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Synthesis of short CdS nanofiber/poly(styrene-alt-maleic anhydride) composites using γ-irradiation

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Assemblies of short CdS nanofibers/poly(styrene-alt-maleic anhydride) were prepared *via* a one-pot procedure in anhydrous ethanol for the first time by γ-irradiation under ambient conditions. The as-prepared copolymer matrix can successfully control the morphology of nanocrystalline CdS and prevent aggregation. Carbon disulfide was the sulfur source while cadmium chloride was the metal ion source. FTIR spectroscopy and X-ray powder diffraction (XRD) were used to characterize the copolymer, and transmission electron microscopy and electron diffraction used to confirm that well crystallized CdS nanofibers were dispersed homogeneously in the copolymer matrix. UV–VIS spectroscopy was also used to examine the quantum-confinement of the CdS nanofibers.

1 Introduction

During the past decade, considerable interest has centered on the synthesis of hybrid organic–inorganic composites from the viewpoint of both fundamental research and applications.[1–6] Such materials can show properties that are a combination of those of the original materials, while others possess improved performance properties not seen in the separate component.[7] In particular, composites consisting of nanosized inorganic particles or fibers dispersed in a continuous polymer matrix have attracted much research attention, and nanosized semiconductor particles such as cadmium sulfide are important dispersed phases within polymer matrices owing to their unique electronic and optical properties, and their potential applications in solar energy conversion, nonlinear optics, photoelectrochemical cells and heterogeneous photocatalysis.[1a,8]

Polymers investigated as matrices for encapsulated semiconductor particles have several advantages over solution-based particle systems in the absense of polymers. Polymeric materials can be processed or manipulated into bulk structures, and solid matrices retain their shapes and do not spill or leak,[3a] while semiconductor–polymer composites are found to be extremely stable.[1b] Moreover, polymers not only act as encapsulants for the particles, but are also capable of passivating the materials, preventing particle agglomeration whilst maintaining a good spatial distribution of the particles, and effectively controlling the particle size and size distribution,[3b,5e] which has an influence on the electronic and optical properties of the semiconductor materials. For example, Lin *et al.*[5e] devised a bimimetic process for the synthesis of CdS in poly(ethylene oxide), in which the inorganic phase displays uniformity of size, morphology, phase and crystallographic orientation. Eisenberg and coworkers[1b] have prepared spherical assemblies of CdS-containing block copolymer reverse micelles in aqueous solution, and found the size of the CdS particles ($2R_{\mathrm{CdS}} \approx 3$ nm) is controlled by the ionic block length of the copolymer.

In most previous reports, however, polymerization and nanoparticle formation were performed separately[1b,c,3a,b,5e] to obtain nanoparticles well dispersed in the polymer matrices. In addition, for some technologically important semiconductors, *e.g.*, metal chalcogenides, most of these synthetic methods have drawbacks including the use of noxious compounds, such as H_2Se and H_2S.[1]

Prompted by the importance of nanostructured materials and the limitations of the above processes, many researchers have developed the γ-irradiation technique to synthesize nanosized particles. Specifically, in 1997, we succeeded in using γ-irradiation to prepare polyacrylamide–silver nanocomposites, in which the silver nanoparticles are dispersed homogeneously within the polyacrylamide network.[9] Compared with other methods, γ-ray irradiation has advantages such as processing under ambient pressure at room temperature with the starting inorganic compounds and organic monomer mixed homogeneously at the molecular level in solution. In addition, the formation of polymer chains is quicker than the growth of nanocrystallites under γ-irradiation. Such chain growth leads to an increase of the viscosity of the system, which limits the further growth and aggregation of nanocrystallites and so makes them well dispersed in the polymer matrix. Although γ-irradiation has led to rapid progress in the preparation of nanoparticles in recent years, much attention has been paid only to the synthesis and characterization of nanometer metal particle–homopolymer[10] and metal sulfides–homopolymer composites.[11]

Here, we have prepared, for the first time, CdS nanofibers in a alternate copolymer of maleic anhydride (MA) and styrene (St) *via* a one-pot procedure using γ-irradiation, and have successfully extended the γ-irradiation technique from the synthesis of inorganic particle–homopolymers to CdS–copolymer composites, avoiding the use of noxious H_2S. The copolymer of maleic anhydride and styrene is expected to show a wide range of applications in industrial use because of its high thermal stability compared with general-purpose thermoplastics.[12–14] In addition, the ordered and regular polymer environment induces nucleation of CdS (matrix preorganization), and initially formed highly polar groups evenly distributed along the chains can effectively control the size and shape of the CdS particles.

2 Experimental

Styrene (St), maleic anhydride (MA), ethanol, CS_2 and $CdCl_2$ used in the present study were all analytical grade reagents; styrene was washed with 10% sodium hydroxide (to remove the inhibitor) and distilled water, and was then distilled under reduced pressure before use.

1.0 g of $CdCl_2$ and 2 ml of CS_2 were dissolved in 90 ml of absolute ethanol by stirring, and 8 ml of St and 8 g of MA were added sequentially to the solution. The solution was deaerated by bubbling with pure nitrogen for 20 min to remove oxygen. 4×10^4 Gy of ^{60}Co γ-ray irradiation was then applied to the solution under ambient conditions for 12 h. After irradiation, the pale yellow product was collected and washed repeatedly with distilled water and ethanol to remove excess of monomers and by-products. The final product was dried *in vacuo* in an oven at room temperature, and ground into a powder for further analysis. The product was insoluble in water and toluene. The obtained sample was weighed, and the yield was calculated based on the molar weight of $CdCl_2$ with CS_2 in excess and that of St with MA in excess. The result showed that the yield of the composites was *ca.* 88%.

Samples were characterized by X-ray powder diffraction (XRD) using a MAC Science Co. Ltd MXP18AHF γA rotation anode X-ray diffractometer with graphite monochromatized Cu-Kα radiation ($\lambda = 1.54178$ Å), employing a scanning rate of 8° min^{-1} in the 2θ range 3–65°. FTIR spectra were measured for samples as KBr pellets to characterize the composition of the copolymer, using a Nicolet Model 759 FTIR spectrophotometer in the wavenumber range 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. The size and morphology of CdS/P(St-co-MA) nanocomposites was investigated by transmission electron microscopy. TEM images were obtained using a Hitachi Model H-800 transmission electron microscope with an accelerating voltage of 200 kV. Samples for TEM analysis were prepared by dispersing the product in distilled water by ultrasonic stirring, and adding a drop of the dispersion onto a substrate consisting of a copper mesh with a carbon film, followed by removal of the excess liquid with a piece of filter paper and drying in air at room temperature.

To determine the concentration of the cadmium sulfide in the copolymer matrix, 0.010 g of a sample was dissolved in 2 mol dm^{-3} analytically pure aqueous hydrochloric acid. The cadmium ion content was determined using an atomic absorption spectrometer (model WYX-40). The sulfur content was determined by wet chemical analysis in which the sample was oxidatively decomposed in dilute HNO_3 solution (2 mol dm^{-3}) in a hydrothermal autoclave at 100 °C for 10 h, and a clear solution was obtained; the sulfur content was determined gravimetrically as $BaSO_4$. C, H, N elemental analysis was performed with a PE-240C elemental analyzer.

The influence of the absorbed doses on the growth of CdS nanocrystallites in the copolymer matrix was studied by recording the UV–VIS absorption spectra of irradiated solutions with different absorbed doses, using anhydrous ethanol as a reference. The solution for UV–VIS study consisted of 0.02 mol dm^{-3} of $CdCl_2$, 2.0% v/v of CS_2, 8.0% v/v of St and 0.05 mol dm^{-3} of MA. The absorption spectra were obtained on a UV-2100 Shimadzu UV–VIS spectrophotometer using quartz cells, by scanning between 340 and 550 nm.

3 Results and discussion

Examination of the IR spectrum of Fig. 1 confirmed that the product contained the copolymer of St and MA. A prominent stretching mode at *ca.* 3500 cm^{-1} indicated the presence of OH from H_2O which might be due to trace H_2O absorbed on the surface of the sample. In fact, the presence of absorbed water is common to all powder samples which were exposed to the atmosphere and was more pronounced for high surface area particles.[15] An aliphatic (CH) stretching band was present at *ca.* 3030 cm^{-1}, arising from the CH units of the aromatic ring. The absorption bands at 1600, 1583, 1492 and 1454 cm^{-1} arise from aromatic C–C stretches, while bands at 761 and 699 cm^{-1} are for the C–H stretch in the mono-substituent of the aromatic ring. The bands at 1775 and 1850 cm^{-1} for the C=O stretch of cyclic anhydride were absent, being replaced by a band at 1729 cm^{-1} for an ester C=O stretch, owing to esterification of the anhydride by ethanol. A band at 1706 cm^{-1} corresponds to the C=O stretch in the carbonyl groups, while that at 1376 cm^{-1} corresponds to C–H stretch from CH_3. The absorption band of the Cd–S bond, which should be at 405 cm,[16] is rather weak and is scarcely resolved owing to the low content of the inorganic component.

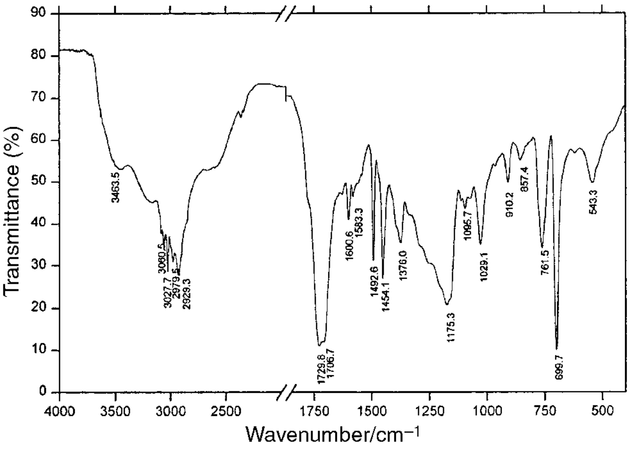

Fig. 1 FTIR spectrum of the sample shown in Fig. 2(a).

Fig. 2(a) shows a typical XRD pattern of a sample prepared by γ-irradiation (4×10^4 Gy). Within experimental error, all the diffraction peaks could be indexed to hexagonal CdS (wurtzite structure) with lattice constants $a = 0.4141$ and $c = 0.6739$ nm. The (101) diffraction peak is unusually strong compared with that of bulk hexagonal CdS [Fig 2(b)], indicating a preferential growth direction in the product. The broad peaks at $2\theta = 10°$ and 19.2° can be attributed to the copolymer of St and MA.

A TEM image of an as-prepared composite (4×10^4 Gy) [Fig. 3(a)] showed an even dispersion of nanocrystallites on the gray background of the copolymer matrix. The copolymer only contains the light elements C, H, O and N and so it appears gray and can not be discriminated from the substrate in the image. By contrast, sulfur and cadmium are heavy elements and thus the observed black short fibers with diameters of <5 nm and lengths from *ca.* 50 to 100 nm correspond to CdS. However, it is difficult to precisely determine the size and the size distribution of CdS by simply viewing the TEM image. The corresponding electron diffraction (ED) pattern [inset of Fig. 3(a)] clearly shows a typical well crystallized diffraction pattern of CdS crystals, rather than diffuse rings characteristic of amorphous copolymer materials. In the ED pattern, three

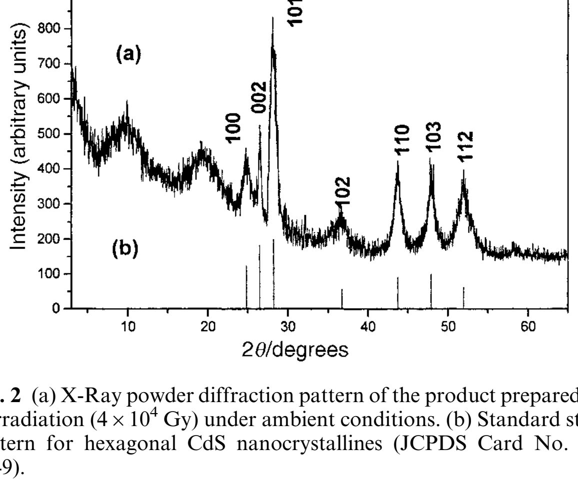

Fig. 2 (a) X-Ray powder diffraction pattern of the product prepared by γ-irradiation (4×10^4 Gy) under ambient conditions. (b) Standard stick pattern for hexagonal CdS nanocrystallines (JCPDS Card No. 41-1049).

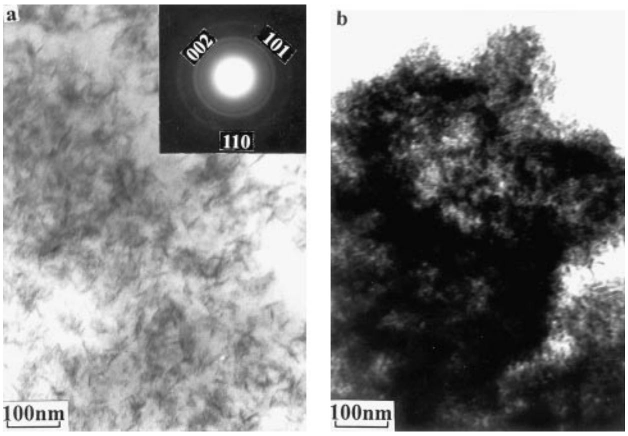

Fig. 3 TEM image and ED pattern (a) of as-prepared CdS/Poly(St-alt-MA) by γ-irradiation (4×10^4 Gy); TEM image (b) of CdS without copolymer under the same conditions.

electron diffraction rings can be clearly distinguished and indexed.

Fig. 3(b) shows the image of fiber-like CdS particles, obtained under similar conditions as in Fig. 3(a) but in the absence of St and MA in the reaction system. CdS particles in this image, although fiber-like, aggregate into secondary phases and differ markedly from those in Fig. 3(a). It is obvious that the St–MA copolymer plays an important role in controlling the size and the monodispersion of the CdS particles.

For the sample shown in Fig. 2, the ratio of cadmium and sulfur in the composites was 1 : 1.09, while the content of cadmium sulfide in the copolymer matrix was *ca.* 3.6 wt% (Elemental analysis. Calc.: C, 68.7; H, 4.77. Found: C, 70.2; H, 4.5%).

The UV–VIS spectra of solutions during preparations of the as-prepared composites were used to explore the influence of the adsorbed dose on the growth of the CdS nanofibers. Fig. 4 shows the progressive red shift absorption onset with increasing irradiation dose, indicating the gradual growth of CdS particles and also a blue shift in the optical absorption maximum (*ca.* 430 nm), relative to bulk CdS (512 nm). The diameter of the CdS nanoparticles was calculated by using the formula from ref. 17. Estimations based on the absorption maximum suggested the presence of particles with an average diameter of 15–30 Å. The differences (in nm) between the position of the onset and the mean position of the shoulders characterize the size polydispersity.[18] Fig. 4 also shows that the size polydispersity of the particles increases with an increase in absorbed dose but this does not change drastically.

In the γ-irradiation process, radiolysis of the anhydrous ethanol solution initially generates many products [eqn. (1)]:[19]

$$C_2H_5OH \xrightarrow{\gamma\text{-irradiation}} e^-_{solv}, H^{\cdot}, CH_3^{\cdot}CHOH, C_2H_5OH^+_{2solv}, CH_3CHO^-_{solv} \quad (1)$$

St monomers are activated by the radicals generated in solution upon irradiation and are converted into St radicals. These St radicals rapidly initiate copolymerization of St and MA, and copolymer chains are propagated, and provide attachment sites for metal sulfide nanoparticles owing to the presence of highly polar groups along the chains. It has been reported that the copolymerization of St and MA gives a copolymer in which the monomers alternate with near perfect regularity along the chain.[20] This is due to the fact that MA with an electron-attracting substituent has electron-accepting character ($e = 2.25$) while St with an electron-releasing substituent has electron-donating character ($e = -0.80$), which leads to a very small value of the product of monomer reactivity ratios ($r_1 \times r_2 = 0.006$).

Furthermore, a polymer of MA was not observed when the monomer MA was treated under the same conditions without St, indicating that monomer MA can not be polymerized itself using γ-radiation under ambient conditions. However FTIR spectra confirm that MA monomer reacts in the mixed reaction system confirming that an alternate copolymer of St and MA is formed when using an excess of MA.

Part of the copolymer undergoes esterification in ethanol with the acid anhydride groups being esterified. In addition, the two carbonyl groups alternate with the aromatic ring, leading to a homogeneous dispersion of carbonyl groups. In most previous studies on inorganic/copolymer composites, the polymer matrices were block copolymers, and particle growth was expected to be restricted to ionic or highly polar microdomains so providing a mechanism for both size control and particle stabilization.[1b,3b] However, such ionic or highly polar microdomains were not necessarily evenly distributed in the block copolymers in contrast to the highly polar carbonyl groups observed here which leads to better control over size and shape of the nanosize particles.

It is clear as a result of reduction of cadmium ions by solvated electrons produced in solution by γ-irradiation, that cadmium ions in lower valence[21] are formed [eqn. (2)]:

$$e^-_{solv} + Cd^{2+} \rightarrow Cd^+ \quad (2)$$

Research on γ-radiation of carbon disulfide indicates the formation of non-ionic intermediates, possibly as $S^{\cdot}$ radicals[22] and free sulfur might be liberated when such radicals collide in solution [eqn. (3)]:

$$CS_2 \xrightarrow{\gamma\text{-irradiation}} CS^{\cdot} + S^{\cdot} \quad (3)$$

Since no free sulfur was observed in our experiments, precipitation of CdS probably prevents the formation of sulfur from $S^{\cdot}$ radicals [eqn. (4)]:[23]

$$S^{\cdot} + Cd^+ \rightarrow CdS \quad (4)$$

To summarize, this work describes the synthesis and characterization of short nanofiber composites of CdS/poly(St-alt-MA). TEM indicated short fiber-like CdS particles with diameters of <5 nm and lengths in the range 70–100 nm. TEM also confirmed the copolymer of maleic anhydride and styrene has the advantages of being able to passivate the inorganic components, and prevent particle agglomeration while maintaining a good spatial distribution of particles.

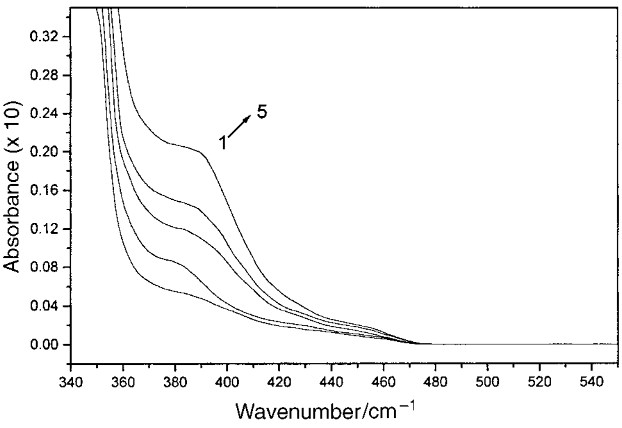

Fig. 4 UV–VIS absorption spectra of the irradiated solutions with varying absorbed doses. (1) 2500 Gy, (2) 3500 Gy, (3) 9500 Gy, (4) 12500 Gy, (5) 15500 Gy. Reference: anhydrous ethanol.

Acknowledgements

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