°C and for 4 hrs. CdS nanoparticles (CdS-3c) exhibit pyramid-like morphology with the hexagonal base, and the ZnS nanoparticles (ZnS-3b) prepared by hydrothermal method of complex Zn-3b (ethyl group) exhibit cubic-like aggregate morphology. Other CdS and ZnS nanoparticles were easy agglomerated and particles morphologies were unclear. A photocatalytic degradation of UV-irradiated Methylene Blue solutions in the presence of ZnS and CdS nanoparticles was also studied in order to examine the nanoparticles influence on photodegradation rates.

Declarations

Conflicts of Interest: The authors declare no conflict of interest.

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Figures
Figure 1

a and b SEM images of as-prepared samples of CdS-3c and ZnS-3b; c and d TEM images of as-prepared CdS-3c and ZnS-3b
Figure 2

EDS spectrum of as-prepared CdS-3c (a) and ZnS-3b (b)
Figure 3

XRD patterns of as-prepared CdS-3c (a) and ZnS-3b (b)
Figure 4

Photodegradation of MB in the presence of as-prepared CdS-3c (a) and ZnS-3b (b)

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