The Synthesis of HgS and CdS Nanoparticles in Polymer Matrices

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SUMMARY: The synthesis of CdS nanoparticles in two different polymer matrices ie. polyacrylamide and polystyrene, is described. In addition, we describe the synthesis of HgS nanoparticles in polyacrylamide. Both the CdS and HgS nanocomposites show blue shifts in the optical spectra in relation to the bulk material. The photoluminescence spectra of both materials show broad emission. The transmission electron microscopy (TEM) images confirm the nanocrystalline nature of the CdS and HgS nanocomposites.

Introduction

The study of nanometer-size crystallites is an exciting area of research, which explores the mesoscopic world in which assemblies containing 10^2-10^3 entities have distinct size-dependent properties.[1,2] Such materials have considerable promise in a wide range of applications.[3,4] Semiconducting nanocrystals have novel optical and electronic properties due to quantum confinement effects and their large surface to volume ratios.[5,6] In the quantum-confined regime it is possible to tune the band gap by the control of the particle size and in principle to achieve targeted optical properties.[7] Nanocrystalline materials generally occur as powders, which are soluble in polar or non-polar solvents depending on their surface coating. The fabrication of devices using nanocrystals requires the particles to be assembled in a medium with suitable characteristics.[8] Organic polymers are good candidates because:

- a wide variety of polymers can be synthesised with tailor-made properties to couple with nanocrystals[3,9-12]
- a high level doping of organically-capped nanocrystals in the medium can be achieved[13]

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- the resultant materials are easy to process, e.g. by spin coating[14]
- there is a potential for high thermal and electrical stability[15]
- there is good spatial distribution of particles, preventing agglomeration
- the particle dispersity and size distribution can be controlled
- the polymer itself can take on the role of the capping agent.

There is also scope for considerable synthetic flexibility:

- pre-prepared nanoparticles can be mixed with polymers to form composite materials[16]
- nanoparticles can be generated *in situ* in a polymer matrix.[17]

Cadmium sulphide nanoparticles have attracted considerable attention mainly because of their relative ease of synthesis and easily studied particle size-dependent optical properties, providing spectral methods for unambiguously identifying and comparing new data with a vast literature of existing data.[18] Various routes, such as the colloidal,[19] organometallic,[20] use of single molecule precursors [21]and synthesis in confined matrices,[22] have been employed for the synthesis of CdS nanoparticles. However there have been very few detailed studies on HgS nanocrystallites because of difficulties associated with its synthesis and the toxicity of mercury.[23 -25] HgS finds application in many fields: in ultrasonic transducers, image sensors, electronic image materials, and non-linear optics.[26] Hasselbarth *et al.* [27] have prepared HgS nanoparticles by a colloidal route and shown by electron diffraction experiments that the structure is that of cubic HgS. There are also reports on other synthetic routes to prepare HgS, such as a sonochemical method,[23-25] microwave-assisted heating method,[26] *etc.* Studies on HgS nanocrystallites deposited in polymer matrices are rare. This paper reports on an effective method of synthesizing CdS and HgS nanocrystallites in polymer matrices.

Experimental

Synthesis of CdS Nanoparticles in a Polyacrylamide Matrix

Acrylamide (1.8 g) was dissolved in water (20 mL). A pre-formed complex of cadmium chloride (0.1 g) and pyridine (2 mL), dissolved in distilled water (30 mL), was added to the above solution. The mixture was stirred well and thiourea (0.038 g) and azoisobutyronitrile (AIBN) (0.5g) were added. The solution was heated to 60 °C and maintained at this temperature for 2 h. As heating proceeded the solution became viscous, with the appearance of a yellow colour due to the formation of CdS. Methanol (60 mL) was then added to the polymer and precipitation resulted. The product was filtered, washed with methanol, and dried.

Synthesis of CdS Nanoparticles in a Polystyrene Matrix

4-Styrenesulfonic acid sodium salt (2g) was dissolved in distilled water (50 mL). Styrene (20 mL) was then added. After then adding polyvinylpyrrolidone (PVP) (2g), the mixture was stirred well. The suspension was heated to 60 °C and benzoyl peroxide (1g) added. Heating was continued for 2 h and the formed solid filtered and washed with water several times. The polymer was suspended in 1:1 HCl (100 mL) and stirred for 24h. It was filtered and washed with water until it was free of HCl. The solid polymer was again suspended in water (100 mL) containing $CdCl_2$ (0.5g) and stirred for 24 h. The cadmium-loaded polymer was washed with water until free of any chloride ions. It was further washed with ethanol and dried under vacuum. The polymer (0.5 g) was dissolved in chloroform (50 mL) in a closed flask under nitrogen atmosphere. H_2S gas (2 mL) was injected into the flask, which was shaken vigorously. The gas was introduced into the headspace above the solution from a gas-tight syringe, with the gas at atmospheric pressure. On shaking, a yellow solution was obtained. It remained stable for days to months.

Synthesis of Mercury Acrylamide

Acrylamide (1.0 g) was dissolved in ethanol (20 mL). Finely powdered HgO (2.5 g) was added to the solution, which was refluxed for 30 minutes. The hot solution was filtered to remove the unreacted HgO. The filtrate, on cooling, gave white crystals of mercury acrylamide. m.p. 222-223 °C. Yield 1.69 g (68.6 %) C, H, N analysis %, experimental (theoretical) C: 21.26 (21.14), H: 2.28 (2.35), N: 8.26 (8.22), IR, ν (cm^{-1}) and tentative assignments: N-H, 3290; C=O, 1670; C=C,1454.

Synthesis of Copolymer of Mercury Acrylamide and Styrene

Styrene (20mL) and mercury acrylamide (1.0 g) were dissolved in THF (100 mL) in a stoppered flask. The solution was flushed with N_2 gas and AIBN (0.5 g) was added. It was heated and maintained at 60°C for 3h with continuous stirring. The solution was then cooled and poured into methanol (250 mL). The precipitated polymer was washed with methanol and dried. m.p. 212-213°C. Yield 15.5 g (81%).

Synthesis of HgS

The copolymer (0.25 g) was dissolved in 20 mL chloroform and reacted with H_2S gas (1.5-4 mL) in a sealed 250 mL flask. The gas was introduced into the headspace above the solution from a gas-tight syringe with the gas at atmospheric pressure. On shaking, yellow to black solutions were obtained. The materials could be cast into films by spin coating.

Instrumentation

UV-Vis Spectroscopy

A Perkin Elmer Lambda 20 UV-vis Spectrophotometer was used to carry out optical measurements. Samples were placed in quartz cuvettes (1 cm path length).

Photoluminescence Spectroscopy

A Jobinyvon-spex-Fluorolog-3-Spectrofluorimeter with xenon lamp was used to measure the photoluminescence of the nanocomposites. The samples were placed in quartz cuvettes (1 cm path length)

X-ray Diffraction (XRD)

Wide-angle X-ray diffraction patterns were recorded using a Philips X'Pert Materials Research Diffractometer. Measurements were taken using a glancing angle incidence detector at an angle 3 ° for 2 θ values over 5 – 60° in steps of 0.04°, with a count time of 2 *s*.

Electron Microscopy

A JEOL JEM-1200EXII Transmission Electron Microscope using a JEOL EM-ACD10 Anti Contamination Device was used for the conventional Transmission Electron Microscopy (TEM) measurements. The operating voltage was 80-100 kV. The EDAX spectra were obtained using the LINK QX2000 Energy Dispersive Analysis System, operating at 25 kV and at a tilt angle of 30°. The samples were deposited onto carbon-filmed grids, using a fine pipette, air-dried and immediately examined under the microscope.

Results and Discussion

In the present study, CdS was grown in two different polymeric matrices- one hydrophilic (polyacrylamide) and the other hydrophobic (polystyrene). The synthetic techniques used for the two systems were also different. For the hydrophilic system the metal ions were suitably complexed and distributed in the polymer medium and then converted to the sulphide by the S^{2-} ions generated by thiourea in aqueous solution. We preferred the use of cadmium ions complexed with pyridine over bare cadmium ions as the precursor. This was done to impart its effect as a Lewis base, to bind the Cd atoms on the outside of the growing particle thereby preventing further growth.[28] Since CdS formation takes place in the presence of the polymer it can have a direct influence on the particle nucleation and growth and hence it controls the size, size distribution and morphology. The initial interaction takes place between the polymer and the metal precursor. In the case of polyacrylamide this has been studied in detail and it has been shown that Cd atoms are coordinatively bound to the amide groups.[29] In the case of the hydrophilic polymer the same synthetic technique could not be applied as for the non-aqueous medium from which the polymer could be synthesised or in which the polymer could be dissolved does not permit the distribution of Cd^{2+}ions into the polymer. Hence the Cd^{2+} ions are initially incorporated into the polymer through the pendant groups by a chemical reaction, followed by reaction of the chloroform solution of the Cd^{2+}-loaded polymer and H_2S. It is argued that the complex formation of the precursor ion before its reaction with the chalcogenide ion often leads to small particles exhibiting a narrow size distribution.[30]

In the case of HgS, a copolymer of mercury acrylamide and styrene has been synthesized. Mercury acrylamide has a C=C bond which, in the copolymerisation reaction, acts as a cross-linking agent. We have prepared and characterised this new compound which could effectively copolymerise with styrene. The product containing the mercury copolymer is soluble in chloroform, which makes it easy to process. The level of loading of mercury in the polymer can be controlled as it depends on the amount of cross-linking agent, mercury acrylamide used in the copolymerisation reaction. However, as the cross-link density increases, so the solubility of the copolymer in chloroform decreases. A solution of the copolymer in chloroform on reaction with H_2S leads to the formation of HgS. Neat films can be cast by spin coating or pouring the chloroform solution on to a clean glass slide and on evaporation of the solvent the film can be peeled off. As the amount of H_2S injected into the chloroform solution of the polymer is increased from 1.5 mL to 2.5mL, 3 mL and 4 mL, the colour of the solution changes from yellow to orange yellow and finally to black. Once the different colours were developed the container was flushed with nitrogen gas and tightly stoppered. The solution has a long shelf-life and does not show any deterioration in colour. Attempts were made to measure the powder XRD of the copolymer and the HgS-polymer composite. The material does not show any peaks corresponding to HgS. This may be due to the low concentration of HgS particles in the matrix.

Optical Properties

The UV-vis absorption spectra of CdS nanoparticles in polyacrylamide and polystyrene matrices are shown in Fig.1a-b. Macrocrystalline CdS has an optical absorption with a band edge around 515 nm . The band edge for both the composite materials is blue shifted in relation to the bulk material.[31] The band edge for CdS/ polyacrylamide is observed at 395 nm (3.13 eV) while that for CdS/polystyrene occurs at 425 nm (2.91 eV). Bulk CdS is reported to have broad emission maxima in the 400-700 nm range due to recombination from surface defects.[32] The photoluminescence spectra of the composites show broad emission curves, with the maxima at 495 nm and 435 nm for CdS/polyacrylamide and CdS/polystyrene respectively (Fig.2a-b). The broad emission spectra and the lack of any features in the absorption spectra is indicative that the particles are not highly monodisperse.

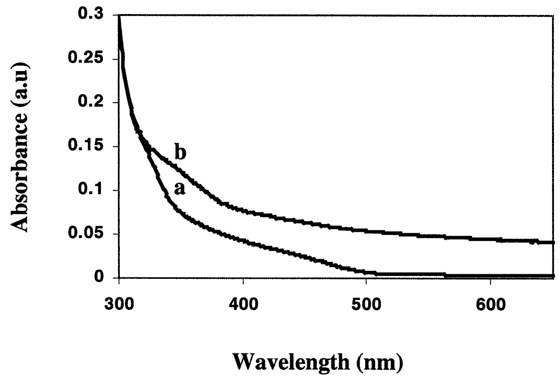

Figure 1. UV/Vis Absorption spectrum of (a) CdS/Polyacrylamide and (b) CdS/Polystyrene nanocomposites

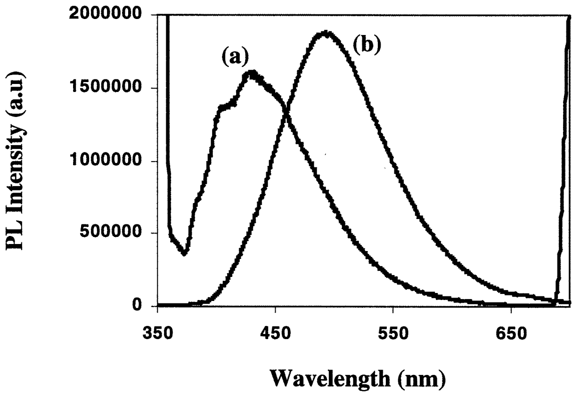

Figure 2. Photoluminesce spectrum of (a) CdS/Polystyrene and (b) CdS/Polyacrylamide nanocomposites

The UV-visible spectrum of the HgS nanocomposite is given in Figure 3. The composite material was dissolved in chloroform and was allowed to react with the required amount of H_2S. The resulting solution was used to measure the absorption spectra. The band gap for the HgS nanocomposite was observed at 2.74 eV (452 nm), which is higher than the band gap (2.0 eV, 620 nm) for bulk HgS^{34} (Figure 2).

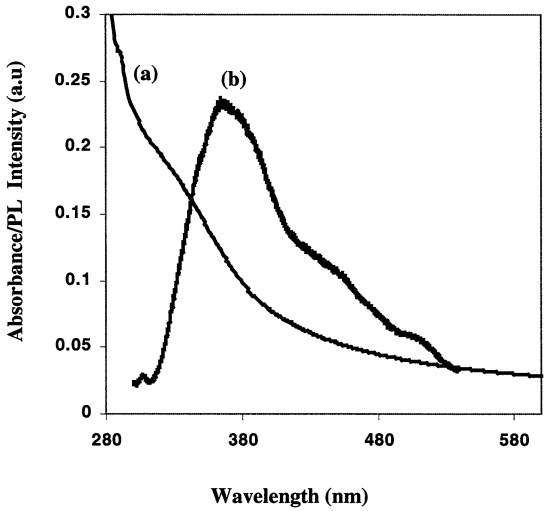

Figure 3. (a) UV/Vis Absorption spectrum ofHgS/Polystyrene nanocompositesand (b) corresponding photoluminescence spectrum

A broad absorption peak with a maximum around 340 nm is observed in the photoluminescence spectrum (Figure 2). This near band edge emission is characteristic of surface-passivated nanoparticles. The observed band gap is also higher than the value, 2.4 eV (516 nm), reported for HgS nanocrystallites synthesised by the sonochemical method.[23-25] The photoluminescence spectrum of the HgS composite shows a broad asymmetric spectrum with an emission maximum at 369 nm (Figure 3). This broad emission curve could be an indication of emission from sulfur vacancies, as observed previously for CdS.

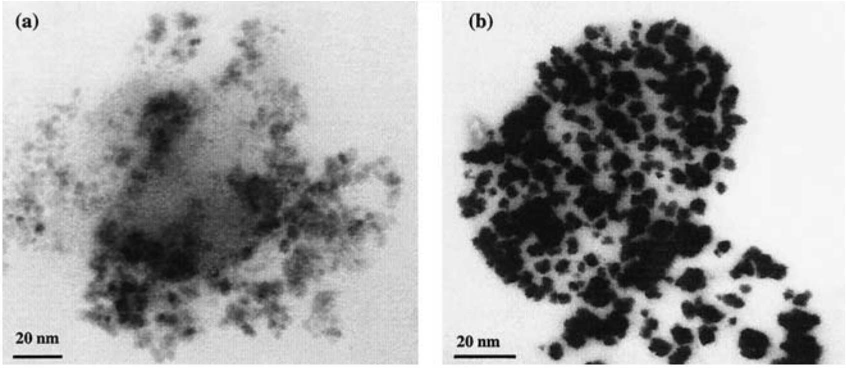

Figure 4. TEM image of (a) CdS/polyacrylamide and (b) CdS/Polystyrene Nanocomposites

Structural Characteristics

The nanocrystalline nature of the CdS and HgS composites is evident in the TEM images. The TEM image of the CdS nanocomposites shows close to spherical particles in the polymer matrix. The particle size calculated from the TEM images is 2-4 nm for CdS/polyacrylamide and 3-5 nm for CdS/polystyrene. Figure 5 shows the TEM image of the HgS polymer nanocomposite film deposited on the copper carbon grid. The image shows particles in the 4-8 nm size range. The agglomeration of the particles during film preparation in chloroform results in particles appearing to be non-uniform and non-homogenous in the polymer matrix. Efforts to obtain an X-ray diffraction pattern for the CdS and HgS nanocomposites were unsuccessful. The absence of diffraction peaks in the XRD spectrum could be due to the low concentrations of CdS and HgS in the polymer matrix.

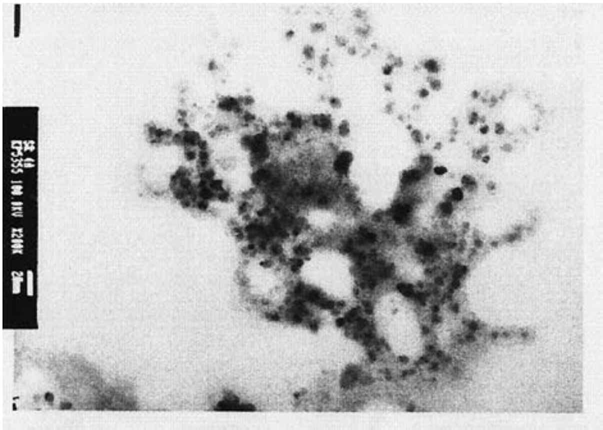

Figure 5. TEM image of HgS /Styrene nanocomposites

Conclusions

We have described a simple route to obtain high quality CdS and HgS nanocomposites. Both the materials show size-dependent optical properties and their particle sizes are confirmed by electron microscopy studies.

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