

# The synthesis of HgS nanoparticles in polystyrene matrix

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A composite of nanodimensional HgS and polystyrene has been prepared by reacting a solution of the copolymer formed from mercury acrylamide and styrene in chloroform solution with H<sub>2</sub>S. The product shows different colours depending on the amount of H<sub>2</sub>S used. The composite material has been characterised by UV, PL, TEM, and XRD techniques. The TEM images show particle sizes of less than 12 nm. The band gaps calculated from the optical spectra are higher than that for bulk material as expected for quantum confined materials.

## Introduction

The study of nanometer size crystallites explores the mesoscopic world of assemblies containing hundreds or thousands of atoms with distinct size dependent properties.<sup>1,2</sup> Such materials have considerable promise in a wide range of applications.<sup>3,4</sup> Semiconducting nanocrystals have optical and electronic properties due to quantum confinement effects and their large surface to volume ratios are also of interest.<sup>5,6</sup> 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.<sup>7</sup> Nanocrystalline materials are generally formed as powders soluble in polar or non-polar solvents depending on the nature of their surface coating. The fabrication of devices using nanocrystals requires the particle to be assembled in a medium with suitable characteristics.<sup>8</sup> Organic polymers are good candidates because: a wide variety of polymers can be synthesised with tailor made properties to couple with nanocrystals,<sup>3,9–12</sup> high levels of doping of organically passivated nanocrystals in the polymeric media can be achieved,<sup>13</sup> the resultant materials are easy to process e.g. by spin coating,<sup>14,15</sup> good spatial distribution of particles prevents agglomeration and facile control of the particle dispersity; the polymer itself can act as a surface passivant for the nanoparticles eliminating the use of an added passivating agent. There is also scope for considerable synthetic flexibility. Prepared nanoparticles can be mixed with polymers to make composite material<sup>16</sup> and the *in situ* generation of nanoparticles in a polymer matrix is another possibility.<sup>17</sup>

Cadmium sulfide has attracted considerable attention mainly because of its relatively easy synthesis, and distinct particle size dependent optical properties.<sup>18</sup> There have been very few detailed studies on HgS nanocrystallites because of difficulties associated with its synthesis and the toxicity of mercury.<sup>19</sup> Mercury sulfide crystallises in three different forms, but the trigonal ( $\alpha$ -HgS) and sphaleritic-type ( $\beta$  HgS) have been the

most extensively studied however there is some controversy concerning the bulk parameters for cubic HgS.<sup>20–23</sup>

Hasselbarth *et al.* have prepared HgS nanoparticles by a colloidal route and they have shown by electron diffraction experiments that the structure is that of cubic HgS.<sup>24</sup> There are also reports on other synthetic routes to HgS including: sonochemical method<sup>19</sup> and microwave assisted heating method.<sup>20</sup> It is possible to synthesise nanocrystallites with diameters between 2 and 10 nm ( $\pm 5\%$ ) by colloidal routes and other methods, the as-prepared particles have their surfaces covered with organic molecules. Some surface sites are unsaturated, which can lead to trapping of charge carriers on surface dangling bonds.<sup>24</sup> This problem has led to a body of synthetic work on core-shell nanocrystallites.<sup>25</sup> These have been further extended to the synthesis of quantum-dot quantum-well (QDQW) structures.<sup>26</sup> HgS has been used to derive QDQW structures which consists of a large band-gap CdS semiconducting core surrounded by a monolayer of smaller band-gap HgS capped by a layer of CdS. Studies on HgS nanocrystallites deposited in a polymer matrices are rare. This paper reports an effective method for the synthesis of HgS nanocrystallites in a polystyrene matrix.

## Experimental

Methanol, tetrahydrofuran (THF), acrylamide, HgO, ethanol, styrene, sodium hydroxide and azobisisobutyronitrile (AIBN) were all analytical grade reagents. Styrene was repeatedly washed with 10% NaOH solution, followed by water and dried over P<sub>2</sub>O<sub>5</sub>. All other chemicals were used as received.

### 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). Infrared spectra were taken on Perkin-Elmer Paragon 1000 FT-IR spectrometer, as KBr pellets.

### Photoluminescence spectroscopy

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

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## X-Ray diffraction (XRD)

The 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  $3^\circ$  for  $2\theta$  values over  $5^\circ$ – $60^\circ$  in steps of  $0.04^\circ$  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 plots were obtained using the LINK QX2000 Energy Dispersive Analysis System operating at 25 kV at a tilt angle of  $30^\circ$ . The chloroform solution of the composite was deposited on to carbon-filmed grids using a fine pipette, air-dried and immediately examined using the microscope.

## Synthesis of mercury acrylamide

Acrylamide (1.0 g) was dissolved in 20 mL ethanol. Finely powdered HgO (2.5 g) was added to the solution and 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.  $222$ – $223^\circ\text{C}$ ; yield 1.69 g (68.6%); C, H, N analysis (%), experimental (theoretical) C: 21.3 (21.1), H: 2.3 (2.4), N: 8.3 (8.2); IR,  $\text{v}/\text{cm}^{-1}$  and tentative assignments: N–H, 3290; C=O, 1670; C=C, 1454.

## Synthesis of copolymer of mercury acrylamide and styrene

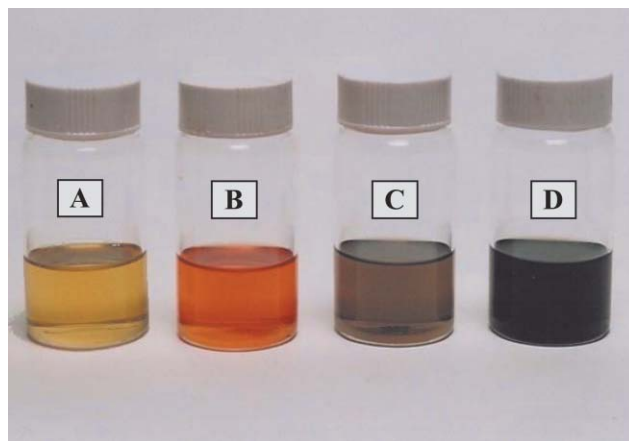
Styrene (20 mL) and mercury acrylamide (1.0 g) were dissolved in THF (100 mL) in a stoppered flask. The solution was flushed with  $\text{N}_2$  gas and AIBN (0.5 g) was added. It was heated and maintained at  $60^\circ\text{C}$  for 3 h with continuous stirring. The solution was cooled and poured into methanol (250 mL). The precipitated polymer was washed with methanol and dried. m.p.  $212$ – $213^\circ\text{C}$ , yield 15.5 g (81%).

## Synthesis of HgS

The copolymer (0.25 g) was dissolved in 20 mL chloroform and reacted with  $\text{H}_2\text{S}$  gas (1.5–4 mL) in a sealed 250 mL container. The gas was introduced into the head space above the solution from a gas-tight syringe with the gas at atmospheric pressure. On shaking yellow to dark brown solutions were obtained. The materials could be cast into films by spin coating.

## Results and discussion

In the present study a copolymer of mercury acrylamide and styrene has been synthesised. Mercury acrylamide has a C=C bond and in a copolymerisation reaction it acts as a cross-linking agent. We have prepared and characterised this new compound which can effectively copolymerise with styrene. The product, mercury containing copolymer, is soluble in chloroform which makes it easy to process. The level of loading of mercury atoms 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 the solubility of the copolymer in chloroform decreases. In the present study the copolymer used was analysed before the synthesis of the composite and it was found to have a mercury content of 0.03 g per g of the copolymer. A solution of the copolymer in chloroform on reaction with  $\text{H}_2\text{S}$  leads to the formation of HgS within the matrix. 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  $\text{H}_2\text{S}$  injected into the chloroform solution of the



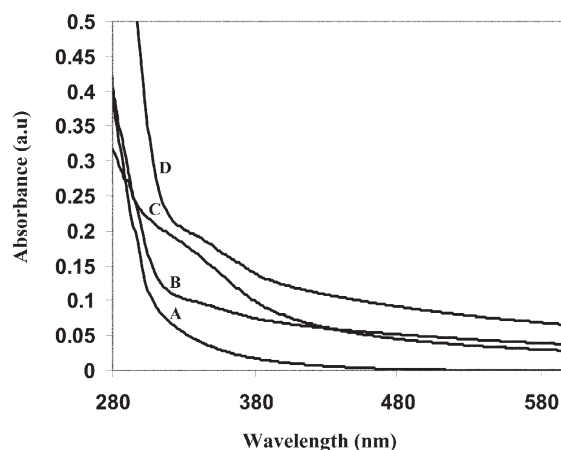
**Fig. 1** HgS-polystyrene nanocomposites prepared by injecting varying amounts of  $\text{H}_2\text{S}$  into a chloroform solution of the mercury containing copolymer. (A) 1.5 mL; (B) 2 mL; (C) 3.0 mL; (D) 4.0 mL.

polymer is increased from 1.5 mL to 2.5 mL, 3 mL and 4 mL, the colour of the solution changes from yellow to orange yellow and finally to dark brown (Fig. 1, samples A–D). Once the different colours have been developed the container is flushed with nitrogen gas and tightly stoppered. The solution has a long shelf-life and does not show any discernable change in colour over more than 6 months. 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. XRD of samples with higher loading of HgS also did not give any peaks due to HgS. However, loading beyond a level of  $5 \times 10^{-4} \text{ mol g}^{-1}$  was not possible because of the lack of solubility of the copolymer with a higher Hg content in chloroform. It can possibly be argued that the XRD signals due to HgS do not appear because either the concentration levels of HgS are not sufficient or because of the lack of good crystallinity and lower polydispersity of the samples.

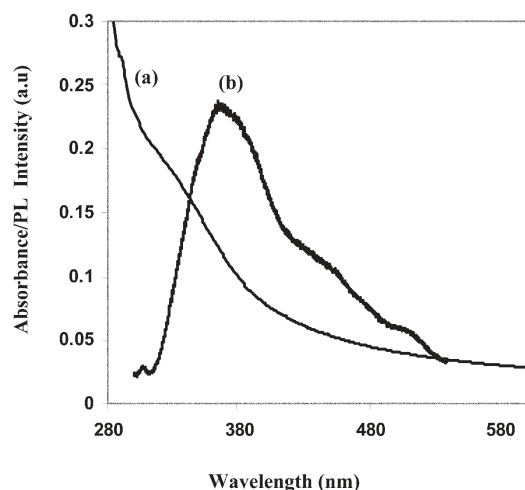
The UV-visible spectra of the composites are given in Fig. 2. The composite material was dissolved in chloroform and was allowed to react with the required amount of  $\text{H}_2\text{S}$  and the resulting solution was used to measure the absorption spectra. A broad absorption peak with a maximum around 340 nm is observed. This optical spectra were used to calculate the band gap from

$$\alpha(\nu) = A(h\nu/2 - E_g)^{m/2}$$

where  $\alpha$  is the absorption coefficient and  $E_g$  is the band gap.<sup>23</sup> For a direct transition  $m = 1$  a plot of  $(\alpha E_{\text{phot}})^2$  vs.  $E_{\text{phot}}$  was



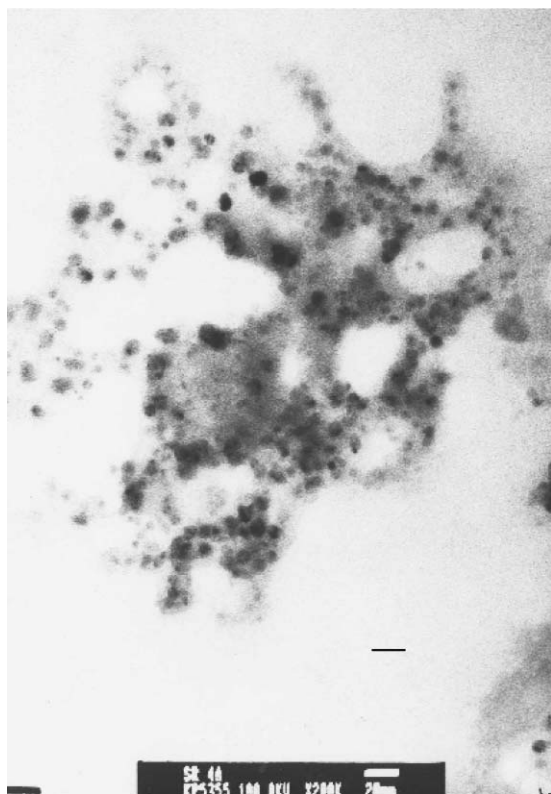
**Fig. 2** UV/Vis absorption spectra of HgS-polystyrene nanocomposites showing change in band edge of samples A–D.



**Fig. 3** (a) UV/Vis absorption spectrum of HgS-polystyrene nanocomposite (sample A) and (b) the corresponding photoluminescence spectrum.

constructed and the value of  $E_{\text{phot}}$  extrapolated to  $\alpha = 0$  gives the band gap,  $E_g$ . The band gaps calculated for samples A to D are 3.01 eV, 2.96 eV, 2.83 eV and 2.74 eV respectively which are higher than the band gap (2.0 eV) of bulk HgS.<sup>27,28</sup> The larger particles are, as might be expected, associated with the materials prepared with greater amounts of hydrogen sulfide. The band gaps observed in the present study for the various samples are higher than the value reported for HgS nanocrystallites synthesised by the sonochemical method.<sup>20</sup> The photoluminescence spectrum of the HgS composite is asymmetric, showing an emission maximum at 369 nm (Fig. 3). This broad emission curve could be due to emission from sulfur vacancies, as observed previously for CdS.<sup>29</sup>

Fig. 4 shows the TEM image of a HgS-polymer nanocomposite film deposited on a carbon coated copper grid. The



**Fig. 4** TEM image of HgS-styrene nanocomposite (sample A) (bar = 20 nm).

TEM images of the composite was compared with that of polystyrene to confirm the presence of HgS particles in the polymer matrix. EDAX analysis also showed mercury and sulfur to be in a 1 : 1 atomic ratio. The picture shows a relatively wide size distribution for the particles, it was difficult to assess precisely the size distribution due to agglomeration. However, it is to be noted that since the method of synthesis of the composite involves the reaction between Hg atoms which are part of the polymer matrix and  $\text{H}_2\text{S}$ , it is most likely that the possibility of phase separation will be much reduced when compared with the samples prepared by the most common method—dissolution of nanoparticles in a solution of the polymer, followed by the evaporation of the solvent to isolate the composite. Moreover the Hg atoms are evenly distributed in the matrix during the polymerisation stage itself; we expect the distribution of HgS particles in the matrix also to be fairly uniform.

## Conclusions

In the present study a convenient method for the synthesis of HgS nanoparticles in a polystyrene matrix has been reported. The composite material is stable, can be spin coated and made into large thin films. The band gap calculated is higher than that for bulk HgS, typical of quantum confined materials. Further studies on the synthesis of related composites are presently being carried out.

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