

# One-Pot Synthesis of a Few Nanocomposites with Poly(*N*-vinylcarbazole) and CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> Nanoparticles with $\gamma$ Irradiation

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**ABSTRACT:** The one-pot synthesis of nanocomposites of a conductive poly(*N*-vinylcarbazole) (PVK) with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles was performed with  $\gamma$  irradiation in a tetrahydrofuran-water mixture (3/1 vol %). For comparison, the CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles were also prepared with  $\gamma$  irradiation with polyvinylpyrrolidone as a stabilizer. Ultraviolet-visible spectroscopy, transmission electron microscopy, X-ray diffraction analysis, and photoluminescence spectroscopy were used for the characterization of CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and

Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles and nanocomposites of PVK with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles. The absorption spectrum of the CdS-nanoparticle-based composite revealed a quantum confinement effect. The emission spectrum of the composite with CdS nanoparticles and PVK indicated the block effect of PVK for surface recombination.  
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**Key words:** irradiation; nanocomposites; nanoparticles

## INTRODUCTION

Nanometer-size metal particle/organic polymer composites have attracted considerable interest in recent years because of the advantageous properties of metals and polymers built into them. The composites also exhibit different characteristics than the individual components of the composites. They have a wide range of applications, including electromagnetic interference shielding, heat conduction, static electricity discharge, and conversion of mechanical signals to electrical signals.<sup>1–5</sup>

Several metal/polymer nanocomposites have been prepared with a one-pot synthesis with  $\gamma$  irradiation in aqueous solutions.<sup>6,7</sup> Selvan et al.<sup>8</sup> reported the preparation of gold/polypyrrole nanocomposites by vapor phase polymerization for use in applications in molecular electronics. Huang et al.<sup>9</sup> used an ultraviolet

irradiation technique for the preparation of silver/polyimide nanocomposites.

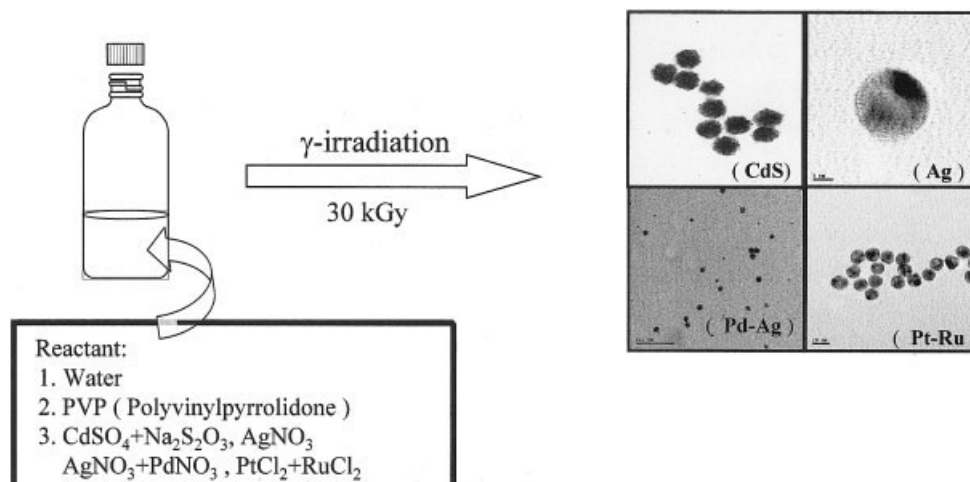
Our research group reported the preparation of silver/polyester and silver/nylon nanocomposites by  $\gamma$  irradiation and the details of characterization.<sup>10</sup> For making antibacterial fibers, silver nanoparticles were dispersed onto polyester and nylon fibers through condensation polymerization. Silver nanoparticles were present as aggregates in the polyester matrix. On the other hand, a uniform dispersion of silver nanoparticles was noticed in a nylon matrix. CdS/polyacrylonitrile nanocomposites were also prepared by  $\gamma$  irradiation and emulsion polymerization.<sup>11</sup> The presence of polyacrylonitrile in the composite provided better thermal stability. However, the composite could not have suitable conductivity for use in applications related to electroluminescence.

We are reporting here the radiolytic preparation of a few nanocomposites with poly(*N*-vinylcarbazole) (PVK) as one component. PVK is a well-known photoconductive polymer possessing a high glass-transition temperature ( $T_g$ ) and good processability,<sup>12</sup> and its use as the host polymer in polymeric photorefractive composites has been well established.<sup>13–15</sup> PVK has been proven to be a good candidate for new-generation high- $T_g$  polymers and can show multifunctional properties for electrooptic and photorefractive

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**Scheme 1** Preparative procedure, using  $\gamma$  irradiation, for CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles.

applications. In this work, composites of PVK with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles were prepared with  $\gamma$  irradiation. The nanoparticles were prepared separately by  $\gamma$  irradiation, and a comparative account of the properties of the composites and nanoparticles was made. The nanoparticles and composites of PVK with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles were characterized by ultraviolet-visible (UV-vis) spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), and photoluminescence (PL) spectroscopy.

## EXPERIMENTAL

### Materials

Cadmium sulfate hydrate (3CdSO<sub>4</sub> · 8H<sub>2</sub>O) and sodium thiosulfate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O) were obtained from Junsei Chemical Co., Ltd. (Kyoto, Japan). Silver nitrate (AgNO<sub>3</sub>; 99.8%) was purchased from Kojima Chemicals Co., Ltd. (Japan). Palladium nitrate (PdNO<sub>3</sub>), H<sub>2</sub>PtCl<sub>6</sub> · xH<sub>2</sub>O (37.5% Pt), RuCl<sub>3</sub> · xH<sub>2</sub>O (41.0% Ru), *N*-vinylcarbazole, and acrylic acid were analytical-reagent-grade (Aldrich-Sigma). Poly(vinylpyrrolidone) (PVP; average molecular weight = 10,000) was obtained from Tokyo Kasei (Japan). Other chemicals of reagent grade were also used.

For the preparation of the nanoparticles and nanocomposites, PVP and 2-propanol were used as a colloidal stabilizer and a radical scavenger, respectively. While the composites were being made, acrylic acid was used for dispersing the nanoparticles in the matrix of PVK.

### Radiolytic preparation of PVP-stabilized CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub> and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles

#### PVP-stabilized CdS nanoparticles

Scheme 1 shows the preparative approach for the PVP-stabilized CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub>

nanoparticles with  $\gamma$  irradiation. An aqueous solution consisting of sodium thiosulfate (0.05M) as a sulfur source and cadmium sulfate (0.05M) and PVP was prepared. The solution was irradiated by a Co-60  $\gamma$ -ray source. The yellow precipitate was collected by centrifugation. The precipitate was washed successively with absolute alcohol and distilled water and dried in vacuo at 50°C for 7 h.

#### PVP-stabilized Ag nanoparticles

A solution of AgNO<sub>3</sub> (25.3 g) in 2-propanol (3.3 mL) was prepared. PVP (0.5 g) was added to the AgNO<sub>3</sub> solution and diluted to 500 mL with distilled water. The residual oxygen in the solution was removed via bubbling with pure nitrogen for 30 min, and the solution was irradiated with a Co-60  $\gamma$ -ray source.

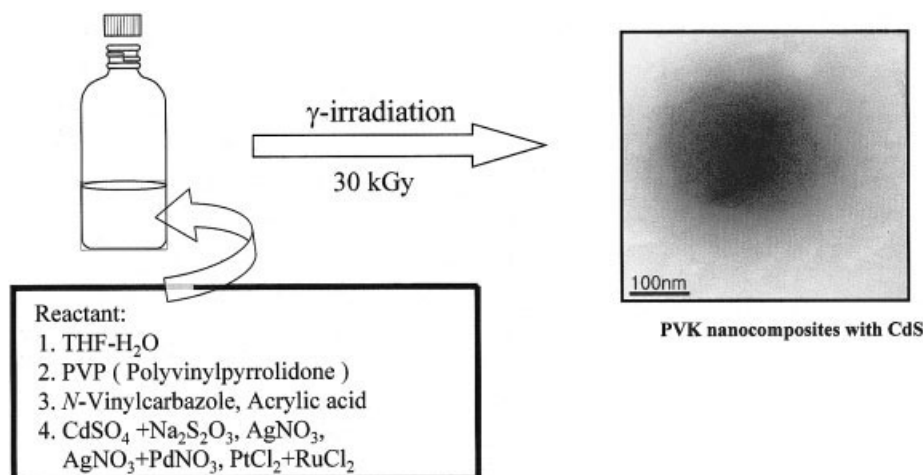
#### PVP-stabilized Pd<sub>50</sub>-Ag<sub>50</sub> and Pt<sub>50</sub>-Ru<sub>50</sub> alloy nanoparticles

The alloy nanoparticles (Pd<sub>50</sub>-Ag<sub>50</sub>) were prepared as follows: PdNO<sub>3</sub> (43.4 mg, 0.18 mmol) and AgNO<sub>3</sub> (31.4 mg, 0.18 mmol) were dissolved in 200 mL of water. PVP (8.68 mg) and an adequate volume of isopropyl alcohol were added. Nitrogen gas was bubbled through the solution for 30 min to remove oxygen. The solution was then irradiated by  $\gamma$ -rays of a Co-60 source under atmospheric pressure at the ambient temperature. A total irradiation dose of 30 kGy (dose rate =  $1.0 \times 10^4$  Gy/h) was used. Pt<sub>50</sub>-Ru<sub>50</sub> alloy colloids were prepared with a similar procedure. Dark brown colloids were obtained in both cases.

### Radiolytic preparation of the PVK nanocomposites with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles

#### PVK nanocomposites with CdS nanoparticles

Scheme 2 describes the preparation procedure for the PVK nanocomposites with CdS. A solution (200 mL)



**Scheme 2** Preparative procedure, using  $\gamma$  irradiation, for PVK nanocomposites with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles.

with sodium thiosulfate (0.77 g) as a sulfur source, cadmium sulfate (0.68 g), *N*-vinylcarbazole (0.84 g), acrylic acid (0.30 g), and PVP was prepared in a tetrahydrofuran (THF)-water mixture (1/3 vol %). The solution was irradiated by a Co-60  $\gamma$ -ray source. A yellow powder was collected after centrifugation of the  $\gamma$ -ray-irradiated solution, sequential washing with absolute alcohol and water, and drying in vacuo at 50°C for 7 h.

#### PVK nanocomposites with Ag nanoparticles

A solution with AgNO<sub>3</sub> (0.34 g), *N*-vinylcarbazole (0.84 g), acrylic acid (0.30 g), and PVP (1.0 g) was prepared in a THF-water mixture (3/1 vol %, 200 mL). Nitrogen gas was purged for 30 min through the solution, and the solution was then subjected to irradiation by a Co-60  $\gamma$ -ray source (Co-60  $\gamma$ -ray irradiator).

#### PVK nanocomposites with Pd<sub>50</sub>-Ag<sub>50</sub> alloy nanoparticles

PdNO<sub>3</sub> (0.22 g), AgNO<sub>3</sub> (0.16 g), *N*-vinylcarbazole (0.84 g), acrylic acid (0.3 g), and PVP (1.0 g) were dissolved in a THF-water mixture (200 mL). After nitrogen gas was passed for 30 min, the solution was irradiated by  $\gamma$ -rays of a Co-60 source under atmospheric pressure at the ambient temperature. A total irradiation dose of 30 kGy (dose rate =  $1.0 \times 10^4$  Gy/h) was used.

#### PVK nanocomposites with Pt<sub>50</sub>-Ru<sub>50</sub> alloy nanoparticles

H<sub>2</sub>PtCl<sub>6</sub> · xH<sub>2</sub>O (0.22 g), RuCl<sub>3</sub> · xH<sub>2</sub>O (0.16 g), and PVP (1.0 g) were dissolved in 200 mL of a THF-water mixture solution. After the removal of the dissolved

oxygen from the solution by the passage of nitrogen for 30 min, the solution was irradiated by  $\gamma$ -rays of a Co-60 source (total irradiation dose = 30 kGy with dose rate =  $1.0 \times 10^4$  Gy/h) under atmospheric pressure at the ambient temperature.

#### Characterization

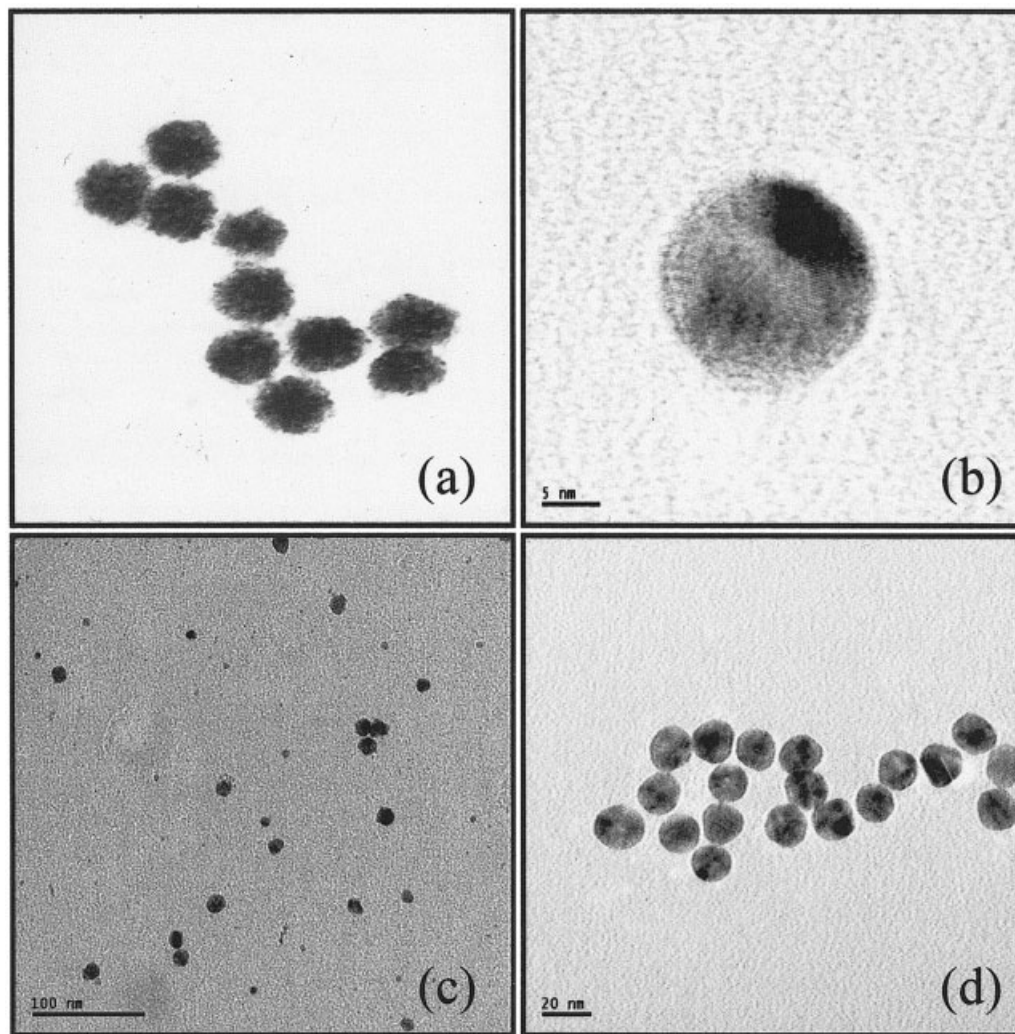
The absorption spectrum of the PVP-stabilized CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles and PVK nanocomposites with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles were recorded with a Shimadzu UV-240 UV-vis spectrophotometer (Tokyo, Japan) with quartz cells. TEM photographs of the samples were recorded with an energy-filtered transmission electron microscope (EM 912 Omega, Carl Zeiss, Oberkochen, Germany) installed at the Korea Basic Science Institute. The PL spectra were recorded with a Shimadzu model RF-5301PC spectrofluorometer at an excitation wavelength of 270 nm.

## RESULTS AND DISCUSSION

### Radiolytic preparation of PVP-stabilized CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> colloids and their characterization

Figure 1 shows the TEM images of CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles prepared by  $\gamma$  irradiation in the presence of PVP as a colloidal stabilizer. Spherical CdS nanoparticles with a uniform size were formed [Fig. 1(a)]. However, much smaller particles aggregated into secondary particles because of their much smaller dimensions and higher surface energy. This limited the precise determination of the size and size distribution of the particles by the simple viewing of the TEM image [Fig. 1(a)]. On the other hand, 5-nm Ag nanoparticles with a uniform size distribution



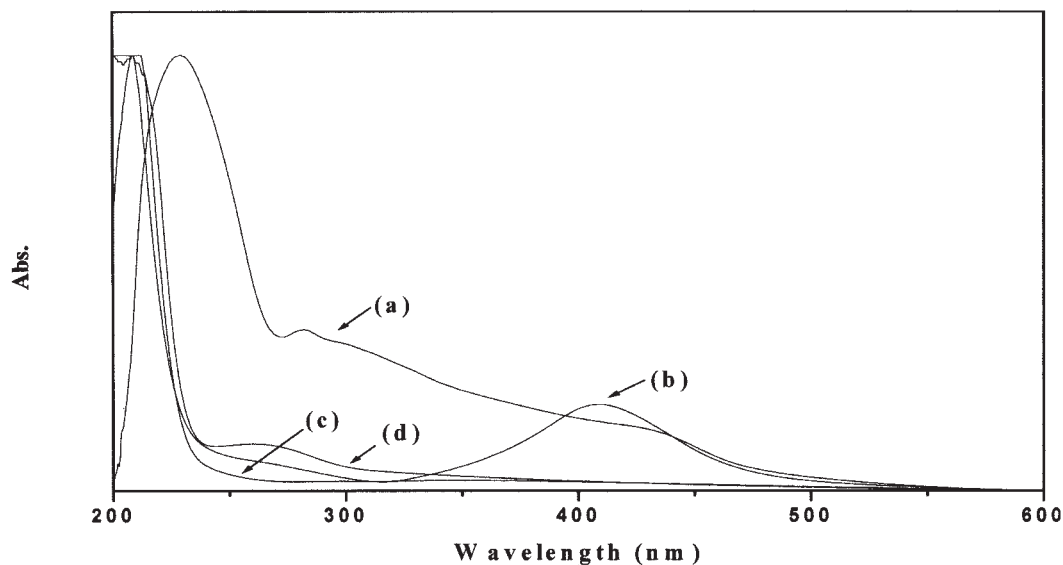


**Figure 1** TEM images of PVP-protected (a) CdS, (b) Ag, (c) Pd<sub>50</sub>-Ag<sub>50</sub>, and (d) Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles prepared by  $\gamma$  irradiation.

were obtained by  $\gamma$  irradiation [Fig. 1(b)]. The mechanism of the formation of Ag nanoparticles with  $\gamma$  irradiation has been described elsewhere.<sup>10</sup> The precursors of the bimetallic nanoparticles of Pd<sub>50</sub>-Ag<sub>50</sub> were PdNO<sub>3</sub> and AgNO<sub>3</sub> salts with an equal molar ratio. A TEM image of bimetallic Pd<sub>50</sub>-Ag<sub>50</sub> nanoparticles [Fig. 1(c)] indicates that particles of different sizes on the nanometer scale were present. However, in the case of Pt<sub>50</sub>-Ru<sub>50</sub> alloy nanoparticles, uniform-size particles were formed with a narrow size distribution [Fig. 1(d)]. PVP-stabilized Pt<sub>50</sub>-Ru<sub>50</sub> alloy nanoparticles have found applications as catalysts for methanol electrooxidation; an indirect methanol fuel cell is known.<sup>16-18</sup>

Figure 2 shows the UV-vis spectra of the PVP-stabilized CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> colloids prepared by  $\gamma$  irradiation in an aqueous solution. The blueshifted absorption onset [Fig. 2(a); <500 nm] for the solution of CdS nanoparticles from the CdS nanocrystals (512 nm) shows that there could be a quantum

confinement effect.<sup>19,20</sup> This may be due to the smaller size of the nanoparticles, as evident from the TEM images [Fig. 1(a)]. Another interesting feature in the absorption spectra of PVP-stabilized CdS colloids [Fig. 2(a)] is the redshifting in the peak position (ca. 250 nm) corresponding to PVP. This could be evident from a comparison of the absorption spectra of Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> colloids [Fig. 2(b-d)]. For the colloids of Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub>, there was no shift in the absorption peak corresponding to PVP. A probable reason for the redshifting in the peak position of the stabilizer for the PVP-stabilized CdS nanoparticles may be the interaction between metal sulfide nanoparticles and the groups in the backbone of PVP. The protective capabilities of PVP through interactions with N atoms or C=O groups have been recently reported.<sup>21</sup> In PVP-stabilized Ag colloids, a characteristic absorption peak appeared at 400 nm [Fig. 2(b)]. UV-vis absorption has been proven to be a sensitive method for the detection of colloidal silver



**Figure 2** UV-vis spectra of PVP-stabilized (a) CdS, (b) Ag, (c) Pd<sub>50</sub>-Ag<sub>50</sub>, and (d) Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles prepared by  $\gamma$  irradiation.

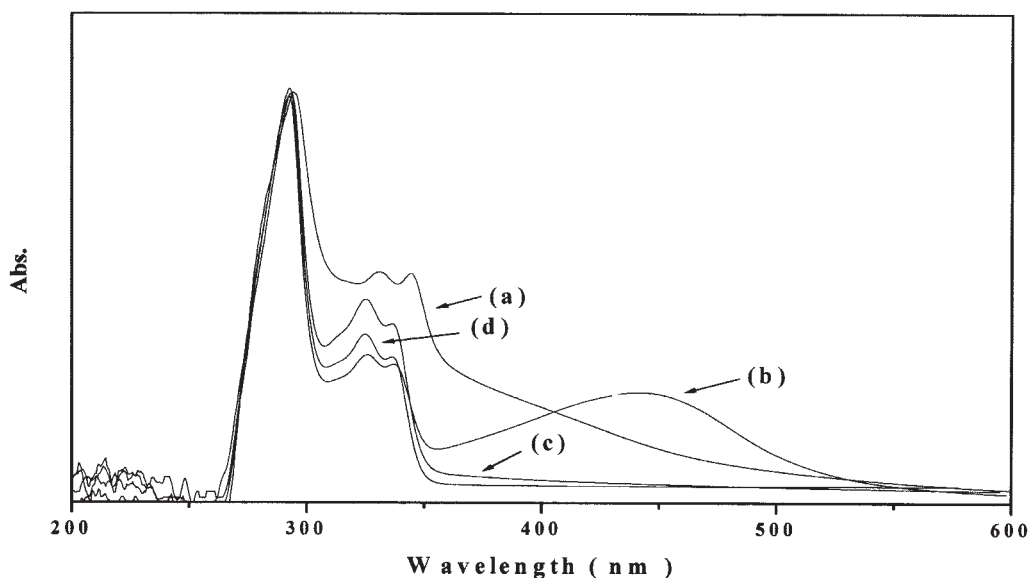
because silver nanoparticles exhibit a characteristic absorption peak at about 400 nm that can be attributed to surface plasmon excitation.<sup>22-24</sup> Pd<sub>50</sub>-Ag<sub>50</sub> and Pt<sub>50</sub>-Ru<sub>50</sub> alloy colloids did not show any absorption characteristics in the visible region.

#### Radiolytic preparation of PVK nanocomposites with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles and their characterization

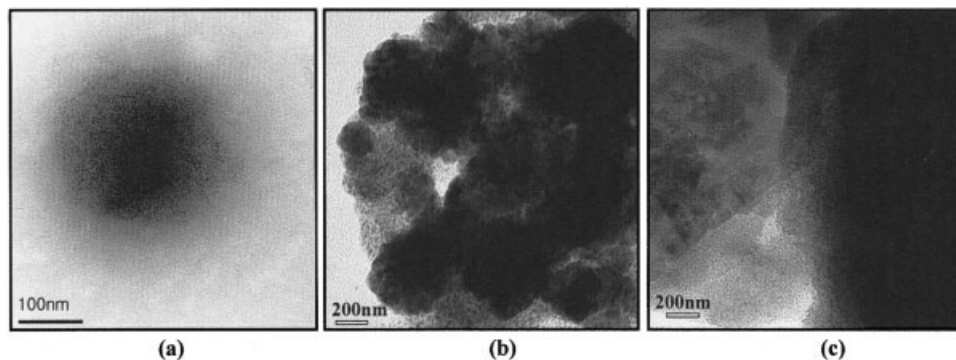
Before composites with PVK were made, the possible formation of copolymers was checked by  $\gamma$  irradiation. Copolymers up to a yield of ~90% could be obtained

for various ratios of *N*-vinylcarbazole to acrylic acid in the presence of PVP as a colloidal stabilizer. *N*-Vinylcarbazole and acrylic acid with a molar composition of 1/1 mol % were selected for preparing PVK nanocomposites with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles.

Figure 3 shows the UV-vis spectra of the PVK nanocomposites with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles. In Figure 3(a), for the PVK nanocomposites with CdS nanoparticles, additional absorption peaks around 270 and 350 nm could be seen corresponding to the presence of the PVK copolymer. Be-



**Figure 3** UV-vis spectra of PVK-stabilized (a) CdS, (b) Ag, (c) Pd<sub>50</sub>-Ag<sub>50</sub>, and (d) Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles prepared by  $\gamma$  irradiation.



**Figure 4** TEM images of PVK nanocomposites with (a) CdS, (b) Pd<sub>50</sub>-Ag<sub>50</sub>, and (c) Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles prepared by  $\gamma$  irradiation.

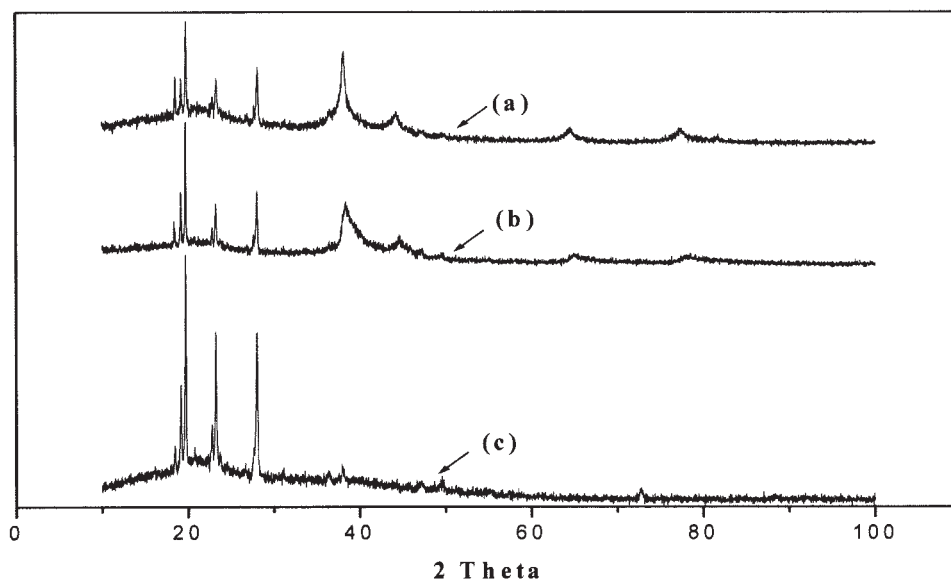
sides that, a quantum confinement effect also could be seen through the blueshifted onset of absorption.<sup>19,20</sup> This may again be considered due to the smaller size of the nanoparticles as witnessed from a TEM image [Fig. 1(a)]. For the PVK nanocomposite with Ag nanoparticles, a significant shift in the surface plasmon excitation peak [Fig. 3(b)] could be noticed, and this was probably due to the covering of the Ag nanoparticles with PVK.<sup>22–24</sup> The absorption peaks in the range of 300–500 nm of PVK were very much suppressed for the nanocomposites of PVK with Pd<sub>50</sub>-Ag<sub>50</sub> and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles. The origin of the suppression of the peaks is not known.

Figure 4 shows TEM images of the PVK nanocomposites with CdS, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles. The particles of the PVK nanocomposites with CdS were spherical and uniform. The precise size determination was hindered by the presence of aggregates. In Figure 4(b,c), we can see that the Pd<sub>50</sub>-Ag<sub>50</sub>

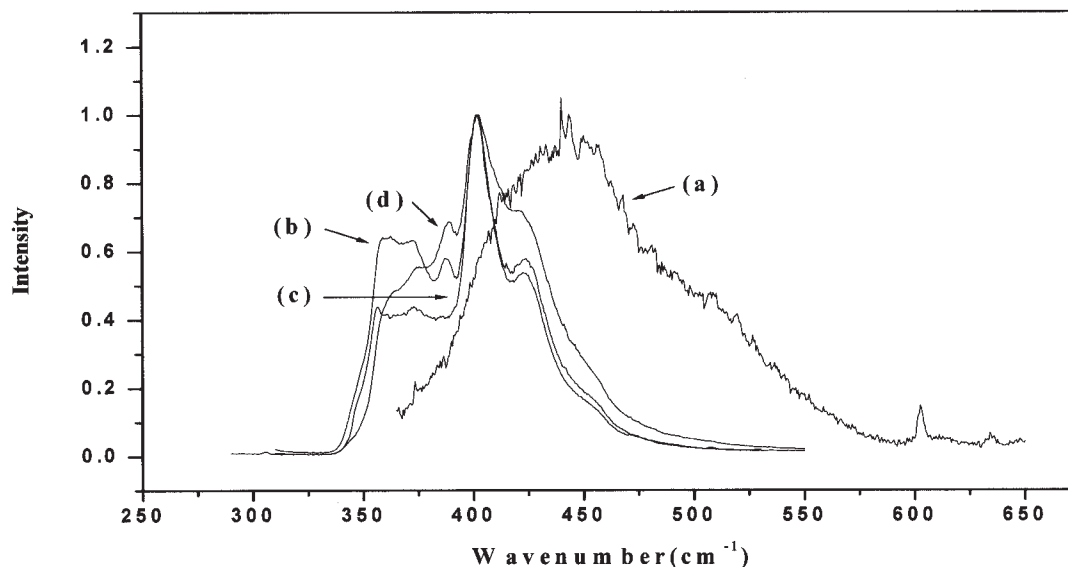
and Pt<sub>50</sub>-Ru<sub>50</sub> alloy nanoparticles were homogeneously dispersed in the matrix of PVK.

In a previous report on the XRD analysis of CdS nanoparticles and CdS/PAN nanocomposites,<sup>11</sup> the average size of the CdS nanoparticles was determined with the Scherrer equation.<sup>25</sup> However, in this study, the data from the XRD analysis for the PVP nanocomposites with Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles could not be used to determine the size of the particles. However, the XRD patterns showed crystalline regions for the composites (Fig. 5).

Figure 6 shows the PL spectra of the PVK nanocomposites with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles prepared by  $\gamma$  irradiation. Recently, studies on the charge carrier transport in PVK : CdS quantum dot hybrid nanocomposites have been conducted.<sup>26</sup> The photoconductive composites obtained by the doping of PVK with semiconductor nanoparticles exhibited not only increased photoconductivity due to sen-



**Figure 5** XRD patterns of PVK nanocomposites with (a) Ag, (b) Pd<sub>50</sub>-Ag<sub>50</sub>, and (c) Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles prepared by  $\gamma$  irradiation.



**Figure 6** PL spectra of PVK nanocomposites with (a) CdS, (b) Ag, (c) Pd<sub>50</sub>-Ag<sub>50</sub>, and (d) Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles prepared by  $\gamma$  irradiation.

sitization of photocharge generation but also the presence of nanoparticles leading to a distinct increase in the effective mobility of the charge carriers. We made PVK nanocomposites with CdS by a one-pot synthesis with a radiation method. Nanosized CdS had two emission peaks at 540 and 470 nm. The former was attributed to the recombination of charge carriers immobilized in traps of different energies, whereas the latter originated from exciton transition. For the PVK nanocomposite with CdS, a blueshift in the exciton and recombination peaks was noticed [Fig. 6(a)]. We presume that the blueshift for the recombination or near-band recombination peak may be due to the block effect of PVK present in the composite. However, the PL spectra of the PVK nanocomposites with Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles predominantly showed emission characteristics around 350–450 nm due to the PVK copolymer.

## CONCLUSIONS

A simple one-pot synthesis, using a radiation method, was effectively used for the preparation of PVK nanocomposites with CdS, Ag, Pd<sub>50</sub>-Ag<sub>50</sub>, and Pt<sub>50</sub>-Ru<sub>50</sub> nanoparticles. The existence of the metal or alloy particles on the nanometer scale in the composites based on PVK adds scope for generating newer materials with tunable luminescent and electronic properties.

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