

# Preparation and Characterization of CdS and CdS/Polyacrylonitrile Nanocomposites by $\gamma$ -Irradiation and Emulsion Polymerization

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**ABSTRACT:** CdS and CdS/polyacrylonitrile (PAN) nanocomposites were prepared by  $\gamma$ -irradiation and emulsion polymerization. The CdS and CdS/PAN nanocomposites were characterized by powder X-ray diffraction, infrared spectroscopy, Fourier transform Raman spectroscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and thermal analysis (thermogravimetric analysis/dynamic thermal analysis). In photoluminescence spectroscopy analysis, the maximum peak of CdS/

PAN nanocomposites prepared by  $\gamma$ -irradiation and emulsion polymerization was at about 485 nm, whereas the maximum peak of CdS nanocomposites was at about 460 nm. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2335–2342, 2004

**Key words:** irradiation; emulsion polymerization; nanocomposites; X-ray; TEM

## INTRODUCTION

In recent years, research on metal–polymer nanocomposites and their properties has attracted considerable attention because of their potential applications in catalysts, electronics, and nonlinear optics.<sup>1–5</sup> These composites not only combine the advantageous properties of metals and polymers but also exhibit many new characteristics that single-phase materials do not have. Precious metals such as silver and gold have been studied most extensively among metal–polymer nanocomposites.

Many metal–polymer nanocomposites have been prepared in one step with  $\gamma$ -irradiation in an aqueous solution.<sup>6,7</sup> Selvan et al.<sup>8</sup> reported the synthesis of gold–polypyrrole nanocomposites by vapor-phase polymerization for molecular electronics. Huang et al.<sup>9</sup> reported that a silver–polyimide nanocomposite was prepared with a convenient ultraviolet irradiation technique.

In a previous study,<sup>10</sup> we also reported that silver–polyester and silver–nylon nanocomposites were prepared by the dispersion of silver nanoparticles, which were prepared by  $\gamma$ -irradiation, onto polyester and nylon during condensation polymerization for anti-

bacterial fibers. It was found that the silver nanoparticles aggregated in the polyester matrix, whereas the silver nanoparticles dramatically dispersed in the nylon matrix. However, little has been reported on the preparation of polymeric nanocomposites in one step with  $\gamma$ -irradiation.

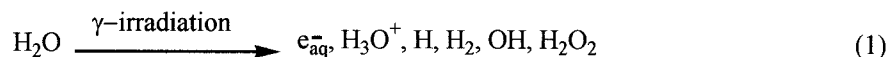
The emulsion polymerization of vinyl and acryl monomers has received much attention for practical and academic reasons and with a view toward the synthesis of polymers for biomedical, coating, and adhesive applications. Wang and Pan<sup>11</sup> reported on polymer–metal nanocomposites, poly(styrene-*co*-acrylonitrile)nickel, the postemulsion polymerization of acrylonitrile (AN) and styrene, the subsequent coupling of poly(styrene-*co*-acrylonitrile) and a small amount of PdCl<sub>4</sub> as a reduction agent, and nickel-ion reduction with poly(acrylonitrile-*co*-styrene)palladium. However, less has been reported on the emulsion polymerization of vinyl and acryl monomers in the presence of nanocomposites prepared by  $\gamma$ -irradiation.

We report here the preparation of CdS and CdS/polyacrylonitrile (PAN) nanocomposites in one step by  $\gamma$ -irradiation at room temperature and ambient pressure. The CdS/PAN nanocomposites were also prepared by the emulsion polymerization of AN in the presence of a CdS nanocomposite. The CdS and CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation and emulsion polymerization were characterized by Fourier transform infrared (FTIR), Fourier transform (FT) Raman spectroscopy, transmission electron micros-

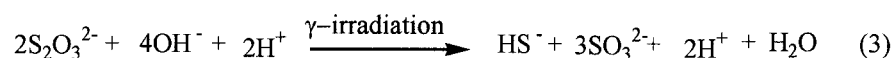
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### 1. Reduction of cadmium ions by $\gamma$ -irradiation.



### 2. Decomposition of sodium thiosulfate by $\gamma$ -irradiation.



### 3. Formation of CdS.



**Scheme 1** Mechanism of the formation of CdS nanocomposites with  $\text{Na}_2\text{S}_2\text{O}_3$  as the sulfur source.

copy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and thermal analysis [thermogravimetric analysis (TGA)/dynamic thermal analysis (DTA)]. Furthermore, photoluminescence (PL) spectra were made.

## EXPERIMENTAL

### Materials

Analytical cadmium sulfate ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ) and sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) as sulfur sources were obtained from Junsei Chemical Co., Ltd. (Kyoto, Japan). Carbon disulfide ( $\text{CS}_2$ ) as a sulfur source, AN, potassium persulfate (KPS), and sodium lauryl sulfate (SLS) as a surfactant were purchased from Aldrich Co. Poly(vinyl pyrrolidone)

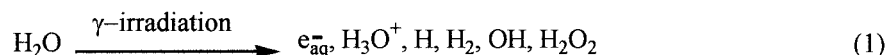
(PVP; weight-average molecular weight = 10,000) as a colloidal stabilizer was obtained from Tokyo Kasei (Japan). The other chemicals, being reagent-grade, were also used without further purification.

### Preparation of CdS and CdS/PAN nanocomposites in one step with $\gamma$ -irradiation

CdS nanocomposites in one step with  $\gamma$ -irradiation

A typical solution was prepared by the dissolution of analytically pure sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ; 0.05M) as a sulfur source and cadmium sulfate (0.05M) in water in the presence of PVP as a colloidal stabilizer and isopropyl alcohol as a radical scavenger. The solution was irradiated with a cobalt 60  $\gamma$ -ray source. A yellow precipitate was collected by centrifugation and

### 1. Reduction of cadmium ions by $\gamma$ -irradiation.



### 2. Decomposition of carbone disulfide by $\gamma$ -irradiation.



### 3. Formation of CdS.



**Scheme 2** Mechanism of the formation of CdS nanocomposites with  $\text{CS}_2$  as the sulfur source.

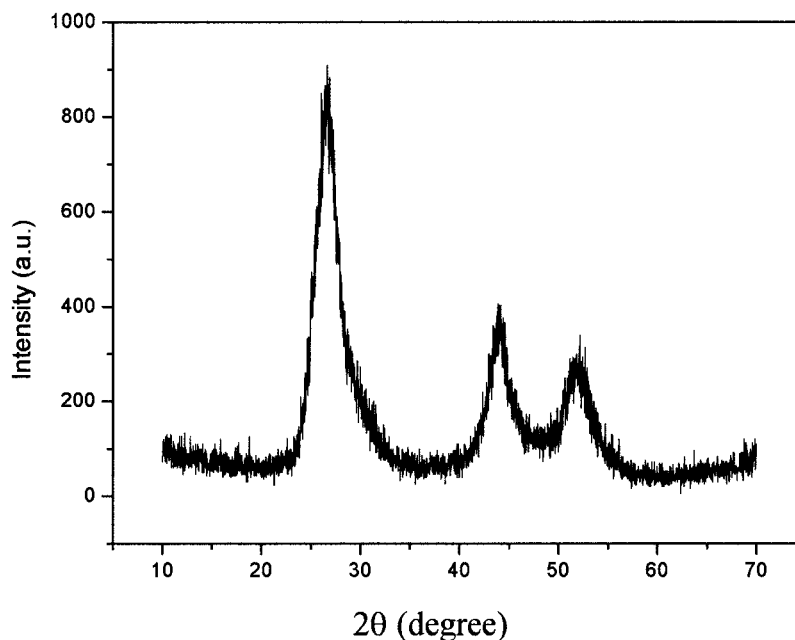


Figure 1 XRD pattern of the CdS nanocomposites prepared by  $\gamma$ -irradiation.

was washed with diluted acetic acid, absolute alcohol, and distilled water, in that sequence, for the removal of the byproduct. The final product was dried *in vacuo* at 50°C for 7 h.

The CdS nanocomposites were also prepared with cadmium sulfate (0.05M), CS<sub>2</sub> (0.025M) as a sulfur source, and PVP as a colloidal stabilizer in a solution of an ethanol/water mixture and by  $\gamma$ -irradiation. A yellow precipitate was collected by centrifugation and washed with diluted acetic acid, absolute alcohol, and distilled water, in that sequence, for the removal of the byproduct. The final product was dried *in vacuo* at 50°C for 7 h.

CdS/PAN nanocomposites in one step with  $\gamma$ -irradiation

The solution was prepared by the dissolution of cadmium sulfate (0.05M), Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, AN (7 vol %) without purification, PVP, and isopropyl alcohol in water. The solution was irradiated with a cobalt 60  $\gamma$ -ray source. A yellow precipitate was collected by centrifugation and washed with diluted acetic acid, absolute alcohol, and distilled water, in that sequence, for the removal of the byproduct. The final product was dried *in vacuo* at 50°C for 7 h.

#### Preparation of PAN and CdS/PAN nanocomposites by emulsion polymerization

AN was distilled under reduced pressure for the removal of the inhibitor.<sup>11</sup> The precursor was prepared by the stirring of AN (161 mL), itaconic acid (0.97 g), *n*-methylol acrylamide (5.01 g), methyl methacrylate (51 mL) as a crosslinking agent, and SLS (4.0 g) as a surfactant in H<sub>2</sub>O (76 mL). The itaconic acid and *n*-methylol acrylamide, containing carboxylic acid and amine groups, were used because the carboxylic acid and amine groups were coupled with the CdS nanoparticles. The prepared precursor and KPS (6.0 mL, 3 wt % with respect to the total amount of H<sub>2</sub>O) as an initiator were added to the CdS solution (142 mL), and they reacted at 80°C for 3 h with mechanical stirring at 400 rpm. The total amount of H<sub>2</sub>O was about 219 mL. PAN as a base polymer was also prepared by emulsion polymerization without CdS nanocomposites.

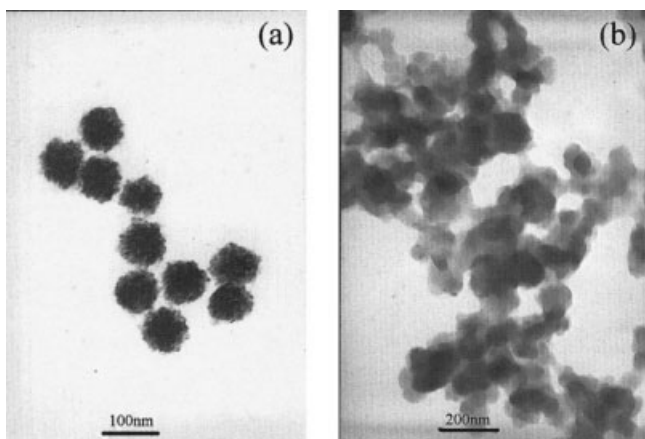
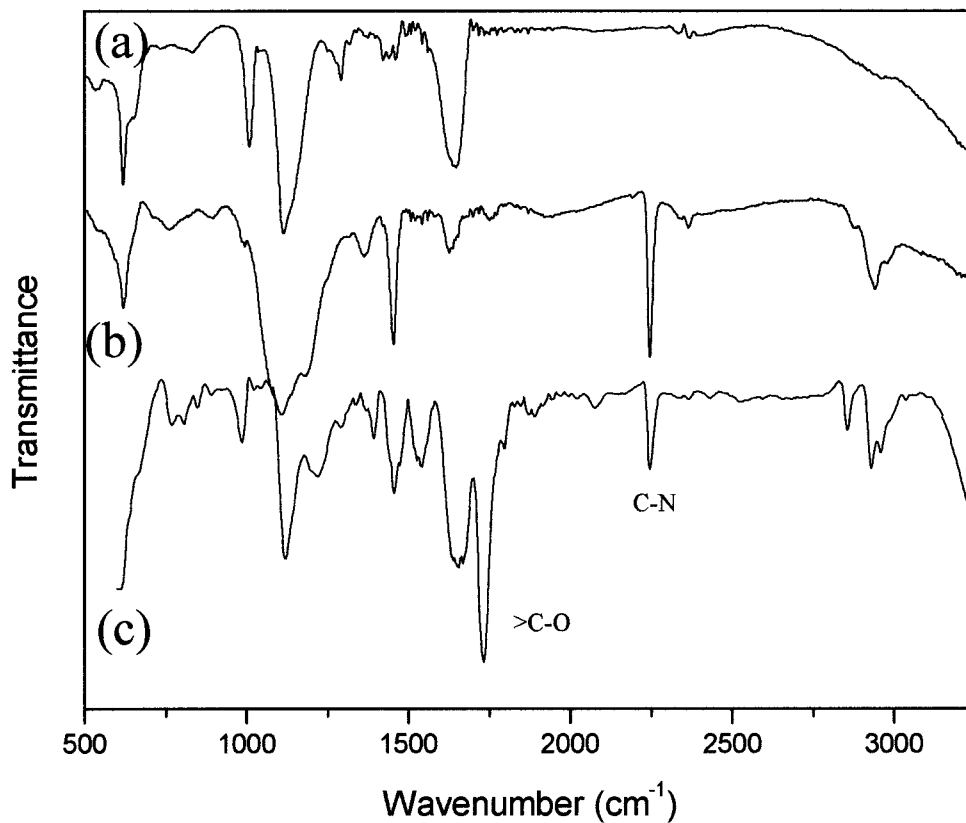
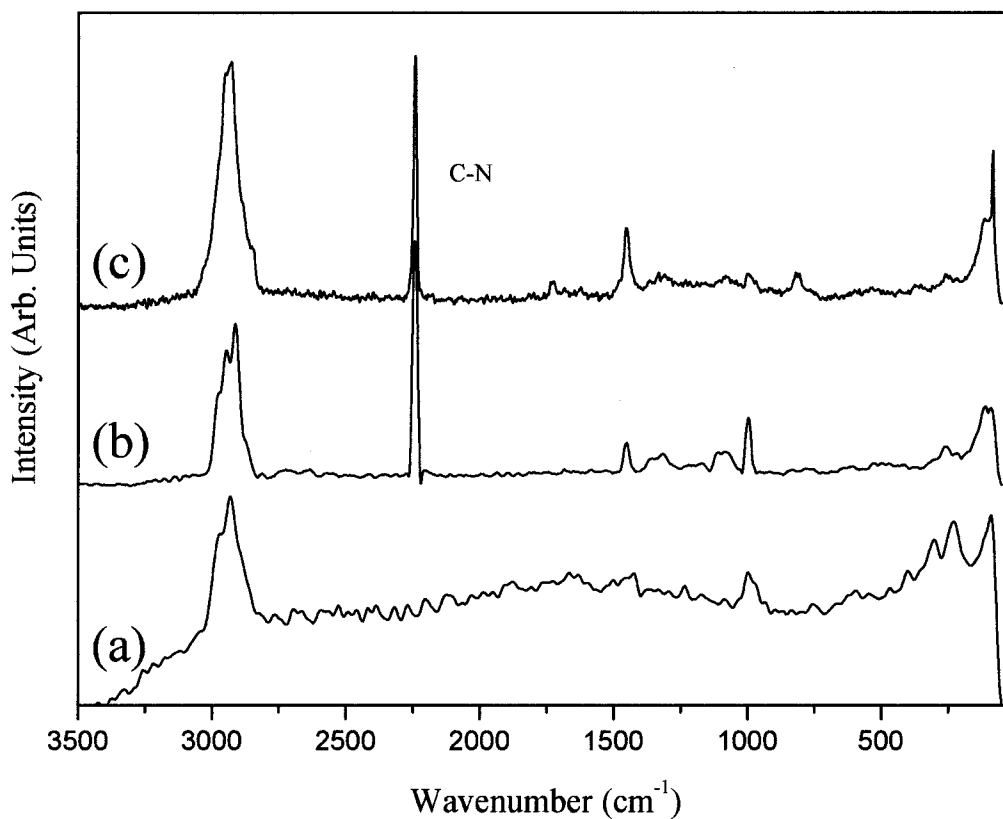


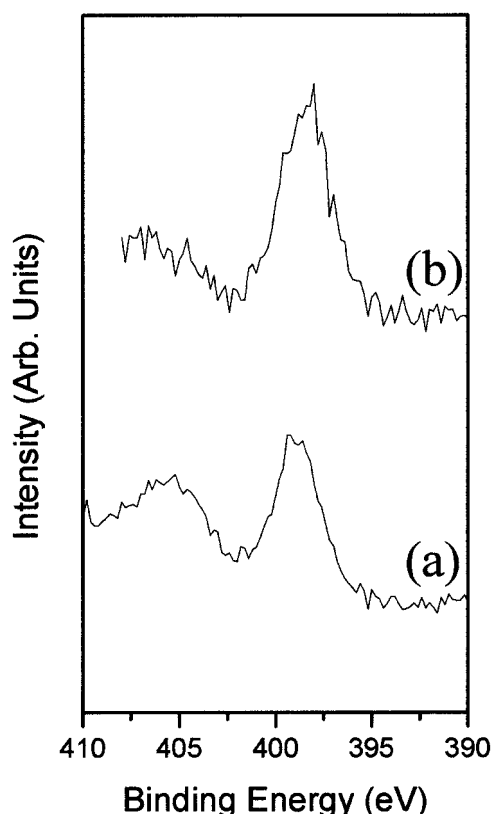
Figure 2 TEM images of (a) CdS (bar = 100 nm) and (b) CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation (bar = 200 nm).



**Figure 3** FTIR spectra of (a) CdS, (b) CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation, and (c) CdS/PAN nanocomposites prepared by emulsion polymerization.



**Figure 4** FT Raman spectra of (a) CdS nanocomposites, (b) CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation, and (c) CdS/PAN nanocomposites prepared by emulsion polymerization.



**Figure 5** XPS spectra of (a) CdS nanocomposites and (b) CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation.

### Measurements

The XRD spectra of the CdS and CdS/PAN nanocomposites were obtained with an X-ray diffractometer (RA/FR 571, Enraf Nonius, Deift, The Netherlands). Photographs of the samples were obtained with TEM (H-7100, Hitachi, Tokyo, Japan). FTIR spectra of the samples were obtained with Nujol mulls with an infrared (IR) spectrophotometer (model 983, PerkinElmer, Boston, MA). The near-infrared FT Raman spectra were recorded with a Bruker FT-106 Raman module equipped with a Ge detector cooled by liquid nitrogen and connected to a Bruker FTIR 66 interferometer. The XPS spectra of the samples were obtained with an Escalab 220i (VG Scientific, Waltham, MA) equipped with a full  $180^\circ$  hemispherical electrostatic analyzer to examine the chemical state of the constituent elements. The PL spectra were recorded with a Shimadzu RF-5301PC spectrophotometer (Japan). The excitation wavelength was 270 nm. TGA/DTA of CdS and CdS/PAN were performed with a TGA 2950 (DuPont Co., Wilmington, DE) at a heating rate of  $10^\circ\text{C min}^{-1}$  in the temperature range of 50–700°C.

## RESULTS AND DISCUSSION

For the preparation of CdS and CdS/PAN nanocomposites,  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{CS}_2$  as were selected sulfur

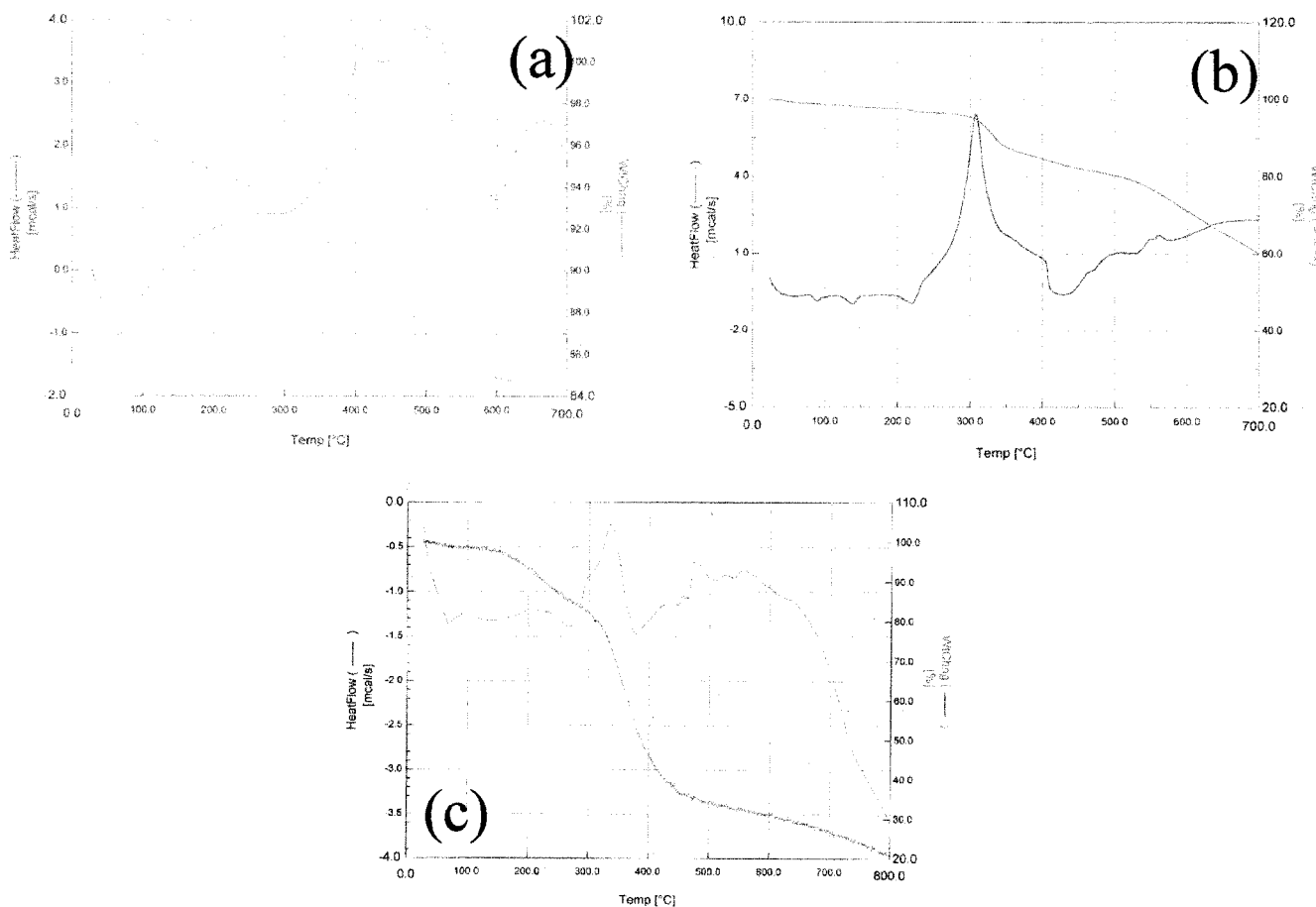
sources. The radiolytic yield of the CdS nanocomposite with  $\text{Na}_2\text{S}_2\text{O}_3$  as a sulfur source was greater than 96%. The radiolytic yield was less than 5% when  $\text{CS}_2$  was used as a sulfur source. Scheme 1 shows the formation mechanism of CdS nanocomposites with  $\text{Na}_2\text{S}_2\text{O}_3$  as a sulfur source. In Scheme 1(1), the hydrated electron,  $\text{H}_3\text{O}^+$ ,  $\text{H}$ ,  $\text{H}_2$ ,  $\text{OH}$ , and  $\text{H}_2\text{O}_2$  during  $\gamma$ -irradiation are generated in a water solution. The cadmium ion ( $1+$ ) is prepared by the reduction of a hydrated electron and a cadmium ion ( $2+$ ) in Scheme 1(2).  $\text{Na}_2\text{S}_2\text{O}_3$  is converted into a sulfur ion in Scheme 1(3,4). Finally, CdS is synthesized by the reaction of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  in Scheme 1(5).

Scheme 2 shows the formation mechanism of CdS nanocomposites with  $\text{CS}_2$  as a sulfur source. As shown in Scheme 2(1), a hydrated electron occurs during  $\gamma$ -irradiation. In Scheme 2(2), the cadmium ion ( $1+$ ) is prepared by the reaction of a hydrated electron and a cadmium ion ( $2+$ ). In Scheme 2(3), the carbon sulfur radical and sulfur radical occur during  $\gamma$ -irradiation. Finally, cadmium sulfide is synthesized during the reaction of the cadmium ion ( $1+$ ) and sulfur radical.

Figure 1 shows the XRD pattern of the CdS nanocomposites created by  $\gamma$ -irradiation. The XRD pattern shows that the products were crystallite powders. The average crystallite sizes were calculated from the peaks of the XRD pattern by the Scherrer equation.<sup>12</sup> The average size of the CdS nanocomposites was about 2.7 nm.

Figure 2 shows TEM images of CdS and CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation. As shown in Figure 2(a), the CdS nanocomposites were spherical particles of uniform size, but small particles aggregated into secondary particles because of their extremely small dimensions and high surface energy. Therefore, it was difficult to precisely determine the size and size distribution of the nanoparticles from the TEM image alone. As shown in Figure 2(b), for pure polymers, which often consist of light atoms such as O, H, and C, TEM images are very weak. Thus, PAN dyed with CdS had to contribute to the image of this product. In Figure 2(b), we see that CdS was homogeneously dispersed in the PAN matrix in the as-prepared nanocomposite.

Figure 3 shows the FTIR spectra of CdS and CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation and emulsion polymerization. In FTIR spectra of the CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation and emulsion polymerization, the characteristic band at  $2243\text{ cm}^{-1}$ , due to a cyano group, could be observed, whereas the cyano band was not observed for CdS nanocomposites. In emulsion polymerization, the characteristic peak at  $1735\text{ cm}^{-1}$ , due to a



**Figure 6** TGA/DTA curves of (a) CdS nanocomposites, (b) CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation, and (c) CdS/PAN nanocomposites prepared by emulsion polymerization.

carbonyl peak, was measured in the matrix. Organic molecules with specific functional groups, such as  $-\text{NH}_2$ ,  $-\text{COOH}$ , and  $-\text{SH}$ , are well-known interaction groups of nanometal and nanocluster surfaces. For increased hydrophilic properties, small amounts of itaconic acid with carboxylic acid groups and methylolacryl amide with amine and alcohol groups were added because the metal nanoparticle was aggregated in a polymeric backbone with hydrophobic properties.<sup>10</sup> According to the results of the FTIR analysis, the CdS/PAN nanocomposites were successfully prepared.

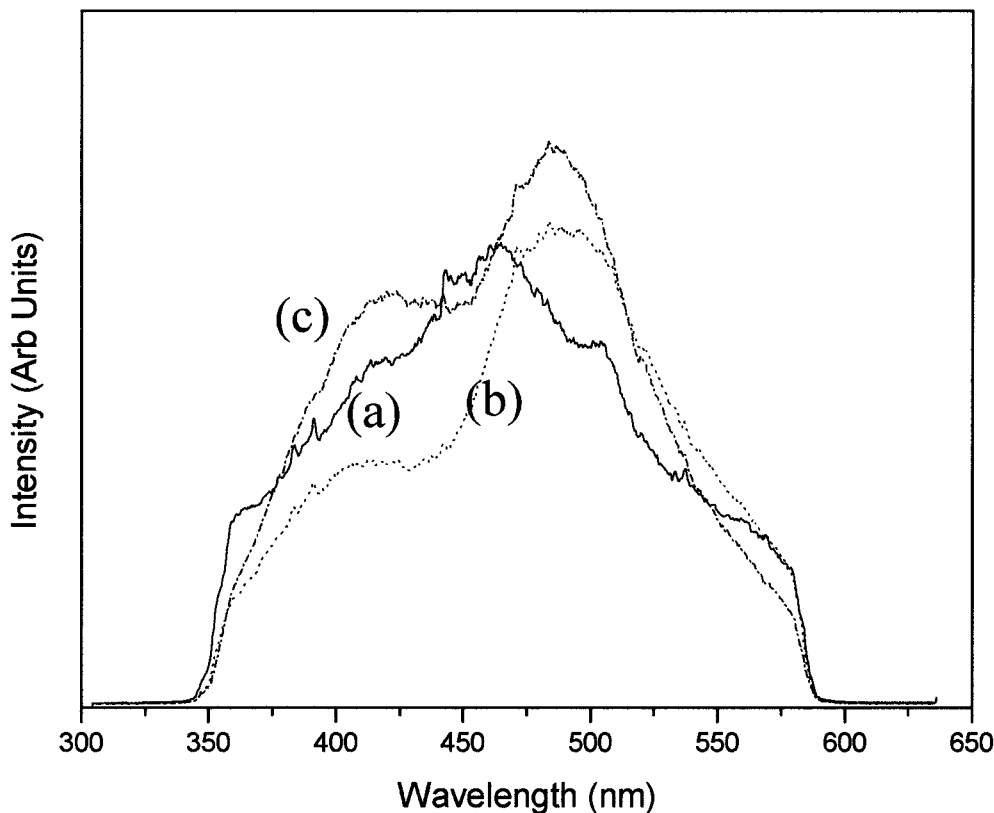
Figure 4 shows FT Raman spectra of CdS and CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation and emulsion polymerization. In Figure 4(b,c), the characteristic stretching band at  $2243\text{ cm}^{-1}$ , due to CN stretching, and the band at  $987\text{ cm}^{-1}$ , due to  $\text{CH}_2$  in-phase twisting of PAN, can be observed. The band at  $1450\text{ cm}^{-1}$ , due to  $\text{CH}_2$  deformation of PAN, can also be observed.

Figure 5 shows the XPS spectra of CdS and CdS/PAN composites prepared by  $\gamma$ -irradiation. The characteristic binding energy of CdS was observed

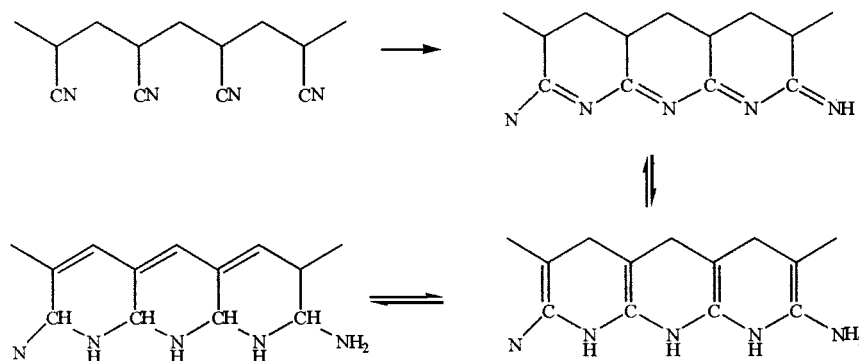
at 399 and 405 eV, respectively. According to these results, the CdS and CdS/PAN nanocomposites were successfully synthesized in one step with  $\gamma$ -irradiation.

Figure 6 shows the thermal analysis (TGA/DTA) of CdS and CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation and emulsion polymerization. In Figure 6(a), two weight losses (TGA data, right curves) can be observed in the range of 70–100°C due to moisture and in the range of 300–520°C due to sulfur dioxide ( $\text{SO}_2$ ); they are endothermic and exothermic processes (DTA data, left curves), respectively. The weight loss at 700°C is about 16%. In Figure 6(b), four weight losses (TGA data, right curves) can be observed in the range of 70–230°C and in the range of 250–320°C due to HCN degradation of PAN, in the range of 350–530°C due to the degradation of sulfur oxides of CdS nanoparticles, and in the range of 520–700°C due to PAN backbone degradation. The weight loss of CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation is about 60% because of the thermally stable cyclic structure of PAN moieties.<sup>13</sup>





**Figure 7** PL spectra of (a) CdS nanocomposites, (b) CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation, and (c) CdS/PAN nanocomposites prepared by emulsion polymerization.



In Figure 6(c), the first weight loss at 100°C was due to moisture vaporization; the second loss in the range of 200–300°C was due to dehydration of the carboxylic acid group in poly(itaconic acid); and the third weight loss in the range of 300–700°C was due to the degradation of the polymer backbone. The weight loss of CdS/PAN nanocomposites prepared by emulsion polymerization was about 80%.

Figure 7 shows the PL spectra of CdS and CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation and emulsion polymerization. In Figure 7(a), the maximum peak was measured at about 460 nm for CdS nanocomposites, whereas the maximum peak was

measured at about 485 nm for CdS/PAN prepared by  $\gamma$ -irradiation and emulsion polymerization. These results imply that the excited electron was transferred into the PAN matrix. The characteristic band at 410 nm of the CdS/PAN nanocomposites was observed because of the polymer matrix.

## CONCLUSIONS

The CdS and CdS/PAN nanocomposites were prepared by  $\gamma$ -irradiation and emulsion polymerization. The obtained CdS and CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation and emulsion polymeriza-

tion were characterized by powder XRD, IR spectroscopy, FT Raman spectroscopy, TEM, XRD, XPS, and TGA/DTA. From these results, we drew the following conclusions:

1. CdS and CdS/PAN nanocomposites were successfully prepared by  $\gamma$ -irradiation and emulsion polymerization.
2. In PL spectroscopy analysis, the maximum peak of CdS/PAN nanocomposites prepared by  $\gamma$ -irradiation and emulsion polymerization was red-shifted with respect to that of CdS composites.

## References

1. Wang, S.; Yang, S.; Yang, C.; Li, Z.; Wang, J.; Ge, W. *J Phys Chem B* 2000, 104, 11853.
2. Qiao, Z.; Xu, J.; Zhu, Y.; Qian, Y. *Mater Res Bull* 2000, 35, 1355.
3. Zhang, Z.; Zhang, L.; Wang, S.; Chen, W.; Lei, Y. *Polymer* 2001, 42, 8315.
4. Zhu, Y.; Qian, Y.; Li, X.; Zhang, M. *Nanostruct Mater* 1998, 10, 673.
5. Qiao, Z.; Xie, Y.; Chen, M.; Xu, J.; Zhu, Y.; Qian, Y. *Chem Phys Lett* 2000, 321, 504.
6. Xu, X.; Yin, Y.; Ge, X.; Wu, H.; Zhang, Z. *Mater Lett* 1998, 37, 354.
7. Qiao, Z.; Xie, Y.; Huang, J.; Zhu, Y.; Qian, Y. *Radiat Phys Chem* 2000, 58, 287.
8. Selvan, S. T.; Hayakawa, T.; Nogami, M.; Möller, M. *J Phys Chem B* 1999, 103, 7441.
9. Huang, J.-C.; Qian, X.-F.; Yin, J.; Zhu, Z.-K.; Xu, H.-J. *Mater Chem Phys* 2001, 69, 172.
10. Choi, S.-H.; Lee, K.-P.; Park, S.-B. *Stud Surf Catal*, 2003, 146, 93.
11. Wang, P. H.; Pan, C.-Y. *Eur Polym J* 2000, 36, 2297.
12. Klug, H. P.; Alexander, L. E. *X-Ray Diffraction Procedure*; Wiley: New York, 1974; Chapter 9.
13. Sahiner, N.; Perkel, N.; Güven, O. *Radiat Phys Chem* 1998, 52, 271.