

Radiolytic synthesis of Pd-M (M=Ag and Ni) and Pt-M (M=Ru and Ni) alloy colloids

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Abstract—Pd-M (M=Ag and Ni) and Pt-M (Ru and Ni) alloy colloids were successfully prepared in aqueous solution by γ -irradiation using poly(vinylpyrrolidone), PVP, as stabilizer. The PVP-stabilized Pd-M and Pt-M nanoparticles were characterized by UV-Vis spectroscopy, Transmission Electron Microscopy (TEM) and Electrophoretic Light Scattering (ELS) analysis. The influence of molecular size of the PVP on the size and size distribution of the alloy nanoparticles was followed. Pd-Ag nanoparticles were formed by employing PVP with different molecular weights. The size of Pd-Ag alloy nanoparticles was determined by TEM photograph and ELS spectra, respectively. From the TEM photographs, the average diameter of Pd-Ag nanoparticles does not show strong dependence on the molecular weight of the PVP. On the other hand, the average diameter of Pd-Ag alloy colloids prepared by PVP with Mw=40,000 was consistently larger than that of Pd-Ag alloy colloids prepared by PVP with Mw=10,000. A plausible scheme is given to explaining this. The size and size distribution of Pt-M (Ru and Ni) alloy colloids are presented.

Key words: γ -Irradiation, Pd-Ag Alloy Colloids, Pd-Ni Alloy Colloids, Pt-Ru Alloy Colloids, Pt-Ni Alloy Colloids, Poly(vinylpyrrolidone)

INTRODUCTION

Nanoparticles offer higher catalytic efficiency per grams than larger sized materials due to their large surface-to-volume ratios. The field of nano-catalysis has been very active and numerous review articles have been published [Neiman et al., 2001; Henglein et al., 1988; Mandal et al., 2001; Chung et al., 2003] during the past decade on heterogeneous catalysts. Preparation and characterization aspects of the heterogeneous catalysts with nanoparticles supported on solid surface as well as in the colloid states have been reviewed [Neiman et al., 2001; Henglein et al., 1988; Mandal et al., 2001; Chung et al., 2003].

From the catalysts' point of view, bimetallic nanoparticles showed superiority over monometallic nanoparticles due to their improved catalytic activities. They also exhibit newer properties that the monometallic catalysts may not have [Chung et al., 2004; Izgaliev et al., 2004].

Studies have been directed to the preparation of monometallic and bimetallic colloids in aqueous solution in the presence of stabilizer using chemical reducing agents. The preparation of the nanocomposite became possible as the precursor metallic salts have good/enough solubility in aqueous systems [Galo et al., 2000; Remita et al., 1999].

In our previous reports [Choi et al., 2003, 2004], we described the preparation of a few precious metallic nanoparticles by γ -irradiation without having any added reducing agent. The precious metallic nanoparticles were formed by hydrated electrons generated

by γ -irradiation in aqueous solution [Choi et al., 2003, 2004]. However, studies on the preparation of Pd-Ni, Pt-Ru, and Pt-Ni alloy colloids in the presence of polymeric stabilizer have not been reported so far.

We report here the preparation of poly(vinylpyrrolidone), PVP, stabilized Pd-M (M=Ag and Ni) and Pt-M (M=Ru and Ni) alloy colloids by using γ -irradiation in aqueous solution. The Pd-M and Pt-M alloy colloids were characterized by UV spectroscopy, Transmission Electron Microscopy (TEM) and Electrophoretic Light Scattering (ELS) Spectrometry. The results on the size and size distribution of PVP-stabilized Pd-M and Pt-M alloy colloids are discussed.

EXPERIMENTAL

1. Materials

PdNO₃, H₂PtCl₆·xH₂O (37.5% Pt), RuCl₃·xH₂O (41.0% Ru), NiNO₃ and NiCl₂ were analytical reagent grade and supplied by Aldrich-Sigma Co. AgNO₃ was purchased from Kojima Chemicals Co., Ltd. (Japan). PVP samples (*M_w* av. 10,000 and 40,000) were obtained from Tokyo Kasei (Japan). Other chemicals of reagent grade were also used.

2. Preparation of PVP-Stabilized Pd-M (M=Ag and Ni) and Pt-M (M=Ru and Ni) Alloy Colloids by γ -Irradiation

The typical procedure for the preparation of Pd-Ag alloy colloids is as follows: PdNO₃ (43.4 mg, 0.18 mmol), AgNO₃ (31.4 mg, 0.18 mmol) and PVP (8.68 mg) were dissolved in 200 mL of distilled water. Nitrogen was bubbled through the solution for 30 min to remove oxygen. The solution was irradiated by γ -ray of Co-60 source under atmospheric pressure and ambient temperature. A total irradiation dose was 30 kGy (a dose rate=1.0×10⁴ Gy/hr) was used.

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Pd-Ni, Pt-Ru, and Pt-Ni alloy colloids were prepared with a similar procedure. Pd-M (M=Ag and Ni) and Pt-M (M=Ru and Ni) alloy colloids were dark brown colored.

3. Measurements

The absorption spectra of the PVP-stabilized Pd-M and Pt-M alloy colloids were recorded with UV-240 Shimadzu UV-VIS spectrophotometer using quartz cells. Transmission Electron Microscopy photographs of the samples were recorded by using Energy Filtered Transmission Electron Microscope (EF-TEM, EM 912 Omega, Carl Zeiss, Germany) installed at the Korea Basic Science Institute, Korea. An Electrophoretic Light Scattering (ELS) spectrophotometer (OTUSKA, ELS-8000) installed at Korea Basic Science Institute, Korea was used to record the ELS spectra of the colloids.

RESULTS AND DISCUSSION

1. Preparation and Characterization of PVP-Stabilized Pd-M (M=Ag and Ni) Alloy Colloids in Aqueous Solution by γ -irradiation

Solutions containing various molar compositions of PdNO₃ and AgNO₃ were irradiated by γ -ray of Co-60 source in an aqueous solution in the presence of PVP as a stabilizer. Dark brown colored homogeneous precious monometallic and bimetallic colloids were obtained. Fig. 1 shows the UV-visible spectra of the PVP-stabilized Pd-Ag alloy colloids prepared for various molar compositions. Interestingly, the alloy colloids, Pd-Ag, show only a band around 266 nm without having significant absorption in the visible region. Also, the characteristic band corresponding to the excitonic plasmon res-

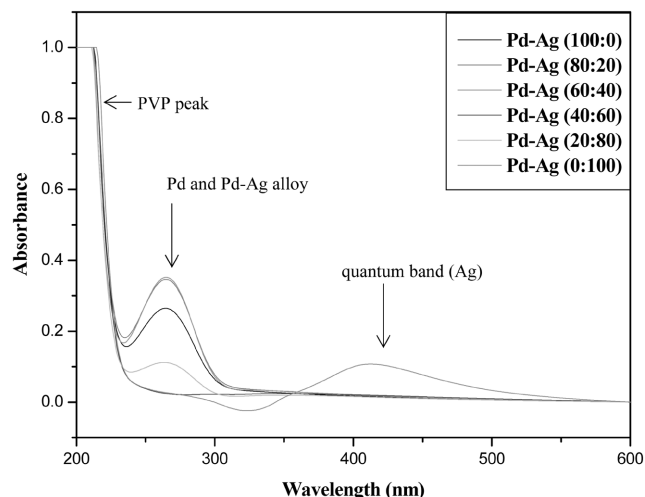


Fig. 1. UV-VIS spectra of PVP-protected Pd-Ag alloy nanoparticles with 100 ppm prepared by γ -irradiation.

onance peak of Ag colloid [Kapoor 1998; Bohren et al., 1983] is not prominent in Pd-Ag colloids. The peak at 266 nm is assigned to the d-d intra band transitions of Pd particles. This assignment finds further support from the UV-visible spectrum of the palladium salt solutions before γ -irradiation. The peak was virtually absent before irradiation.

It is normally expected that the alloy colloids of Pd-Ag should show the bands corresponding to Ag and Pd. In the present study,

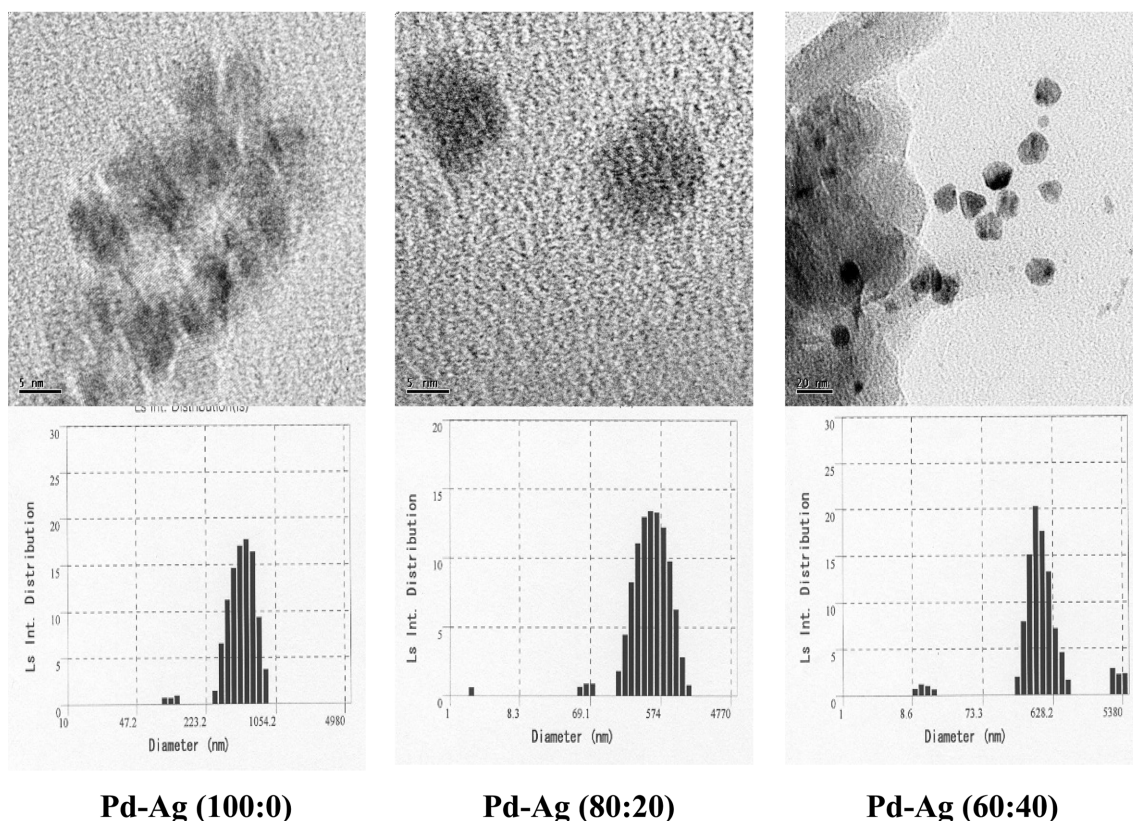


Fig. 2. TEM images and ELS spectra of PVP-protected Pd-Ag alloy nanoparticles prepared by γ -irradiation.

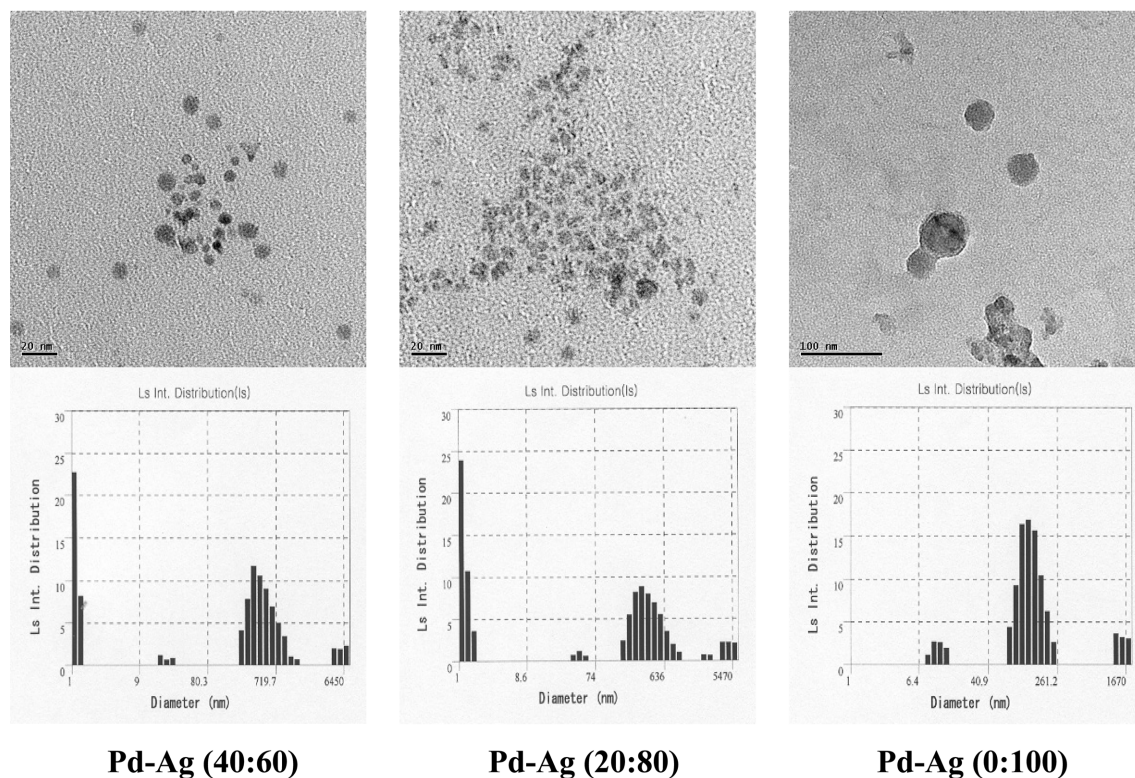


Fig. 3. TEM images and ELS spectra of PVP-protected Pd-Ag alloy nanoparticles prepared by γ irradiation.

the Ag-Pd bimetallic nanoparticles colloid shows no prominent absorption peaks corresponding to Ag plasmon resonance. The presence of a VIII B group element (Pd) in bimetallic nanoparticles generally suppresses the surface absorption plasmon of a I B element (Ag) [Wu et al., 2001; Toshima et al., 1998; Harada et al., 1993; Liu et al., 1992] and therefore no distinct absorption peak was observed in the present case. Similar observations were also reported by others [Torigoe et al., 1993].

Figs. 2 and 3 show TEM images and ELS spectra of the PVP-stabilized Pd-Ag nanoparticles for various molar composition ratios of Pd-to-Ag. TEM images (Fig. 2 and 3) show that uniform sized Pd and Ag nanoparticles were formed by γ -radiation induced reduction of the respective metal ions. ELS spectra (Figs. 2 and 3) indicate that there can be agglomeration of the primary metal particles to form secondary particles. Pd-Ag alloy nanoparticles formed from the molar composition ratios of Pd to Ag as 80 : 20, 60 : 40, 80 : 20 are having uniform size distributions. Larger sized Pd-Ag

alloy particles were formed on increasing the molar proportions of Ag ions. Secondary particles are seen in the TEM images and this probably due to the agglomeration of initially formed smaller nanoparticles by γ irradiation.

Two set of experiments were carried out to find the influence of PVP on the size and size distribution of the Pd-Ag alloy nanoparticles. In the first set, alloy particles were formed with PVP having different molecular weight (M_w =10,000 and 40,000). In another set, alloy particles were formed for various weight ratios (%) of PVP (10, 20, and 50 of metal ions-to-PVP by selecting PVP with a weight average molecular weight of 10,000. TEM and ELS analysis were used to follow the size and size distribution of the nanoparticles, respectively. Interestingly, the information from TEM did not agree with that from ELS. As per the TEM photographs, the average diameters of Pd-Ag nanoparticles do not show strong dependence on the molecular weight of the PVP used during the preparation (Table 1). On the other hand, the average diameter of Pd-Ag alloy colloids

Table 1. Size of the Pd-Ag alloy nanoparticles depending on the precious metal ions-to-PVP^a

	Pd-Ag (100 : 0)			Pd-Ag (80 : 20)			Pd-Ag (60 : 40)			Pd-Ag (40 : 60)			Pd-Ag (20 : 80)			Pd-Ag (0 : 100)		
	10	20	50	10	20	50	10	20	50	10	20	50	10	20	50	10	20	50
Size determined by TEM (nm)	15.2	4.2	4.2	13.3	9.9	5.1	18.3	12.5	5.0	12.0	6.4	4.6	10.0	4.4	4.6	43.2	38.8	24.1
		(4.3)			(7.5)			(7.8)			(4.6)			(5.4)			(36.3)	
Size determined by ELS (nm)	124.9	157.0	251.1	50.7	83.1	195.7	47.9	129.2	177.1	152.7	154.1	247.8	107.8	189.1	330.0	44.6	131.0	169.8
		(414.0)			(348.3)			(393.9)			(410.4)			(331.2)			(209.2)	

^aWeight ratio of the precious metal ions-to PVP was ca. 10, 20, and 50. The PVP stabilizer (M_w =10,000) was used. The parenthesis was used the PVP stabilizer of M_w =40,000.

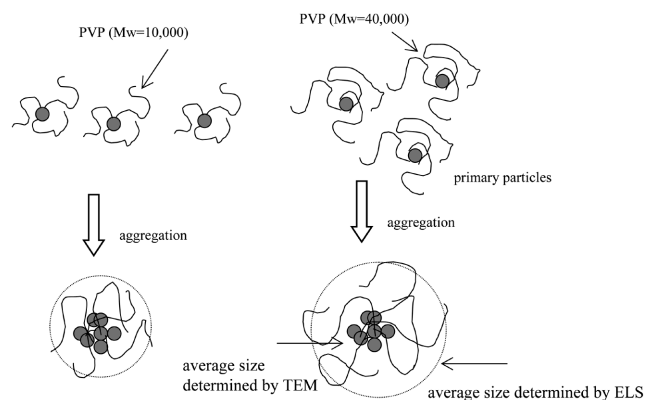


Fig. 4. Aggregation mechanism of the PVP-protected Pd-Ag alloy nanoparticles.

prepared by PVP with Mw=40,000 was consistently larger than that of Pd-Ag alloy colloids prepared by PVP with Mw=10,000. We believe that this discrepancy arises from the difference in viewing the particles between TEM and ELS measurements (Fig. 4). While TEM photographs represent the size obtained by viewing the particles through accessible paths, ELS measurement utilizes a wider area that includes coiled chains of PVP (Fig. 4) to view the particles. In the case of the size determination of the alloy nanoparticles prepared with different weight ratios of PVP, TEM photographs indicate that average size of Pd-Ag alloy colloids decreases with an increasing PVP (Table 1) contents. However, as per the ELS data, an increasing trend for the average size of the Pd-Ag alloy particles could be noticed with increasing weight ratios of PVP. This implies

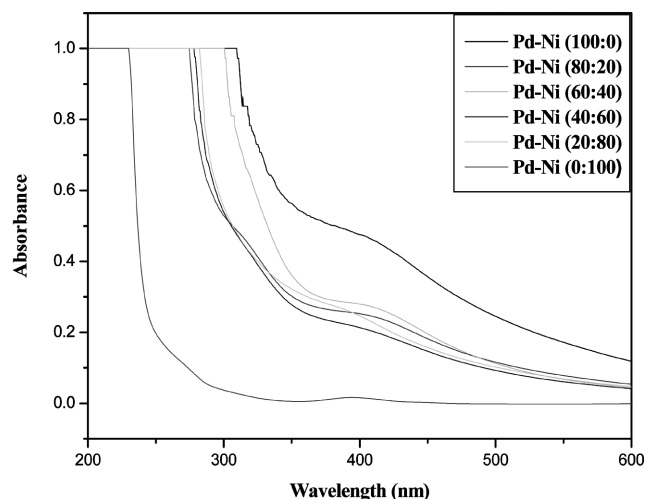


Fig. 5. UV-VIS spectra of PVP-protected Pd-Ni alloy nanoparticles with 1,000 ppm prepared by γ -irradiation.

that the average size of the particles is typically determined by the morphological environment in the presence of the stabilizer (Fig. 4).

Fig. 5 shows the UV-vis spectra of the PVP-stabilized Pd-Ni alloy colloids prepared for various molar compositions of the Pd-to-Ni ions. No obvious peak could be seen for the colloids. However, the intensity of the shoulder around 450 nm showed an increasing trend with increasing the molar composition of Pd ions used for the preparation. This gives a clue for the formation of alloy (Pd-Ni) particles on employing γ -irradiation for the reduction of the combined metal ions.

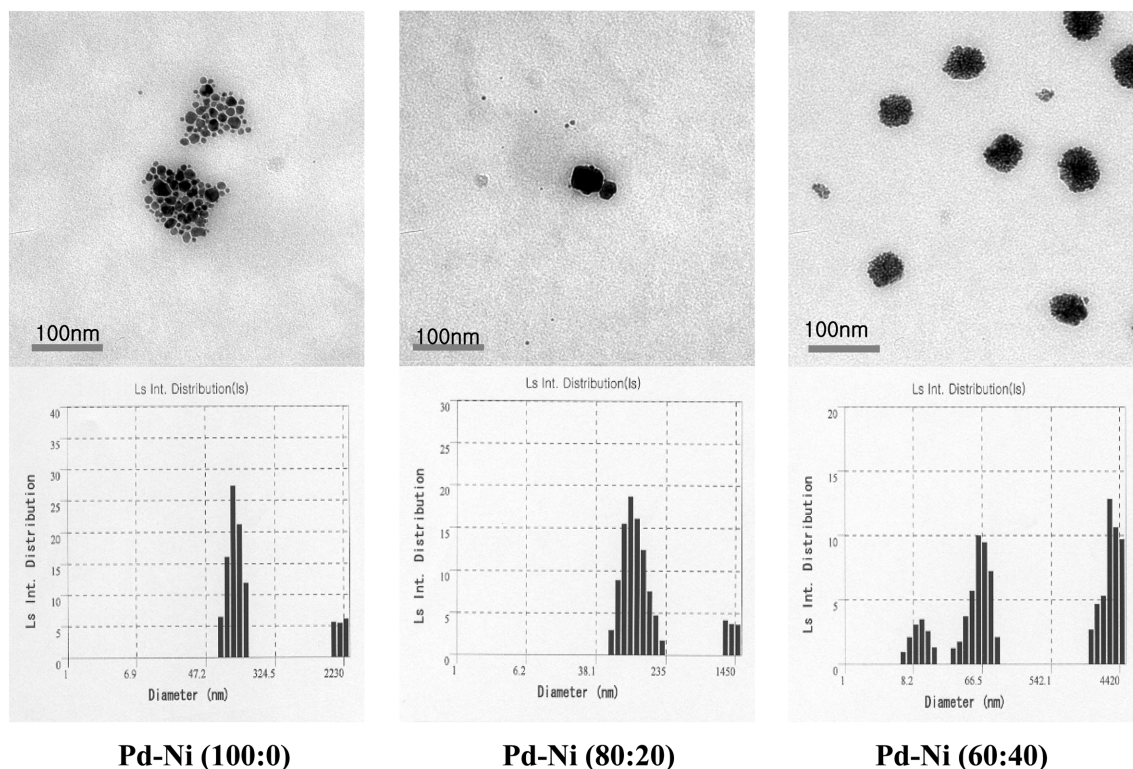


Fig. 6. TEM images and ELS spectra of PVP-protected Pd-Ni alloy nanoparticles prepared by γ -irradiation.

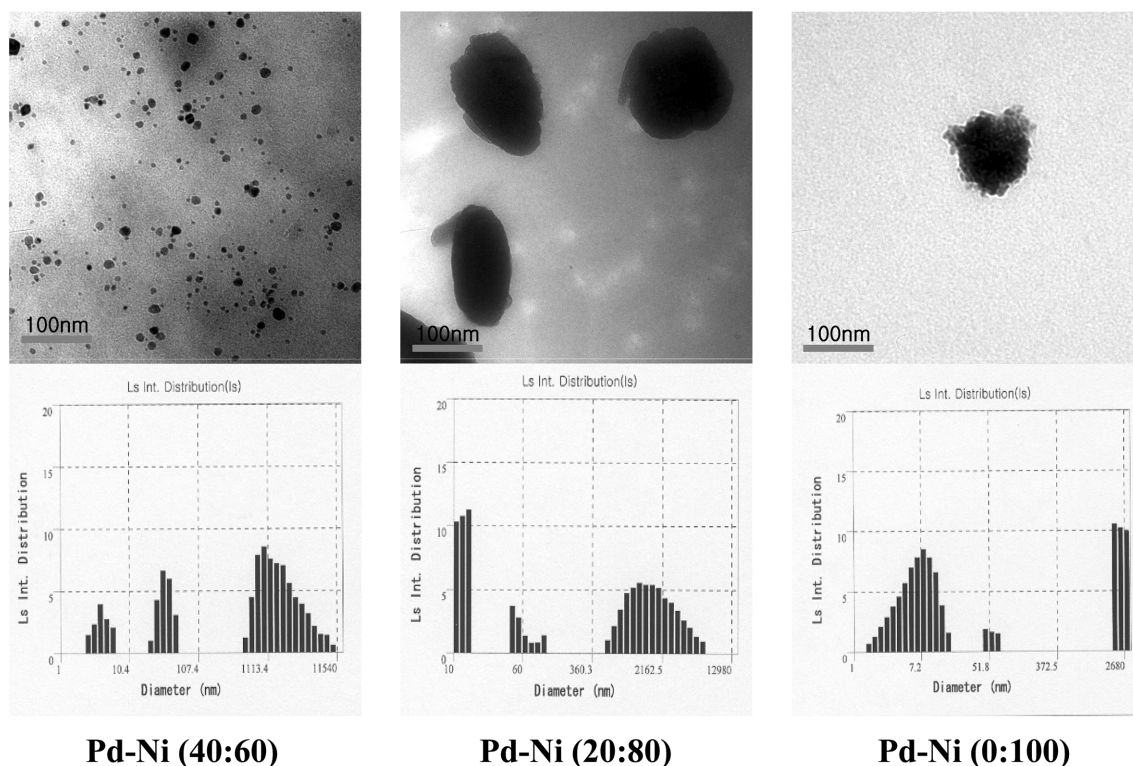


Fig. 7. TEM images and ELS spectra of PVP-protected Pd-Ni alloy nanoparticles prepared by γ -irradiation.

Fig. 6 and 7 show TEM images and ELS spectra of the PVP-stabilized Pd-Ni nanoparticles prepared for the various molar composition ratios of Pd-to-Ni ions. A fixed weight ratio (20%) of metal ions-to-PVP was used for all the cases. An increase in the average size of Pd-Ni alloy nanoparticles could be seen on increasing the molar composition of Ni ions (see, Fig. 6 and 7). ELS data indicates the presence of another particle distribution other than the alloy nanoparticles (Fig. 6 and 7). This may probably be due to the secondary agglomeration of the primary particles after its initial formation through γ -radiation.

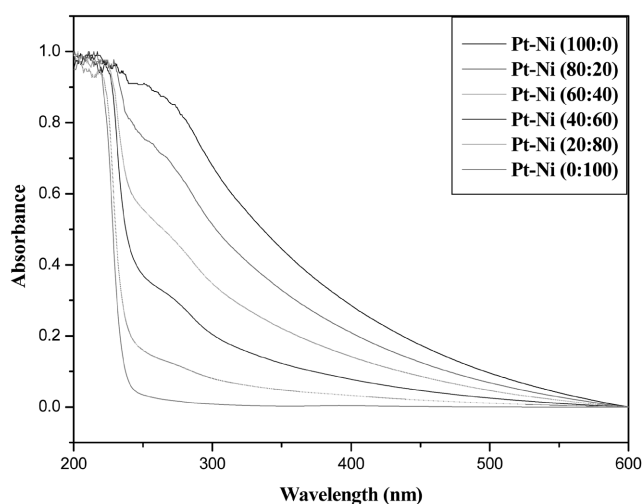


Fig. 8. UV-VIS spectra of PVP-protected Pt-Ni alloy nanoparticles with 1,000 ppm prepared by γ -irradiation.

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2. Preparation and Characterization of PVP-Stabilized Pt-M (M=Ni and Ru) Alloy Colloids in Aqueous Solution by γ -irradiation

Fig. 8 shows the UV-vis spectra of the PVP-stabilized Pt-Ni alloy colloids with various molar compositions of the Pt-to-Ni ions. No prominent peak was observed specific to the alloy nanoparticles. However, a progressive increase in the intensity for the band around 270 nm was noticed with increasing the Pt ions molar ratios.

Fig. 9 and 10 show TEM images and ELS spectra of the PVP-stabilized Pt-Ni nanoparticles with various molar ratios of Pt-to-Ni ions. A uniform distribution in the size of the nanoparticles was noticed. Here again, the formation of secondary particles could be inferred. The PVP-protected Pt-Ru alloy and Pt-Ru/carbon-based composites can be used as catalysts in direct methanol fuel cell [Park et al., 2004; Wei et al., 2004]. The present study uses γ -irradiation for producing the bimetallic colloids in contrast to the previously reported chemical methods.

Fig. 11 and 12 show TEM images and ELS spectra of the PVP-stabilized Pt-Ru nanoparticles with various composition ratios of Pd-to-Ru ions. Though the size distribution of primary particles is uniform, clusters of secondary particles were also formed after the initial nucleation of primary particles.

CONCLUSIONS

Alloy colloids such as Pd-Ag, Pd-Ni, Pt-Ni, and Pt-Ru were successfully prepared by γ -irradiation in aqueous solutions in the presence of PVP as stabilizer. The more coiled configuration of the stabilizer keeps the alloy nanoparticles in deep and tentatively shows higher size for the particles through scattering measurements.

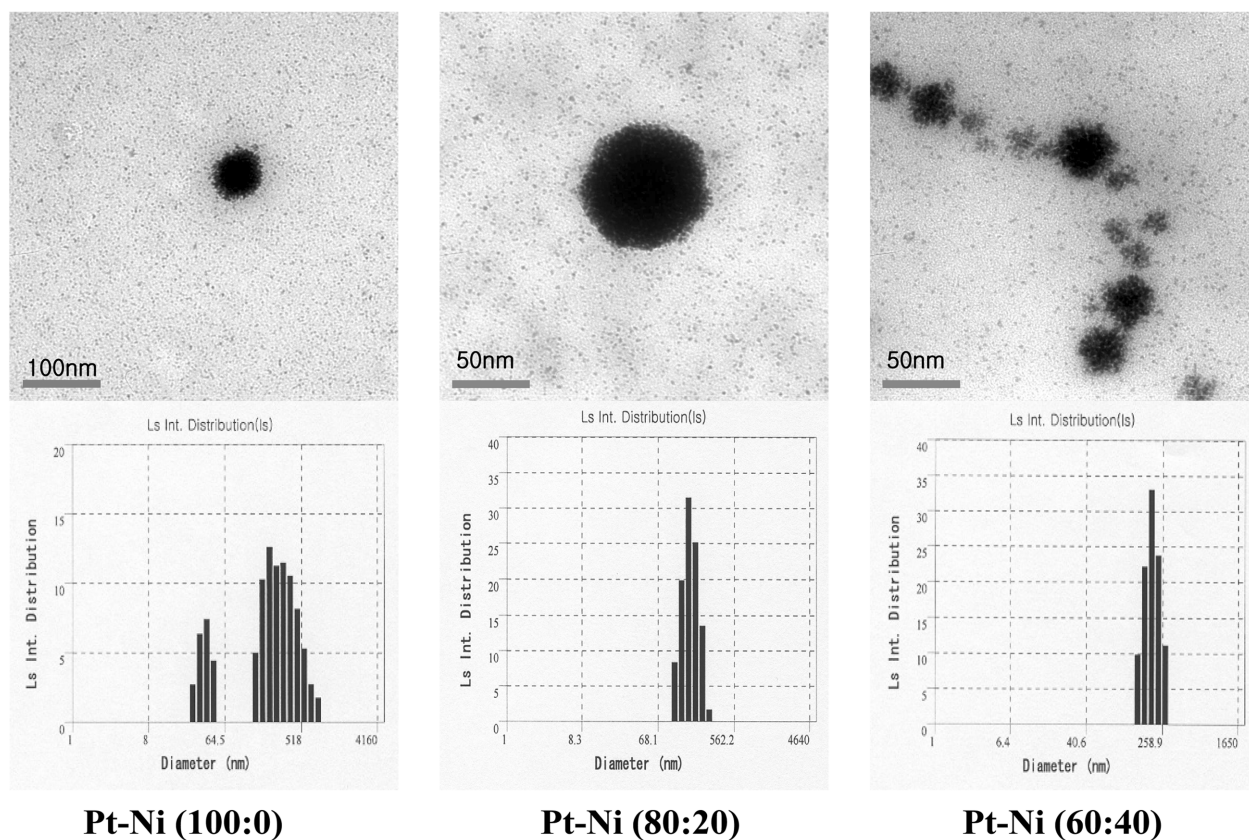


Fig. 9. TEM images and ELS spectra of PVP-protected Pt-Ni alloy nanoparticles prepared by γ irradiation.

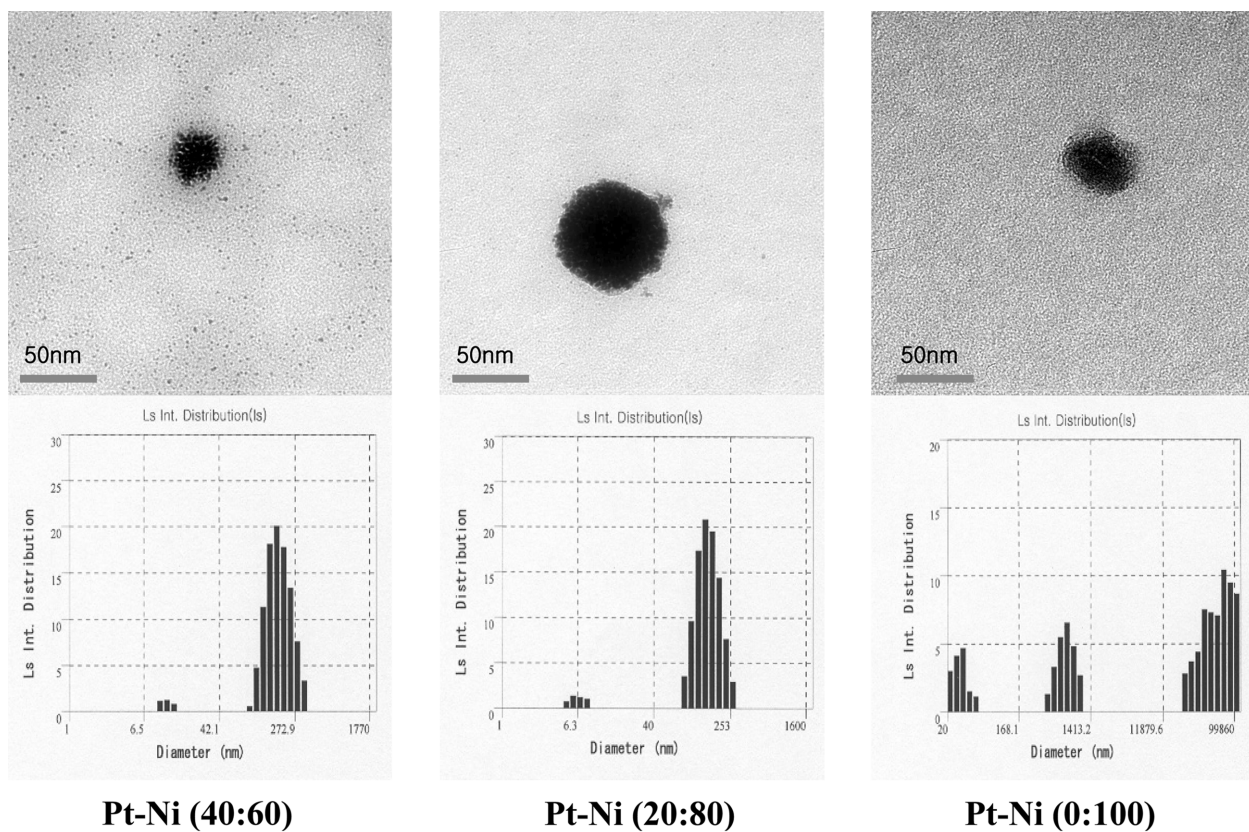


Fig. 10. TEM images and ELS spectra of PVP-protected Pt-Ni alloy nanoparticles prepared by γ irradiation.

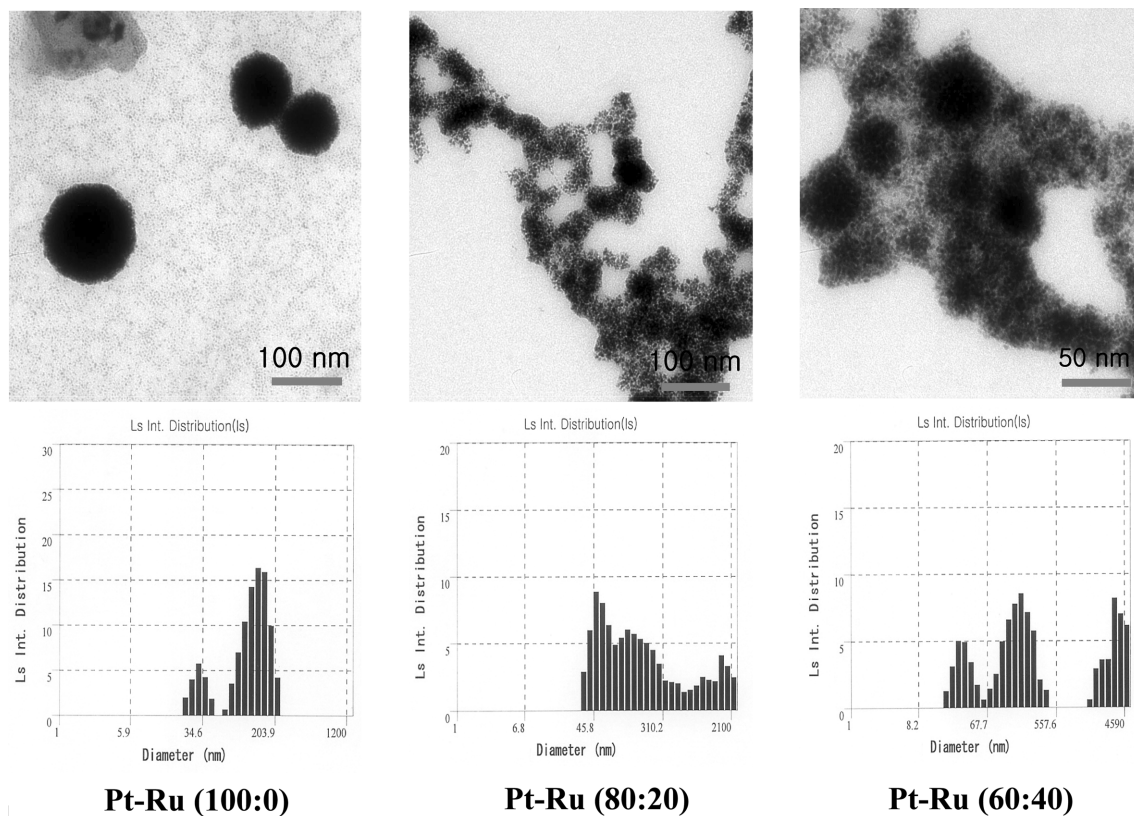


Fig. 11. TEM images and ELS spectra of the PVP-protected Pt-Ru alloy nanoparticles prepared by γ -irradiation.

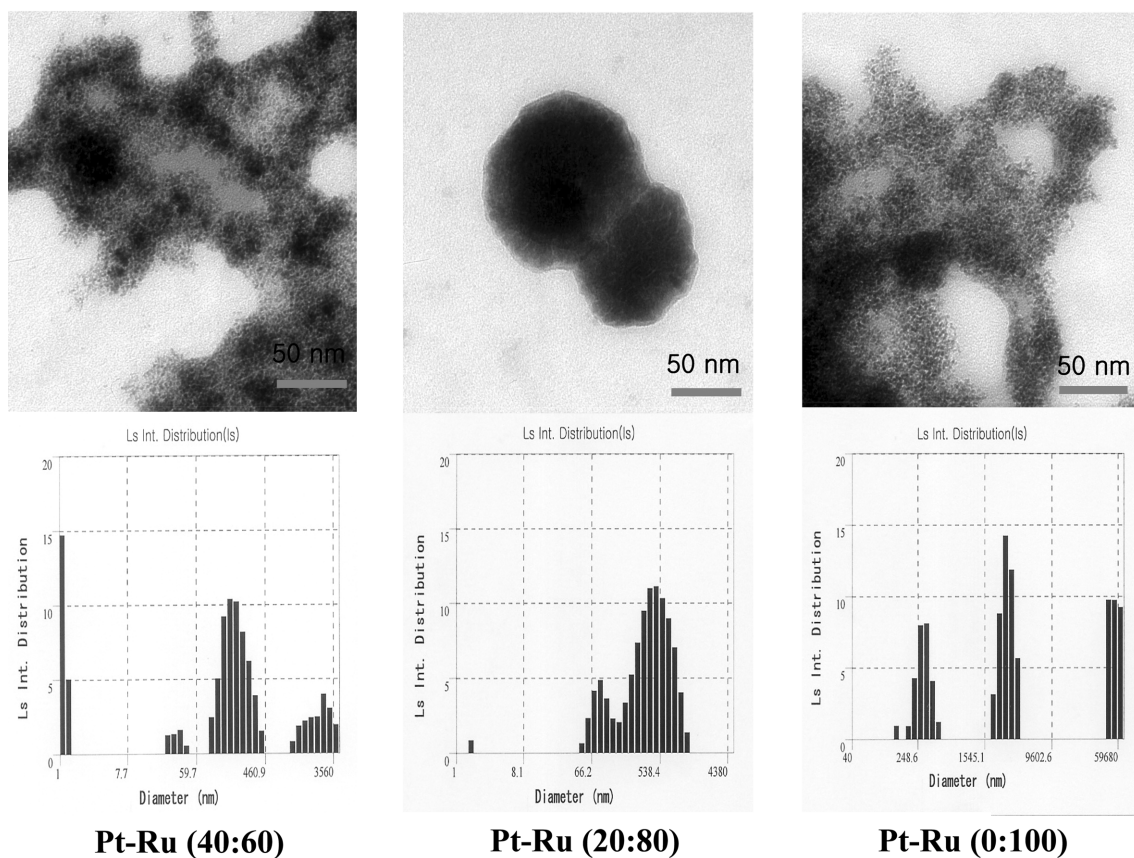


Fig. 12. TEM images and ELS spectra of the PVP-protected Pt-Ru alloy nanoparticles prepared by γ -irradiation.

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