# Preparation of ZnS-PSA Nanocomposites by *in situ* Simultaneous Polymerization-precipitation of ZnS Nanoparticles Using γ-Radiation

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Poly(St-co-AA)(PSA)-semiconductor ZnS nanocomposites with well homogeneously dispersed semiconductor nanoparticles in the copolymer matrix were prepared by in situ simultaneous polymerization-precipitation of ZnS nanoparticles using γ-radiation. These synthesized nanocomposites were further characterized by XRD and TEM measurements.

Much attention has been paid to the preparation and characterization of inorganic-organic polymer nanocomposites, owing to their optical, electrical, catalytic, mechanical properties[1-3] and potential application in microelectronics.[4,5] Many methods have been applied to synthesize the semiconductor / polymer nanocomposites. Organizing the semiconductor nanoparticles in an orderly fashion in a matrix may provide a potential application of their special properties. Polymers can be expected to provide good mechanical and optical properties, conferring high kinetic stability on nanometer-sized semiconductor particles.

Meissner et al[6] firstly reported a system involving a dispersed semiconductor / polymer arrangements by embedding monograins CdS particles on the order of 40 μm diameter in a thin, unconducting polyurethane membrane. Later a new method of incorporation of a dispersed semiconductor CdS throughout an ionically conductive Nafion polymer membrane was developed.[7,8] Recently PbS / S-MA (styrene-methylacrylic acid copolymer),[11] CdS / PS-P2VP[polystyrene-block-poly(vinylpyridine)s] composite,[10] CdS / polystyrene,[9] PbS / E-MAA (ethylene-15% methylacrylic acid copolymer )[12] and monolayer of $PbI_2$ / MD (molecular deposition )-LB films[13] have been synthesized using a variety of methods. Currently the multisemiconductor nanocomposite $Cu_2S$ / CdS / ZnS was also synthesized successfully in polystyrene system by ion exchange.[14] The synthesis of CdS / PVK (N-polyvinyl carbazole) composite by using $Cd_{10}S_4$ $(C_6H_5)_{12}$ as precursor has been reported for the first time by Y. Wang et al.[15] Some block copolymer systems / metal sulfide nanoparticles have prepared by adding $H_2S$.[17] At present, the use of amphiphilic block copolymer(ABC) micelles opens a doorway to utilize these materials as "nanoreactors" for the formation of the inorganic nanocrystals.[16-18]

Here we report a novel method for the preparation of ZnS-copolymer nanocomposites by γ-radiation at room temperature and atmospheric pressure. In this method, $ZnCl_2$, $Na_2S_2O_3 \cdot 5H_2O$ and organic monomers are mixed homogeneously at the molecular level in the solution, and the formation of nanocrystalline ZnS particles ($S^{2-}$ ions are from the decomposition of sodium thiosulfate ($Na_2S_2O_3$) upon γ-irradiation[19,20]) and polymerization of monomers are simultaneous in solution. The polymerization proceed by keeping the pace with the formation of ZnS, leading to a homogeneous dispersion of nanocrystalline ZnS particles in the copolymer matrix.

In a typical procedure, an aqueous solution (100 mL) containing $ZnCl_2$ (1.36g) and $Na_2S_2O_3 \cdot 5H_2O$ (4.96g) was prepared in advance. 20 mL of the solution was then added to a mixture of 25g styrene, 5g acrylic acid, 0.5g SDS and 2g isopropyl alcohol. This mixture was stirred drastically until a stable emulsion (w/o) formed. After bubbling with $N_2$, the emulsion was stirred continuously and irradiated in the field of a $^{60}Co$ γ-ray source for 10 h with a radiation dosage of $3.0 \times 10^4$ Gy. After irradiation, the product was collected and washed with distilled water. Finally, the product was dried in vacuum at 50 ℃.

SDS is acted as emulsifier, and is also used to prevent the small ZnS particles from coming into close contact and undergoing further aggregation. Isopropyl alcohol, which is a scavenger of oxidative radicals such as $OH^{\cdot}$, is thus added to improve the yield of ZnS nanoparticles. The products are white powder. The average size of these white powder is about 50 nm.

X-ray powder diffraction (XRD) was carried out on a Rigaku $D_{max}$ $\gamma_A$ X-ray diffractometer with Cu-$K_\alpha$ radiation ($\lambda$ = 0.154178 nm ). Transmission electron microscopy (TEM) image was taken with a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200Kv.

Figure 1 shows the XRD pattern of the ZnS / PSA nanocomposite obtained by γ-radiation method. The broad peak at $2\theta = 19.7^\circ$ is attributed to the diffraction of non-crystalline copolymer (PSA) phase. The other three peaks with $2\theta$ values of $28.3^\circ$, $47.6^\circ$, $56.3^\circ$ correspond to the three crystal planes of 111, 220 and 311 of crystalline ZnS nanoparticles, respectively. Empolying Scherrer's equation,[21] the average size of ZnS nanoparticles was estimated to be 3 nm.

Figure 2 shows the TEM image of the same sample of Figure 1. From Figure 2, we can see that the nanocomposite containes

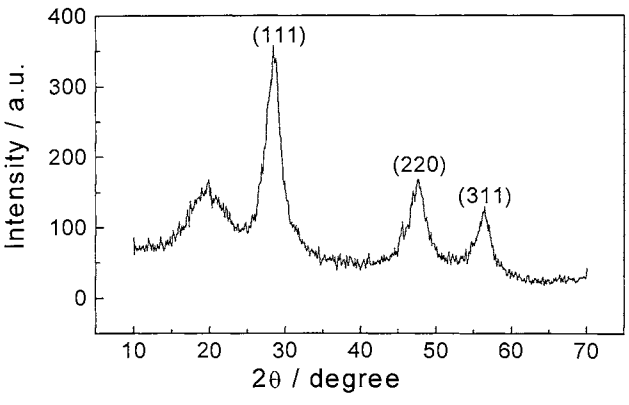


**Figure 1.** X-Ray diffraction pattern of ZnS-PSA nanocomposites.

fine crystalline ZnS particles homogeneously dispersed and well separated in the PSA matrix. Figure 2 also reveals that small particles aggregate into secondary particles (about 50 nm) because of their extremely small dimensions and high surface energy. Further studies demonstrate that the average size of ZnS nanoparticles in the absence of styrene and acrylic acid is larger than that of the ZnS nanoparticles in the ZnS-PSA nanocomposite under the same experimental condition. The reason is that the reaction medium became more and more viscous with the proceeding of polymerization of the styrene and acrylic acid, which is favorable for preventing the formed ZnS nanoparticles from aggregating. Other polymer systems (PAA, PMMA, etc.) and other metal sulfides (CdS, PbS, etc.) nanocomposites may be also prepared by this method.

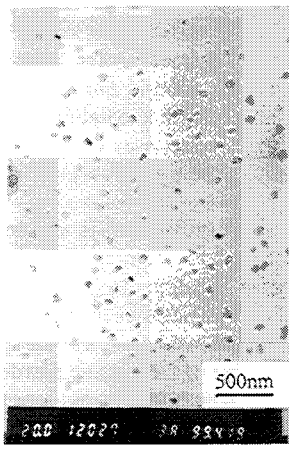


**Figure 2.** TEM image of ZnS-PSA nanocomposites.

In summary, the ZnS-PSA nanocomposite with well homogeneously dispersed ZnS nanoparticles in the copolymer matrix were synthesized successfully by a novel in situ simultaneous co-polymerization of monomers and precipitation of ZnS nanoparticles using γ-radiation. The present in situ γ-radiation technique may provide a new route for other polymer system and other metal sulfides semiconductor-copolymer (CdS-PSA, PbS-PSA, CdS-PAA, etc.) hybrid nanocomposites. The electrical and photocatalytic properties of semiconductor-copolymer nanocomposite materials are worthy of further study. They may be a functional materials applied in optical, electrical and photocatalytic fields.

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**References and Notes**

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