

A Novel in situ Ultraviolet Irradiation Polymerization–Photolysis Technique for Fabrication of Polyacrylamide-MS (M = Cd, Pb, Zn) Nanocomposites at Room Temperature

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Polyacrylamide (PAM)-MS (M = Cd, Zn, Pb) inorganic-polymer nanocomposites with homogeneously dispersed semiconductor nanoparticles of narrow size distribution in the polymer matrices were prepared by a novel in situ ultraviolet irradiation polymerization–photolysis (UIPP) technique at room temperature.

Synthesis and characterization of inorganic–organic polymer nanocomposites have received much intensive research,¹ owing to their optical, electrical, catalytic, and mechanical properties,² and potential applications in microelectronics.³ Many methods have been employed to prepare the semiconductor-polymer nanocomposites. Meissner et al.⁴ first reported a system involving a dispersed semiconductor/polymer arrangements by physically embedding monograins CdS particles on the order of 40 μm diameter in a thin, unconducting polyurethane membrane and examined various photoprocesses. Recently, CdS/polystyrene,⁵ CdS/PS-P2VP[poly-styrenes-block-poly(vinylpyridine)s] composite,⁶ PbS/S-MA(styrene-methylacrylic copolymer),⁷ PbS/E-MAA(ethylene-15% methacrylic acid copolymer) composites⁸ have been prepared in different polymer matrices using a variety of methods. Y. Wang and N. Herron reported for the first time the synthesis of CdS/PVK(N-polyvinylcarbazole) polymer composite by using Cd₁₀S₄(C₆H₅)₁₂ as precursor.⁹ Hirai reported the preparation of semiconductor nanoparticle-polyurea composites using reverse micellar system via in situ diisocyanate polymerization¹⁰.

In our previous work, we reported a novel in situ simultaneous polymerization–hydrolysis (SPH) technique for the fabrication of polyacrylamide-semiconductor MS (M = Cd, Zn, Pb) nanocomposites¹¹ and a novel in situ simultaneous copolymerization–decomposition (SCPD) technique for the preparation of poly(acrylamide-co-styrene)–semiconductor CdE (E = S, Se) nanorods nanocomposites.¹² In this letter, we introduce a novel in situ ultraviolet irradiation polymerization–photolysis (UIPP) technique to polyacrylamide (PAM)-semiconductor MS (M = Cd, Pb, Zn) nanocomposites in aqueous systems. The present in situ UIPP technique is based on the mechanism of the simultaneous occurring of the polymerization of organic monomer and the formation of the semiconductor MS nanoparticles upon ultraviolet irradiation. It was found that the produced MS semiconductor nanoparticles were well homogeneously dispersed in the PAM matrices and have narrow size distribution. Compared to the previous SPH and SCPD techniques, the present UIPP technique can be carried out at room temperature, resulting in that the produced MS semiconductors were of smaller particle size and displayed stronger quantum confinement effect.

In a typical preparation procedure of the PAM-CdS nanocomposites with the present in situ ultraviolet irradiation polymerization–photolysis (UIPP) technique, a 30 W, column-like, low-pressure, mercury lamp (λ = 253.7 nm) was employed as an ultraviolet light source. The reagents of 0.001 mol CdSO₄ and 0.001 mol

thioacetamide (TAA, CH₃CSNH₂), as sulfur source, were added to 100 mL 5.0 mol/L acrylamide (AM) monomer aqueous solution. Then, 0.01 g AIBN (2, 2'-azobisisobutyronitrile) as radical initiator was added to the above solution. The resulting mixture solution was irradiated for 24 h in the present ultraviolet light source. The product obtained was washed with distilled water and absolute ethanol, dried at room temperature and grounded into powders for characterization.

The X-ray powder diffraction (XRD) pattern for the product was determined at a scanning rate of 0.02°s⁻¹ in 2θ ranging from 5°–65°, using a Japanese Rigaku Dmax γ_A-ray diffractometer with high-intensity Cu Kα radiation (λ = 0.151478 nm). 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.

Figure 1 (a) shows the XRD pattern of the produced CdS-PAM nanocomposite by the present in situ UIPP technique. The broadening peak at about 17° was corresponding with the PAM phase. The other diffraction peaks can be assigned to the cubic phase CdS. Due to the interference from the broad diffraction peaks for the PAM phase, not all diffraction peaks of the CdS nanoparticles can be observed in the XRD pattern of the CdS-PAM nanocomposite. However, the diffraction peaks for CdS cubic phase in the range of 2θ bigger than 40° can be obviously seen. The configuration of the XRD pattern was similar to that of CdS-PAM nanocomposite by our previous SPH technique.¹¹ The only difference lied in more broadened in diffraction peaks of CdS nanocrystals than that by SPH technique, indicating that the CdS particle size in CdS/PAM nanocomposite by the present UIPP technique is smaller than that by the SPH technique. The average size of the CdS nanoparticle was about 4.5 nm calculated by the Scherrer formula.

Figure 2 (a) presents the UV–Vis absorption spectrum of the CdS-PAM nanocomposite obtained by the present in situ UIPP technique for 24 h, which was dispersed in distilled water with pure PAM in distilled water as reference solution. The featured-spectrum shows that the onset of the absorption peak of the CdS nanoparticles was observed at about 466 nm, which shifts toward blue zone compared with that of the bulk material (512 nm).¹³ The blue shift was caused by strong quantum confinement effect, due to the decreasing in particle size.¹⁴ The average size of the CdS nanoparticles in the CdS/PAM nanocomposite is about 4.1 nm calculated by the Brus method based on the blue shift of UV–Vis absorption spectrum.¹⁴ The predicted CdS particle size is well correspondent with the result calculated by the XRD pattern of the present CdS/PAM nanocomposite according to the Scherrer formula. The band gap of the CdS nanoparticles was calculated about 2.66 eV, larger than that of the bulk materials (2.5 eV)¹³. The strong exciton feature indicated a narrow particle size distribution of the CdS nanoparticles dispersed in the CdS/PAM nanocomposite produced by the present UIPP technique.¹⁵

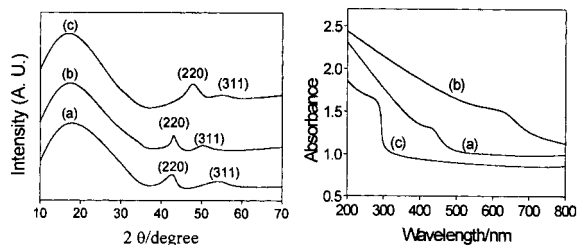


Figure 1. (left) The XRD patterns of the produced MS-PAM nanocomposites, (a) CdS-PAM; (b) PbS-PAM; (c) ZnS-PAM.

Figure 2. (right) The UV-Vis absorption spectra of MS-PAM nanocomposites, (a) CdS-PAM; (b) PbS-PAM; (c) ZnS-PAM.

Figure 3 (a) presents a representative TEM image of the CdS-PAM nanocomposite powders obtained by the present in situ UIPP technique for 24 h. The image shows that the CdS nanoparticles were homogeneously dispersed in the PAM matrix. The CdS particle size was observed about 4.5 nm, in good agreement with the results by the XRD pattern and the UV-Vis absorption spectrum.

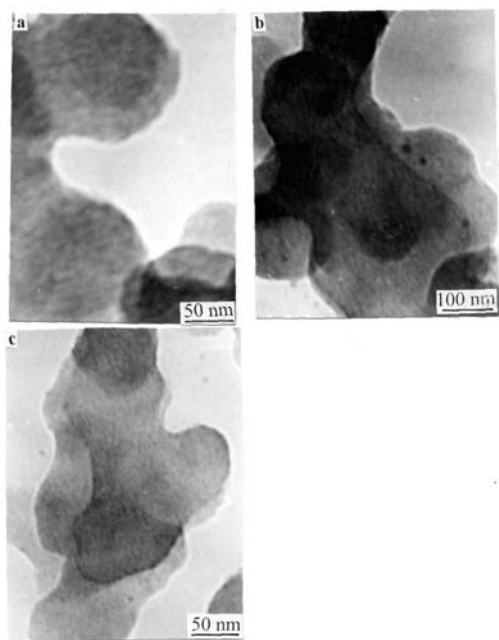
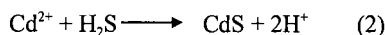
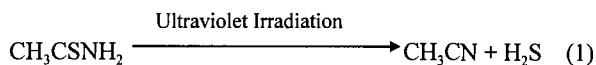


Figure 3. The TEM images of the produced MS-PAM nanocomposites, (a) CdS-PAM; (b) PbS-PAM; (c) ZnS-PAM.

It is well known that the AIBN initiates polymerization of the acrylamide (AM) monomer into poly-acrylamide (PAM) upon the present ultraviolet irradiation at 254 nm. Accompanying with the proceeding of polymerization reaction, the photolysis of thioacetamide (TAA) is also simultaneously favored under the irradiation, leading to the release of S^{2-} and the formation of CdS nanoparticles. The in situ production of the CdS nanoparticles results in a well homogeneous dispersion throughout the PAM matrix. The formation process of CdS nanoparticles by photolysis of TAA can be formulated as following eqs (1) and (2)¹⁶:



Here, it should be noted that although the TAA absorbed UV light, it could not produce free radicals that initiate acrylamide polymerization as did the radicals from AIBN.

We also employed the present in situ UIPP technique to prepare PbS-PAM and ZnS-PAM nanocomposites under substitution of $\text{Pb}(\text{NO}_3)_2$ and ZnCl_2 for CdSO_4 . Figures 1(b) and 1(c) show the XRD patterns of the produced PbS-PAM and ZnS-PAM nanocomposites by the present in situ UIPP technique. Both of the produced PbS and ZnS nanoparticles can be indexed to the cubic phase. The particle size calculated by Scherrer formula was 10.3 nm for PbS nanoparticle in the PbS-PAM nanocomposite and 4.8 nm for ZnS nanoparticle in the ZnS-PAM nanocomposite. The UV-Vis absorption spectra of the PbS-PAM and the ZnS-PAM nanocomposites were shown in Figure 2 (b) and (c), respectively. The absorption onsets were 325 nm for the ZnS nanoparticle and 754 nm for the PbS nanoparticle. Both of them displayed blue shift, compared to those of bulk materials (λ_{onset} of bulk ZnS: 335 nm, band gap: 3.7 eV; λ_{onset} of bulk PbS: 3200 nm, band gap: 0.41 eV).¹³ The estimated particle size and band gap by Brus method were 4.4 nm and 3.82 eV for the ZnS nanoparticle, and 9.8 nm and 1.64 eV for PbS nanoparticle, which were in good agreement with the results by XRD pattern. The appearance of the exciton bands in the both spectra demonstrated that the ZnS and PbS nanoparticles dispersed in PAM matrices were also of narrow size distribution. The Figures 3(b) and 3(c) show the TEM image of the PbS-PAM and ZnS-PAM nanocomposites. From the Figure 3, the PbS and ZnS nanoparticles were clearly seen to dispersed in PAM matrices and have narrow size distribution although much few larger particles existed. The average sizes of particles were about 10 nm for PbS particle and 4.5 nm for ZnS particle respectively, well correspondent with the values estimated by the above Brus method.

The PAM-semiconductor MS (M = Cd, Pb, Zn) nanocomposites were prepared by a novel in situ ultraviolet irradiation polymerization-photolysis (UIPP) technique. The MS particles produced with narrow distribution of particle size were found to disperse homogeneously in the polymer matrices and to display the strong quantum confinement effect.

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References and Notes

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