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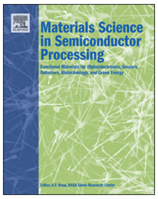

Synthesis and characterization of castor oil and ricinoleic acid capped CdS nanoparticles using single source precursors

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ABSTRACT

We report the synthesis of castor oil and ricinoleic acid capped CdS nanoparticles by the thermolysis of piperidine (**1**) and tetrahydroquinoline (**2**) dithiocarbamate complexes of cadmium(II) at temperatures varying from 190 °C to 300 °C. Reaction parameters such as time and temperature were varied to study their effect on the properties and morphology. The optical properties of CdS were typical of particles that displayed quantum confinement effects. X-ray diffraction studies revealed the existence of both cubic and hexagonal phases depending on the reaction conditions. Ricinoleic acid capped CdS gave cubic phase particles whereas castor oil capped CdS gave both cubic and hexagonal phases dependent on the reaction temperature and the type of complex used. The morphology of the particles varied from oval-short rods to spherical shaped particles with sizes ranging from 10 to 22 nm. Rhodamine B (RhB) dye photodegradation studies of a representative CdS nanoparticles' sample have been carried out in the presence of halogen light and studied using UV–visible spectroscopy.

1. Introduction

Among the various semiconductors, cadmium sulfide nanoparticles have been given considerable attention by researchers and scientists due to their size dependent unique optical and electronic properties. These properties make them useful in optoelectronic applications including solar cells [1], light emitting diodes [2], nonlinear optics [3] and heterogeneous photo catalysis [4].

In the last few decades, considerable effort has been expended towards developing synthetic methods of preparation for CdS and other II–VI semiconductor nanoparticles [5–9]. Despite the many synthetic approaches reported in the literature, a persistent challenge is the need to develop synthetic methods which are environmentally friendly and economically viable. Recent focus has been on the development of greener methods for nanoparticle synthesis [10–12]. One approach is the use of non-toxic solvents and/or capping groups in the synthetic methodology [13–15]. Passivating agents are frequently used to inhibit nanoparticle overgrowth and aggregation and also control the structural characteristics of the resultant particles in a precise manner [16]. Common capping agents used include amines, phosphines and thiols [17–22]. However, most of these capping agents are toxic, expensive and require complicated synthetic processes [23,24]. As a result, the need of employing greener methods of synthesis which use renewable and bio-based capping agents has grown over the years. Olive oil [25], oleic acid [26], anacardic acid [13] and castor oil [11] are examples of greener capping agents and dispersants that are already reported in literature.

Castor oil, a naturally occurring triglyceride, has been recently investigated for its use in nanoparticles synthesis [27–30]. The oil consists of different fatty acids with ricinoleate making about 90% of the total fatty acid chains [31]. Castor oil is extracted from the seeds of the castor oil plant, *Ricinus communis*. It is obtained as a colorless to very pale yellow liquid with a distinct taste and odor, and has a boiling point of 313 °C [30]. Due to its easy availability, low cost, non food competition, high boiling point, high viscosity and environmental considerations, castor oil seems to have a huge potential as a green capping agent. Hydrolysis of the oil gives ricinoleic acid, a mono-unsaturated 18-carbon fatty acid, as the major component [32]. Unlike other fatty acids, ricinoleic acid has a hydroxyl functional group on C-12 which makes it and castor oil in general more polar than most fat acids. In the current work, castor oil and its major constituent, ricinoleic acid are used as greener capping agents and dispersants in the synthesis of CdS nanoparticles using heterocyclic dithiocarbamate complexes as single source precursors. To our knowledge this is the first report of the thermolysis of single molecular precursors in castor oil and

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ricinoleic acid. The prepared nanoparticles were characterized and a representative sample tested as catalysts in the photodegradation of RhB dye using fluorine lamp as the source of light. We hope that this work will lead to more studies on the use of greener solvents for nanoparticle synthesis.

2. Experimental

2.1. Chemicals

Castor oil was extracted from castor seeds; ricinoleic acid was isolated from castor oil. Rhodamine B dye (> 95%), tri-*n*-octylphosphine (TOP) 90%, piperidine (99%) and 1,2,3,4, tetrahydroquinoline (98%) were purchased from Sigma-Aldrich. Petroleum ether (90%), potassium hydroxide (90%), anhydrous magnesium sulfate, sulfuric acid (98%), hexane, chloroform, methanol (99.5%), carbon disulfide (99.5%), sodium hydroxide (98%), cadmium chloride monohydrate (99%) and acetone were purchased from Merck chemicals. All chemicals were used as purchased without any further purification.

2.2. Instrumentation

Infrared spectra were recorded on a Bruker FT-IR tensor 27 spectrophotometer directly on small samples of the compounds in the range 200–4000 cm^{-1}. Optical measurements were analyzed using a Varian Cary 50 UV–visible spectrophotometer in which the samples were placed in silica cuvette (1 cm path length), using hexane as a reference solvent. Photoluminescence of the particles was analyzed using a Perkin-Elmer, LS55 Luminescence spectrometer. The samples were placed in a quartz cuvette (1 cm path length) and all measurements were done at room temperature. Samples were prepared by placing a drop of dilute solution of nanoparticles on Formvar-coated grids (150 mesh) for TEM and holey carbon grids for HRTEM. The samples were allowed to dry completely at room temperature and viewed using a JEOL 1400 TEM and JEOL 2100 HRTEM. viewing was done at an accelerating voltage of 120 kV (TEM) and 200 kV (HRTEM), and images captured digitally using a Megaview III camera; stored and measured using soft imaging systems iTEM software (TEM) and Gatan camera and Gatan software (HRTEM). Powder diffraction patterns were recorded in the high angle 2θ range of 20–70° using a Bruker AXS D8 diffractometer equipped with a nickel filtered Cu Kα radiation ($\lambda = 1.5418$ Å) at 40 kV, 40 mA and at room temperature. The scan speed and step sizes were 0.2 min^{-1} and 0.01314 respectively.

2.3. Extraction of castor oil and isolation of ricinoleic acid

Castor oil was extracted from castor seeds using a method reported by Akpan et al. 2006, in which hexane was used as the extracting solvent in a soxhlet apparatus [33]. Its isolate, ricinoleic acid was isolated from the oil by a method reported by Vaisman et al. 2007 [34]. In a typical process, 60 g of KOH in 500 ml of ethanol were added in 250 g of castor oil and refluxed. After 3 h, 1.5 L of distilled water acidified by 50 ml conc. H_2SO_4 in 150 ml of H_2O was added. Two layers were formed in which the organic layer was collected, washed with warm distilled water and dried over $MgSO_4$. The mixture was filtered to yield ricinoleic acid.

2.4. Synthesis of precursors

The method used in the preparation of the ligands and complexes is similar to that reported in our previous work [22].

2.5. Synthesis of nanoparticles

0.5 g of complex (**1**) or (**2**) was dissolved in 6.0 mL of castor oil. The mixture was then injected into 6.0 g of hot castor oil in a three neck flask at 190 °C /230 °C /270 °C /300 °C under nitrogen gas flow. After the reaction time of 30 min/1 h and 2 h, an aliquot of the sample was taken, to which methanol was added resulting in the formation of a flocculent precipitate. The precipitate formed and the solvent were separated by centrifugation, and dispersed in hexane to give yellow castor oil capped CdS nanoparticles. Similar procedures were followed using ricinoleic acid (RA) as both a dispersing medium and a capping agent.

2.6. Photodegradation

The photocatalytic activity of representative samples of the as-prepared materials was evaluated by the degradation of RhB dye under halogen (fluorine) light irradiation of fluorine lamp. Castor oil capped CdS nanoparticles prepared from complex (**1**) at 190 °C (CdS 1), and 300 °C (CdS 2); and ricinoleic acid capped CdS nanoparticles prepared from complex (**1**) at 190 °C (CdS 3), and 300 °C (CdS 4) were used for this study. After the base line setting using water as a blank solvent, absorbance of RhB solution was measured. About 0.015 g of CdS 1 was added in 20 ml of RhB solution and placed in a sealed black box equipped with fluorine lamp as the source of light. At given time intervals, a sample of the reaction mixture was taken and optical absorption spectra were recorded to determine the degradation rate of RhB. Control experiments; without the addition of the catalyst and with a catalyst in absence of light were also carried out. The same procedure was repeated for CdS 2, 3 and 4.

3. Results and discussion

3.1. Characterization of the precursors

Piperidine dithiocarbamate and tetrahydroquinoline dithiocarbamate ligands and their corresponding Cd (II) complexes synthesized were pure and obtained in good yields. White precipitates of piperidine dithiocarbamate ligand and its corresponding cadmium complex (**1**) were obtained while pale yellow powders were obtained for the case of tetrahydroquinoline dithiocarbamate ligand and its cadmium complex (**2**). The compounds are air stable, easy to synthesize and soluble in some organic solvents such as chloroform. Characterization of piperidine and tetrahydroquinoline dithiocarbamate ligands and their corresponding cadmium (II) complexes by ^1H NMR, IR, TGA and CHN have been reported previously [22].

3.2. Castor oil capped CdS nanoparticles

The optical absorption spectra of CdS nanoparticles synthesized from complex (**1**) at different reaction temperatures (190–300 °C) are shown in Fig. 1. The excitonic absorption maxima bands from all temperatures are blue shifted relative to the peak absorption of bulk CdS indicating quantum confinement effects [35]. The band gap energies of the materials at each temperature can be calculated from Tauc plots [36]. The calculated band gap for a 190 °C sample estimated from the Tauc plot (Inset Fig. 1) is 2.25 eV. A slight red shift is observed from the spectra on moving from lower to higher temperatures suggesting an increase in the size of the particles as the reaction temperature is increased (Tauc plots not shown for clarity of the figures). The corresponding PL spectra (Fig. 2) display strong band edge emissions with the maxima at *ca.* 480 nm, a considerable blue shift as compared to the bulk CdS