A novel *in situ* simultaneous polymerization–hydrolysis technique for fabrication of polyacrylamide–semiconductor MS(M = Cd, Zn, Pb) nanocomposites

Yong Zhou,[a] Shuhong Yu,[a] Cuiying Wang,[a] Xiaoguang Li,[b] Yurui Zhu[a] and Zuyao Chen*[a]

[a] *Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: zhz@mail.ustc.edu.cn*

[b] *Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*

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Polyacrylamide(PAM)–semiconductor MS (M = Cd, Zn, Pb) nanocomposites with homogeneously well dispersed semiconductor nanoparticles in the polymer matrices were prepared by a novel *in situ* simultaneous polymerization–hydrolysis technique (SPH).

The synthesis and characterization of inorganic-organic polymer nanocomposites has received much intense research interest,[1] owing to their optical, electrical, catalytic and mechanical properties,[2,3] and potential applications in microelectronics.[4]

Many methods have been exploited to prepare semiconductor–polymer nanocomposites. Organization of semiconductor nanoparticles in an orderly fashion in a matrix may provide potential applications of their special properties, whereas polymers are expected to provide good mechanical and optical properties, conferring high kinetic stability on nanometer-sized semiconductor particles.

Meissner *et al.*[5] first reported a system involving dispersed semiconductor/polymer arrangements by physically embedding monograin CdS particles of *ca.* 40 μm diameter in a thin, nonconducting polyurethane membrane and various photoprocesses were examined. Later, a new method of incorporation of dispersed semiconductor CdS throughout an ionically conductive Nafion polymer membrane was developed.[6] Recently, CdS/polystyrene,[7] CdS/PS–P2VP[polystyrenes–block–poly(vinylpyridine)s],[8] PbS/S–MA(styrene–methylacrylic copolymer)[9] and PbS/E–MAA(ethylene–15% methacrylic acid copolymer) composites have been prepared in different polymer matrices using a variety of methods.[10] The multisemiconductor nanocomposite Cu_2S/CdS/ZnS was also successfully prepared in polystyrene by ion exchange.[11] Wang and Herron reported, for the first time, the synthesis of CdS/PVK(*N*-polyvinylcarbazole) polymer composite by using $Cd_{10}S_4Ph_{12}$ as precursor.[12] Currently, the use of amphiphilic block copolymer (ABC) micelles opens a doorway to utilize these materials as 'nanoreactors' for the formation of inorganic nanocrystals.[1,13] Other block copolymer system/metal sulfide nanoparticles have been prepared by addition of H_2S.[14]

Here, we report a novel *in situ* simultaneous polymerization–hydrolysis technique (SPH) for preparing polyacrylamide–semiconductor MS (M = Cd, Zn, Pb) nanocomposites in aqueous systems. The so-called SPH technique is based on the mechanism of the simultaneous polymerization of organic monomer and formation of semiconductor nanoparticles. It was found that the semiconductor nanoparticles (CdS, ZnS, PbS) were homogeneously well dispersed in the polyacrylamide matrices. The present SPH technique may provide a new route to prepare other metal sulfide–polymer hybrid nanocomposites.

In a typical procedure, the CdS–polyacrylamide (CdS–PAM) nanocomposite was prepared in an aqueous system. 0.01 mol $CdCl_2$ and 0.01 mol NH_2CSNH_2 were added to a 100 ml of 5.0 mol l^{-1} acrylamide(AM) monomer aqueous solution. Then, 0.01 g AIBN (2,2′-azobisisobutyronitrile) as radical initiator was added to the above solution. The mixture solution was put into a stainless-steel tank with a Teflon inner and heated in an oven at 140 °C for 12 h. The product obtained was washed with distilled water and absolute ethanol, dried at room temperature and ground into a powder for characterization.

The X-ray powder diffraction (XRD) pattern for the product was determined at a scanning rate of 0.02° s^{-1} in the 2θ range from 5–65°, using Japanese Rigaku Dmax γ_A-ray diffractometer with high-intensity Cu-Kα radiation (λ = 0.151478 nm) and a graphite monochromater was set at the diffracted radiation. The UV–VIS absorption spectrum was recorded with a Shimadzu UV-200 spectrophotometer. TEM images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV.

Fig.1 shows the XRD pattern of a CdS–PAM nanocomposite obtained by the present SPH technique at 140° for 12 h. The broad peak at *ca.* 23° corresponds to the PAM phase. Cubic phase CdS nanoparticles were obtained. Not all diffraction peaks of the CdS nanoparticles can be observed in the XRD pattern of the CdS–PAM nanocomposite because of interference from the broad diffraction peaks for the PAM phase. However, the diffraction peaks for cubic CdS for $2\theta > 40°$ can clearly be seen.

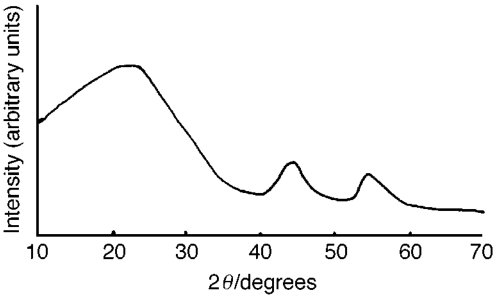


Fig. 1 The XRD pattern of a CdS–PAM nanocomposite prepared by the *in situ* simultaneous polymerization–hydrolysis technique (SPH) at 140 °C for 12 h.

The UV–VIS absorption spectrum of the CdS–PAM nanocomposite, dispersed in ethanol, was measured using pure PAM dispersed in ethanol as a reference solution.

The resulting spectrum shows λ_{max} for the CdS nanoparticles in the CdS/PAM nanocomposite at *ca.* 476 nm, *i.e.* blue-shifted relative to bulk CdS (515 nm).[15]

Fig. 2 shows a TEM image of the CdS–PAM nanocomposite powder. The image shows that the CdS nanoparticles prepared by the present SPH technique were homogeneously well dispersed in the PAM matrix. A histogram of the CdS nanoparticles (Fig. 3) shows a distribution of particle sizes in the range 2–10 nm.

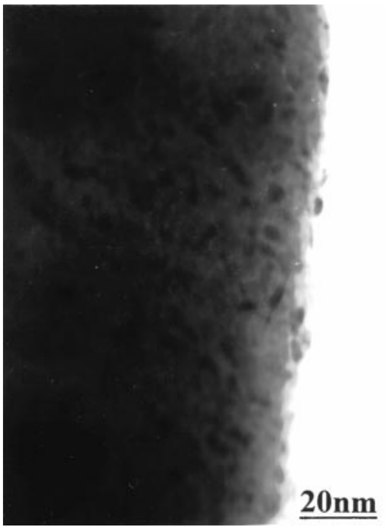


Fig. 2 TEM image of a CdS–PAM nanocomposite prepared by the *in situ* simultaneous polymerization–hydrolysis technique (SPH) at 140 °C for 12 h.

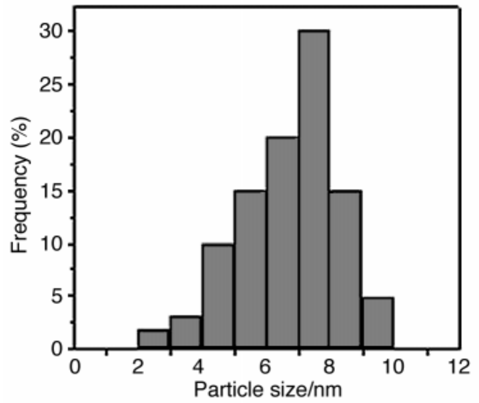
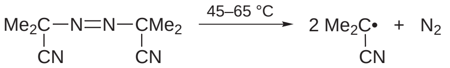


Fig. 3 Higtogram of CdS nanoparticle size in a CdS–PAM nanocomposite prepared by the present *in situ* SPH technique.

It is well known that the radical initiator AIBN decomposes at 45–65 °C, according to eqn. (1).



$$\underset{\text{CN}}{\text{Me}_2\text{C}}{-}\text{N}{=}\text{N}{-}\underset{\text{CN}}{\text{CMe}_2} \xrightarrow{45\text{–}65\ °\text{C}} 2\ \underset{\text{CN}}{\text{Me}_2\text{C}^\bullet} + \text{N}_2 \qquad (1)$$

The resulting radicals initiate the polymerization of the acrylamide (AM) monomer. Accompanying polymerization, CdS nanoparticles are also simultaneously formed by hydrolysis of NH_2CSNH_2 as described in eqns. (2) and (3).

$$\text{NH}_2\text{CSNH}_2 + 2\text{H}_2\text{O} \xrightarrow{\textit{Hydrolysis}} 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{S} \qquad (2)$$

$$\text{Cd}^{2+} + \text{H}_2\text{S} \longrightarrow \text{CdS} + 2\text{H}^+ \qquad (3)$$

Therefore, the obtained CdS nanoparticles can be homogeneously well dispersed in the PAM matrix. Further studies demonstrate that the average size of CdS nanoparticles in the absence of AM monomer obtained under the same preparation conditions as for the CdS–PAM nanocomposite, is *ca.* 20 nm which is larger than that of the CdS nanoparticles in the CdS–PAM nanocomposite. The reason may be that the reaction medium becomes more and more viscous as polymerization of the AM monomer proceeds, which is favorable for preventing the aggregation of initially formed CdS nanoparticles.

Fig. 4 TEM image of a ZnS–PAM nanocomposite prepared by the *in situ* simultaneous polymerization–hydrolysis technique (SPH) at 140 °C for 12 h.

We have also prepared ZnS–PAM and PbS–PAM nanocomposites *via* the present SPH technique by using $Zn(NO_3)_2$ and $Pb(NO_3)_2$ instead of $CdCl_2$. Fig. 4 shows the TEM image for the ZnS–PAM nanocomposite. It was found that the ZnS nanoparticles were also homogeneously well dispersed in the PAM matrix with a size of *ca.* 5–15 nm. The TEM image for the PbS–PAM nanocomposite indicates that the size of the PbS nanoparticles is *ca.* 10–20 nm.

In summary, CdS–PAM, ZnS–PAM and PbS–PAM nanocomposites with homogeneous dispersion of the metal sulfide nanoparticles in the polymer matrices were prepared by a novel *in situ* simultaneous polymerization–hydrolysis technique (SPH). The polymerization reaction of the AM monomer is favorable for preventing the aggregation of initially formed semiconductor nanoparticles. The present *in situ* SPH technique may provide a new route to prepare other metal sulfide semiconductor–polymer hybrid nanocomposites.

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