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Organized assemblies of AOT determine nanoparticle characteristics and their performance as FRET donors

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ABSTRACT

CdS nanoparticles (NPs) have been synthesized in three organized assemblies formed by the surfactant Aerosol-OT (AOT). Although NP synthesis in AOT reverse micelles is well documented, but AOT regular micelles and gels have not been commonly used for NP synthesis in the past. The NP shape, size and particularly crystallinity are found to bear direct correlation to the type of AOT assembly. These CdS NPs were found to be photoluminescent and participate in very effective fluorescence resonance energy transfer (FRET) with a dye, Ethidium bromide (EB). The efficiency of FRET between CdS NPs and EB is found to depend largely on the location of dye in the surfactant assembly and more significantly on the NP characteristics. This is the first report of preparation of CdS NPs in AOT regular micelles and gels and the first report of FRET between CdS NPs and dye in AOT based organized assemblies.

1. Introduction

Quantum confined semiconductor chalcogenide nanoparticles, specially quantum dots (QDs) have been widely studied for the last few decades due to their high photostability, wide absorption and narrow emission profiles, size dependent band gaps etc [1–5]. Semiconductor nanoparticles find wide applications in various fields like labeling, deep-tissue imaging, photonics, sensing, pollutant degradation, detection of nucleic acids, solar cells, light-emitting diodes and in photocatalysis [6–13]. Among the semiconductors, CdSe is the popularly studied [14,15].

Due to their high surface energy, CdS nanoparticles (NPs) tend to form large aggregates in solution [16]. Surfactants are often used to stabilize the NPs [17]. Often surfactants can diminish the toxicity or cytotoxicity of the NPs [18]. In the past, CdS NPs have been synthesized using many different techniques *viz.* sol-gel method [19], solvothermal or hydrothermal method [20] and thermal evaporation technique [21] to name a few. Sodium bis (2-ethylhexyl) sulfosuccinate or Aerosol OT (AOT), an anionic surfactant, has been used in the past for the synthesis of CdS NPs. More specifically, AOT reverse micelles had been used as microreactors [22–24]. CdS NPs have also been synthesized in AOT foam [25]. To the best of our knowledge, till date there have been no reports on the synthesis of CdS NPs in other AOT based assemblies like regular micelles or gels. That AOT spontaneously forms reverse micelles in non polar solvents is well known [26]. Although less popularly known, AOT can also form regular micelles in water above CMC [27–30]. Recently Lai et al. have reported on the formation of gel-like structures in the *n*-hexane/AOT/water system [31,32].

To the best of our knowledge, AOT regular micelles have not been used for the synthesis of any NPs in the past except synthesis of CuNPs reported by our group [33] and there are only few reports of synthesis of NPs in AOT gels [34,35].

In the present work we have synthesized CdS NPs in three AOT based organized assemblies- reverse micelles, regular micelles and gels. These have been completely characterized and a comparative study has been made of the NP characteristics in the various assemblies. Furthermore, the NPs have been found to be fluorescent themselves and they also participate in efficient fluorescence resonance energy transfer (FRET).

FRET is often used as a 'spectroscopic ruler' in biological sciences [36]. FRET also finds applications in energy conversion processes [37], photosensitization [38] and photodynamic therapy [39]. FRET involves non-radiative excited state energy transfer from a donor (D) to an acceptor (A) and can be represented as-

$$D^* + A \rightarrow D + A^* \quad (1)$$

Common FRET donors are quantum dots as they exhibit a stable fluorescence and have fairly high quantum yields. Kagan et al. have reported that CdSe QDs can act as both donor and acceptor in energy transfer processes depending on their size [40]. Sadhu et al. have reported on the shape and composition dependent FRET between CdS nanoparticles as donor and Nile Red dye as acceptor [41]. Zhou et al.

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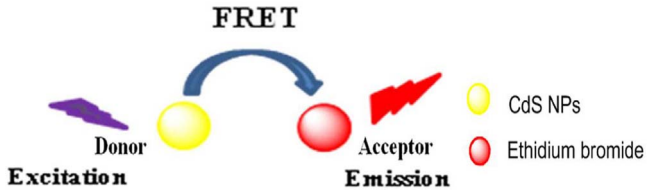

Scheme 1. FRET between CdS NPs as donor and EB as acceptor.

have reported on FRET between QDs and Alexa dye attached to DNA [42]. Matoussi et al. have studied the FRET involving QD in details [43,44].

Most of the earlier FRET studies using CdS NPs were carried out in bulk media [40–42]. For efficient FRET between a donor and an acceptor, a restricted environment can be very useful [45]. To the best of our knowledge, no work on FRET using CdS NPs in restricted media has been reported till date. The CdS NPs synthesized here, in various AOT-based organized assemblies were used as FRET donors while a DNA intercalating dye Ethidium bromide [46–49] was used as acceptor for FRET studies (Scheme 1).

2. Materials and methods

2.1. Materials

AOT [sodium bis (2-ethylhexyl) sulfosuccinate] was purchased from Loba Chemie and was purified and vacuum dried before use. *n*-Heptane (HPLC grade), purchased from spectrochem was at first refluxed with sodium and benzophenone and then down distilled under dry atmosphere. Cadmium nitrate [$Cd(NO_3)_2$. $4H_2O$] and sodium sulfide (Na_2S) were from Merck. Ethidium bromide was purchased from Sigma-Aldrich and double distilled water was used to prepare all the solutions.

2.2. Synthesis of CdS nanoparticles

0.2 M stock solutions of both precursors were used for the synthesis. The final concentrations of both the precursors $Cd(NO_3)_2$. $4H_2O$ and Na_2S were maintained at 1.8×10^{-3} M in all three systems. All studies were carried out at room temperature. The pH of the solutions were in the range 7.8-8.3.

2.2.1. Synthesis in AOT reverse micelles

The synthesis of CdS nanoparticles in AOT reverse micelles was carried out using the procedure described in literature [22–24]. The concentration of AOT is 0.1 M. The w_0 ($[H_2O]/[AOT]$) value was maintained at 15. Synthesis of CdS NPs were also tried at higher w_0 (w_0 = 30). However precipitation occurred within a few minutes. At first, two separate microemulsions containing $Cd(NO_3)_2$. $4H_2O$ and Na_2S were sonicated for 30 min using a mini bath sonicator (Piezo-U-Sonic model). Then the two transparent and colorless microemulsions were mixed together and sonicated for another 15 min. The characteristic yellow color appeared within a few minutes indicating the formation of CdS nanoparticles.

2.2.2. Synthesis in AOT micelles

While carrying out the synthesis of CdS nanoparticles in AOT regular micelles, 1×10^{-2} M AOT was used which is above the reported critical micellar concentration (CMC) of AOT i.e. 5×10^{-3} M [27–30,33]. In this case AOT regular micelles were prepared first in water then $Cd(NO_3)_2$ solution was added, the entire mixture was sonicated for 15 min and then Na_2S solution was added drop wise resulting in the formation of CdS nanoparticles.

2.2.3. Synthesis in AOT gel

For synthesis of CdS nanoparticles in AOT gel, the transparent AOT gel was prepared first by dissolving AOT in *n*-Heptane at [AOT] = 0.1 M. Then water was gradually added. The molar ratio of water to AOT was 1.2. Then the $Cd(NO_3)_2$ precursor solution was added and homogenized by stirring. This was followed by addition of Na_2S solution drop wise with stirring until the characteristic yellow color of CdS nanoparticles appeared within a few minutes.

The yellow-coloured CdS NCs were separated from solvent by ultracentrifugation. The yellow solid was carefully washed using methanol and then dried under vacuum.

2.3. Instrumentation

The UV–vis spectra were recorded in a Shimadzu UV-2401PC spectrophotometer. The fluorescence emission spectra were recorded in a Perkin-Elmer spectrofluorimeter, Model No. LS-55. The excitation wavelength for all the experiment was maintained at 370 nm and both the excitation and emission slits are 5 nm. Fluorescence life times were determined by time correlated single photon counting (TCSPC) using a nanoLED-07 diode (IBH, UK) as the excitation source at 405 nm. The decay curves were analyzed using IBH-6 decay analysis software. Scanning electron microscopy (SEM) studies were performed with a field emission SEM (JSM-6700F JEOL, Japan) to see the surface topology. Dynamic light scattering (DLS) studies were performed with a Nano-ZS (Malvern) instrument, which is equipped with a 4 mW He–Ne laser (λ = 632 nm). Transmission electron microscopy (TEM) studies of the nanoparticles were carried out at a resolution of 1.9 Å with a JEOL JEM-2100 electron microscope. TEM specimens were prepared by placing micro drops of solution on a carbon film supported by a 300 mesh copper grid. Polarising optical microscopy (POM) studies were carried out using a Nikon polarising microscope LV100POL provided with Instec hot- and cold-stage HCS302 and a STC200 temperature controller configured for HCS302. Powder X-ray diffraction (XRD) data were recorded using a Bruker D8 advanced powder X-ray diffractometer employing CuKα radiation (λ = 1.5418 Å).

3. Results and discussion

3.1. AOT gel characteristics

Fig. 1a shows the SEM image of AOT gel. It is observed from the SEM image that the gel is fibrillar in nature i.e. the gel network is composed of closely packed fibrils. This assumption is also supported by the earlier work of Lai et al. [31,32]. POM images shown later also support this. The mechanical properties of the gels were studied by the rheological parameters G' and G" which represent the storage modulus and loss modulus respectively. G' is an indicator of the solid-type nature of the gel and G" is an indicator of the liquid-type nature of the gel. The frequency sweep measurements of the AOT gel (Fig. 1b) indicate that G' is linear for a large range of frequency upto 300 rad/s and is always larger than G" indicating the viscoelastic nature of the gels. The gel is moderately robust as is borne out by medium value of G' (200–300 Pa). The gel is also transparent as borne out by the photograph of gel (Fig. 1c).

3.2. Absorption spectra and band gap (E_g) of CdS nanoparticles

Fig. 2 shows the absorption spectra of CdS nanoparticles in the three AOT based organized assemblies. Spectra in all three assemblies show an absorption shoulder around 390–420 nm which is characteristic of CdS NPs [50–52] and can be assigned to the $1s_h$-$1s_e$ excitonic transitions. The absorption shoulders are well-defined for regular micelles and reverse micelles (w_0 = 15) but a broader shoulder in the gel indicates larger size of CdS NPs in AOT gel. From the absorption spectra, we note that the CdS NPs synthesized in reverse micelles (w_0 = 15) show a pronounced shoulder at 390–400 nm and an