In situ Synthesis and Characterization of Spherical CdS/Polyacrylamide Nanocomposites by γ-Irradiation in W/O Microemulsions

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Spherical CdS/polyacrylamide (CdS–PAM) nanocomposites were successfully synthesized in single step by γ-irradiation in a W/O microemulsion under ambient pressure at room temperature. The final product was characterized by various means such as XRD, IR, UV–vis, PL, ED and TEM. The TEM image clearly showed the homogeneous dispersion of CdS–PAM nanocomposites with the dimension of 50 nm.

Since inorganic/organic polymer nanocomposites own many intriguing optical, electrical, catalytic and mechanical properties and potential applications in microelectronics,[1–4] much attention has been paid to syntheses and characterization of kinds of composites. These composites not only combine the advantageous properties of inorganic materials and polymers, but also exhibit many new characteristics which single-phase materials do not own.

Many methods have been employed to synthesize the semiconductor/polymer nanocomposites. The first system involving dispersed semiconductor/polymer arrangements through embedding monograin CdS particles on the order of 40 μm diameter in a thin, nonconductive polyurethane membrane was reported by Meissner in 1983.[5] Later, a new method of incorporating a dispersed semiconductor CdS throughout an ion-conductive Nafion polymer membrane was developed.[6,7] In the past decade, many semiconductor/polymer nanocomposites, such as PbS/poly(ethylene-15% methacrylic acid),[8] CdS/polystyrenes-*block*-poly(vinylpyridine)s,[9] CdS/poly(*N*-vinylcarbazole)[10] and CdS/polystyrene,[11] had been synthesized via a variety of methods. However, in these methods, to initiate the polymerization of monomers and the formation of semiconductor compounds, a relatively high temperature was often needed.

Recently, γ-irradiation method has been developed for the preparation of various semiconductor/polymer nanocomposites in aqueous solution containing aqueous soluble monomer and inorganic salts.[12–14] However, no reports of the preparation of semiconductor/polymer nanocomposites using this method in a microemulsion system were found in literatures.

Here, we report a novel method for the synthesis of spherical CdS/polyacrylamide (PAM) nanocomposites in single-step by γ-irradiation in a W/O microemulsion system at room temperature and under ambient pressure. In this W/O microemulsion system, octyl phenyl poly(ethylene oxide)-4 (OP-4) and octyl phenyl poly(ethylene oxide)-10 (OP-10) were selected as emulsifiers and kerosene as oil phase. The inorganic salts and AM monomers were dissolved in water before producing the microemulsion.

An aqueous solution containing $CdCl_2 \cdot 2.5H_2O$ (2.28 g), $Na_2S_2O_3 \cdot 5H_2O$ (3.38 g), isopropyl alcohol (10 mL) and AM monomers (5 g) was prepared in advance. The solution (10 mL) was then added into a 40 mL mixture of kerosene and OP-4 (7.0 g). OP-10 was titrated into the mixture under stirring until a transparent microemulsion suddenly formed. After the microemulsion was irradiated in the field of a ^{60}Co γ-ray source for 6 h with an absorption dose of 18 kGy, a bright yellow semi-transparent microemulsion was obtained and de-emulsified by acetone and distilled water. The products were repeatedly washed with distilled water and ethanol, and dried in vacuum at room temperature for 4 h.

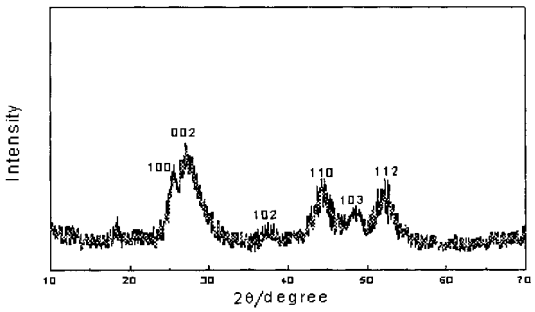

Figure 1. XRD pattern of CdS/PAM nanocomposites prepared by γ-irradiation in a W/O microemulsion, with the absorption dosage of 18 kGy.

Figure 1 shows the XRD pattern of the CdS/PAM nanocomposites obtained by γ-irradiation in the W/O microemulsion. The peaks with 2θ values of 25.7°, 27.0°, 37.8°, 44.1°, 48.4°, 52.4° correspond to the crystal planes of 100, 002, 102, 110, 103 and 112 of hexagonal CdS form by comparison with the data from JCPDS file no. 41-1049, respectively. According to Scherrer's equation,[15] the average size of CdS nano-particles is estimated to be about 2 nm. In addition, a weak absorption peak at 420 nm is found in UV–vis spectrum of the final product. Related to that of the bulk material of CdS (513 nm), an obvious blue shift can be observed. However, no PL peak is shown in the range from 300 nm to 800 nm in PL spectrum of the product.

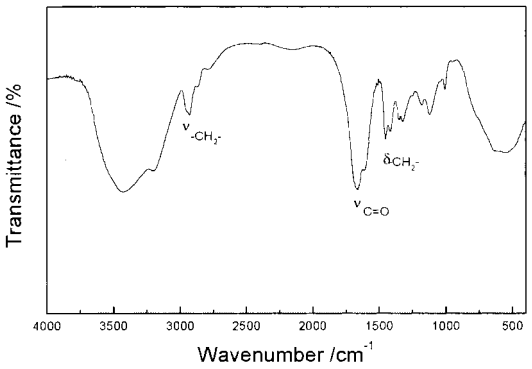

Figure 2. IR spectrum of the sample shown in Figure 1.

The organic content in the composite is so low that only a weak peak at 2θ = 18° is seen in Figure 1. Nevertheless, the presence of polymer can be confirmed by IR spectrum of the product (see Figure 2). Comparing with the standard IR spectra of PAM

and AM monomers,[16] one can find that the IR spectrum of the product is very close to the former, and obviously different from the latter. The strongest peak at 1665.7 cm^{-1} ($\nu_{C=O}$) and the characteristic peaks at 2929.3 cm^{-1} (ν_{-CH_2-}) and 1452.6 cm^{-1}, 1415.5 cm^{-1} (δ_{-CH_2-}) of PAM confirm that AM monomer has successfully polymerized under γ-irradiation.

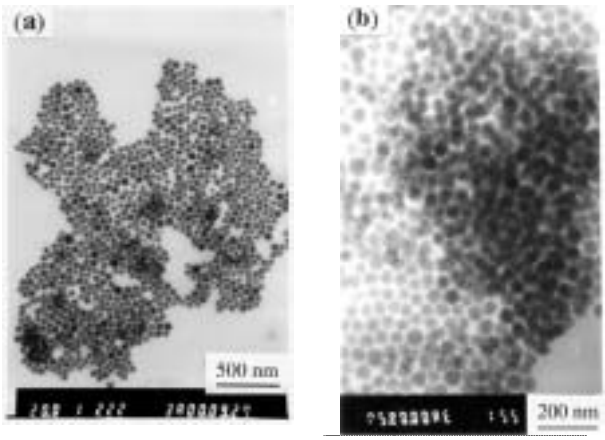

Figure 3. TEM images of the CdS/PAM nanocomposites prepared in a microemulsion system. (a) monodispersed nanospheres, (b) monolayer and multilayer nanospheres.

Figure 3 is the TEM images of the same sample shown in Figure 1. Seen from Figure 3 (a), the nano-composite consists of mono-dispersed nanospheres. The mean diameter of these nanospheres is about 50 nm, which is not in agreement with the result of XRD analysis because a nanosphere was made from polymer and many smaller CdS nanoparticles. Figure 3 (b) is TEM image of another area, from which monolayer and multilayer nano-spheres can be clearly seen. The formation of the hexagonal CdS phase under the present conditions is also confirmed by the electron diffraction (ED) of the sample.

In this W/O microemulsion system, inorganic salts and AM monomers were limited in water droplets with nanoscale size. When the system was irradiated by γ-ray, a series of reactions occurred: Firstly, owing to the radiolysis of water, many active products such as e_{aq}^-, H· and ·OH were produced. Then, the produced radicals could induce polymerization of monomers, and e_{aq}^- could reduce sulfur source to S^{2-}, which reacted with Cd^{2+} to generate CdS. Since the polymerization was faster than the reduction, the viscosity of the system rapidly increased. The further growth of CdS particles was limited. Thus, the composites containing small-sized CdS particles were formed. Meanwhile, isopropyl alcohol, a scavenger of oxidative radicals and chain-transfer reagent, was also added into the system to eliminate the influence of oxidative radicals on the formation of S^{2-} anion and decrease the rate of polymerization. This process can be simplified as follows:

$$H_2O \longrightarrow e_{aq}^-,\ H\cdot,\ \cdot OH,\ \text{etc.}$$

$$n\,CH_2{=}CHCONH_2 \xrightarrow{\text{irradiation}} -(CH_2CH)_n-\ (CONH_2)$$

$$2e_{aq}^- + S_2O_3^{2-} \rightarrow S^{2-}$$

$$S^{2-} + Cd^{2+} \rightarrow CdS$$

$$(CH_3)_2(OH)CH + \cdot OH \rightarrow H_2O + (CH_3)_2(OH)C\cdot$$

In this work, both the size distribution of CdS nanoparticles and the distribution of CdS and PAM in the nanospheres can not be clearly observed by TEM. Nevertheless, according to the above description, one can conclude that CdS nanoparticles were homogeneously dispersed in the matrix of PAM and their dimension–distribution should also be even.

In summary, spherical CdS/PAM nanocomposites have been successfully fabricated in situ by γ-irradiation in a W/O microemulsion system. This novel method combines the advantages of microemulsion and γ-irradiation methods to produce semiconductor nanoparticles or nanocomposites. Furthermore, compared with other methods to prepare semiconductor/polymer nanocomposites,[5–14] the present method owns obvious advantages: Firstly, no extra inducing reagent is needed; Secondly, the reactions can occur under normal pressure at room temperature and can be easily controlled; Thirdly, monomers can be arbitrarily selected without the limitation of solubility in water; and the size of the nanospheres can be controlled by changing the experimental condition such as the kind or the content of emulsifiers and the dose rate of radiation. More important, employing this method, the polymerization of monomers and the formation of CdS nanoparticles can be performed in single step.

XRD pattern measurement was carried out on a Japanese Rigaku D/max γ_A X-ray diffractometer with graphite monochromatized Cu Kα radiation. TEM images were taken on a Hitachi Model H-800 transmission electron microscope. IR spectrum was recorded on a Bruker Vector-22 FT-IR spectrometer. The absorption spectra were examined on an UV-2100 Schimadzu UV-VIS spectrophotometer. The PL spectrum was measured on a Hitachi 850-fluorescence spectrophotometer.

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