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Tuning of chalcogenide nanoparticles fluorescence by Schiff bases

Selvaraj Naveenraj[a], Sambandam Anandan[a,*], Sivan Velmathi[a], Abdullah M. Asiri[b], Muthupandian Ashokkumar[c]

[a] Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India
[b] The Center of Excellence for Advanced Materials Research, King Abdul Aziz University, Jeddah 21413, P.O. Box 80203, Saudi Arabia
[c] School of Chemistry, University of Melbourne, Victoria 3010, Australia

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ABSTRACT

The interaction between chalcogenide (CdS and CdSe) nanoparticles and Schiff bases in the presence and absence of an electron withdrawing (nitro) substituent in organic media has been studied using steady-state and time-resolved fluorescence measurements. The changes in the chalcogenide nanoparticles luminescence properties in the presence of electron or hole acceptors provide information on their electronic properties. For this purpose, platelet-like chalcogenide nanoparticles with average size of ~5–12 nm were synthesized using a simple microwave technique and characterized using UV–vis spectroscopy, XRD and TEM. The fluorescence quenching studies suggest that Schiff bases quench the fluorescence of chalcogenide nanoparticles effectively. Fluorescence lifetime studies suggest the presence of dynamic (collisional) encounters in the interaction of schiff bases with the chalcogenide nanoparticles. A possible quenching mechanism has also been proposed using Fourier transform infrared spectroscopy.

1. Introduction

Studies on chalcogenide nanoparticles have been at the focus of intense research due to their unique size-dependent physicochemical and optoelectronic properties [1]. This size quantization effect allows chemists and material scientists, a distinct opportunity to modify their surface properties in addition to their electronic and chemical properties simply by controlling the particle size [2]. The electronic properties of nanoparticles can be studied by monitoring their luminescence properties in the presence of electron or hole acceptors [3,4].

Chalcogenide semiconductor nanoparticles, such as CdS and CdSe, have been extensively studied due to their potential applications in various fields such as solar cells, field effect transistors, light emitting diodes, photocatalysis, biological fluorescent labels and biological sensors [5–7]. Among the various methods available to synthesize chalcogenide nanoparticles [8–12], microwave technique has attracted significant attention due to the dramatic enhancement in reaction yields, reduction in reaction time, ease of purification, use of less solvent and greater flexibility in reaction conditions [13–15].

Recently, many groups [3,4,16–18] studied the interactions of chalcogenide nanoparticles with different substrates using steady-state and dynamic fluorescence spectroscopy, which are the main constructive tools in monitoring the electronic properties of nanoparticles.

In this work, we have studied the interactions of chalcogenide nanoparticles (CdS and CdSe) with Schiff bases in the presence and absence of an electron withdrawing group. Schiff bases, which are derived from the condensation of primary amines and aldehydes or ketones and characterized by the anil linkage —HC=N—, possess structural similarities with natural biological substances. They have a wide variety of applications in biological, inorganic, clinical and analytical fields [19,20]. They are known to exhibit potent antimicrobial (antibactericidal, antiviral and antifungal), anticonvulsant, anti-inflammatory and insecticidal activities [19–21]. In addition some Schiff bases show pharmacologically useful activities like anticancer (radical scavenging activity), anti-hypertensive, antifertility, analgesic, anthelmintic, and hypnotic activities [21].

2. Experimental

2.1. Materials

Cadmium chloride, sodium sulfide, sodium selenite, hydrazine, salicylaldehyde, 4-nitroaniline and aniline were of analytical grade purchased from Aldrich chemicals and used as received. All solvents used were of extra pure analytical grade.

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* Corresponding author. Tel.: +91 431 2503639; fax: +91 431 2500133.
E-mail addresses: sanand@nitt.edu, sanand99@yahoo.com (S. Anandan).

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2.2. Methods

2.2.1. Microwave assisted synthesis of CdS nanoparticles

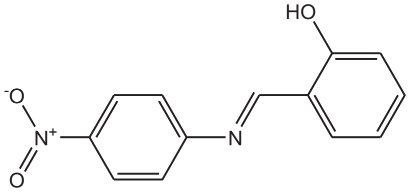
CdS nanoparticles were synthesized using the method by Yang et al. [22] 0.05 M Na_2S, dissolved in distilled water (25 ml), was added drop-wise to a 100 ml round bottom flask containing 25 ml of 0.05 M aqueous solution of $CdCl_2$. The mixture was stirred using magnetic stirrer and then ultrasonicated for homogeneous mixing. After ultrasonication for 1 min, the round bottom flask was connected with a reflux system and was kept in a domestic microwave oven (2450 MHz, Whirlpool). A water cooled condenser outside the microwave oven cavity was connected by a glass joint to the round bottom flask. The reaction was carried out under microwave irradiation for 5 min. After cooling to ambient temperature, the yellow precipitate was centrifuged and washed and then dried under vacuum at 60 °C for about 10 h.

2.2.2. Microwave assisted synthesis of CdSe nanoparticles

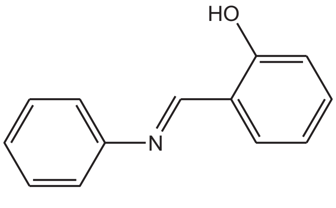
0.05 M Na_2SeO_3 dissolved in distilled water (25 ml) was added drop-wise to the 100 ml round bottom flask containing 25 ml of 0.05 M aqueous solution of $CdCl_2$. The mixture was stirred using magnetic stirrer and 0.075 M hydrazine was added to this mixture while it was kept in an ultrasonic bath for reducing selenite ion to selenide ion. After ultrasonication for 1 min, the round bottom flask was connected with a refluxing system and was kept in a domestic microwave oven (2450 MHz, Whirlpool). A water cooled condenser outside the microwave oven cavity was connected by a glass joint to the round bottom flask. The reaction was carried out under microwave irradiation for 5 min. After cooling to ambient temperature, the red precipitate was centrifuged and washed and then dried under vacuum at 60 °C for about 10 h.

2.2.3. Synthesis of Schiff bases N-salicylidene-4-nitroaniline (SB1) & N-salicylideneaniline (SB2)

Schiff bases, N-salicylidene-4-nitroaniline & N-salicylideneaniline, were synthesized using a method by Sivakumar et al. [23] salicylaldehyde (2 mmol in methanol) was slowly added to 4-nitro aniline (2 mM in methanol). The mixture was stirred for 3 h at room temperature. The completion of the reaction was monitored through TLC for the disappearance of the starting compounds. Then, the solvent was evaporated through rotary evaporator yielding reddish yellow crystals of N-salicylidene-4-nitroaniline. The yield was about 98.3%. The solid thus obtained was dried in vacuum oven. The melting point was found to be 130–132 °C. Following a same procedure, N-salicylideneaniline was synthesized.



N-Salicylidene-4-Nitroaniline (SB1)



N-Salicylideneaniline (SB2)

N-salicylidene-4-nitroaniline:

^1H NMR ($CDCl_3$, δ_{ppm}), (aromatic) 6.9 m 2H, 7.2 m 1H, 7.4 m 5H, 7.6 d 1H (aromatic), 9.0 s 1H (CH = N), 12.3 s, 1H (OH)

IR (KBr plates, (cm^{-1}): 1272, 1395, 1485, 1611, 3056, 3450.

UV λ_{max} (nm): 355, 321.*N-salicylideneaniline*:

^1H NMR ($CDCl_3$, δ_{ppm}) 7.0–7.2 m 2H, 7.3–7.5 dd 4H, 8.2–8.4 d 2H (aromatic), 8.6 s, 1H (CH=N), 12.5 s, 1H (OH)

IR (KBr plates, (cm^{-1}): 1267, 1345, 1463, 1630, 3070, 3427.

UV λ_{max} (nm): 336, 316, 300.

2.2.4. Interactions between microwave synthesized CdS and CdSe nanoparticles and Schiff base N-salicylidene-4-nitroaniline

Microwave synthesized chalcogenide nanoparticles and Schiff bases were soluble in dimethylformamide (DMF). 6×10^{-5} M solution of Schiff base in DMF and 3×10^{-5} M chalcogenide solution were prepared. Twenty microliters of the prepared Schiff base solution was added to 3 ml of 3×10^{-5} M CdS/CdSe solution. The interactions were monitored by steady-state and time resolved fluorescence spectroscopy.

2.3. Analytical procedures

Fourier transform infrared (FTIR) spectra were recorded using a Perkin-Elmer 360 model IR double beam spectrophotometer. The spectra were collected from 4000 to 400 cm^{-1} with 4 cm^{-1} resolution over 40 scans. All spectra were collected against the background spectrum of KBr. UV–vis absorption spectra were recorded on a T90+ UV/Visible Spectrophotometer (PG Instruments, United Kingdom) in the range of 200–800 at a scan rate of 250 nm/min. All spectra were collected against the background spectra of the solvents. Fluorescence emission spectra were recorded on SHIMADZU Spectrofluorophotometer in the range of 360–600 nm at a scan rate of 500 nm/min. The CdS and CdSe samples were excited at a wavelength of 340 nm and 450 nm, respectively. XRD spectra were recorded with a Philips PW1710 diffractometer using Ni filtered Cu radiation. The sample was allowed to equilibrate with atmospheric moisture for at least 24 h prior to recording. The scanning range was 20–60° (2θ) with a step of 0.02° and a count time of 2 s. Fluorescence lifetime measurements were carried out in a picosecond time correlated single photon counting (TCSPC) spectrometer with tunable Ti-sapphire laser (TSUNAMI, Spectra physics, USA) as the excitation source. In TCSPC experiment, the CdS and CdSe samples were excited at a wavelength of 325 nm and 425 nm, respectively. The fluorescence decay curves were analyzed using the software provided by IBH (DAS-6). The surface morphology and particle size of the synthesized nanoparticles were analyzed using TEM (TECNAI G^2 model). Samples were coated on copper grid at normal atmospheric temperature and pressure.

3. Results and discussion

3.1. Characterization of CdS and CdSe nanoparticles

Fig. 1a shows the absorption spectra of microwave synthesized CdS and CdSe nanoparticles dissolved in DMF. They show absorption onsets at 480 nm (2.58 eV) for CdS and 556 nm (2.23 eV) for CdSe, whereas bulk CdS and CdSe particles show absorption onsets at 512 nm (2.42 eV) and 716 nm (1.73 eV), respectively. The apparent blue shift in the absorption onsets for both CdS and CdSe can be attributed to the quantum-size confinement effect [1,2]. From the absorption onset, the mean grain size of semiconductor nanoparticles can be determined using Brus equation