

## Effect of PVP molecular weight and a reducing agent on the preparation of platinum nanoparticles through chemical reduction in ethanol/water

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In this study, we prepared Pt nanoparticles through the reduction of H<sub>2</sub>PtCl<sub>6</sub> solutions containing poly(vinylpyrrolidone) (PVP) as a capping agent and investigated the effects of several reaction parameters, such as the reducing agent-to-Pt molar ratio and the concentration and molecular weight (M<sub>w</sub>) of PVP, on the size, size distribution, and stability of the particles in the resulting Pt colloids. When PVP (M<sub>w</sub> 10,000) was added at a PVP-to-Pt molar ratio of 0.38 in the presence of NaOH, we obtained quasi-spherical nanoparticles having average sizes ranging from 2.0 to 4.0 nm. The particle size increased upon decreasing the molecular weight of PVP; increasing the PVP concentration had only a stabilizing effect. The particle size of the monodisperse Pt nanoparticles, we obtained in the presence of NaOH were larger than those formed in the presence of NaHCO<sub>3</sub>, indicating that the rate reduction of [PtCl<sub>6</sub>]<sup>2-</sup> ions is an important factor influencing the growth of these particles. Furthermore, increasing the reducing agent-to-Pt molar ratio also increased the particle size. To understand their mechanism of formation, we used transmission electron microscopy (TEM) and UV-Vis spectrophotometry to monitor the stabilities and size distributions of the Pt nanoparticles.

**Key words:** Pt nanoparticles, poly(vinylpyrrolidone) (PVP), capping agent, reducing agent, stability, chemical reduction.

### Introduction

The chemical synthesis of nanoparticles of platinum and its alloys has attracted much attention recently because of their potential application as catalysts [1–3]. For example, platinum nanoparticles serve as catalysts for the electrochemical oxidation of carbon monoxide [4], for the elimination of NO generated in combustion processes [2], and in proton-exchange membrane (PEM) fuel cells [5]. In particular, carbon-supported platinum nanoparticles remain the system of choice for use as electrocatalysts in fuel cells [6,7], because of their high electrocatalytic activities for both the oxidation of hydrogen and methanol on the anode and the reduction of oxygen on the cathode. When used as catalysts in fuel cells, the platinum nanoparticles should have small particle sizes and narrow particle size distributions. Consequently, a great deal of effort has been devoted to the development of simple and economical strategies for the preparation of platinum nanoparticles possessing well-controlled sizes and shapes [8–10].

The preparation of Pt nanoparticles through alcohol reduction in the presence of stabilizing agents has been examined widely. Duff et al. reported the synthesis of Pt nanoparticles having sizes in the range 1.5–4 nm in methanol/water mixtures through the methanol reduction

of ionic Pt in the presence of poly(vinylpyrrolidone) (PVP) [11]. Miyake and coworkers reported the preparation of Pt nanoparticles having sizes of 1.7–7.1 nm through alcohol reduction [12]. These methods involve simple operation procedures and ready control over the particle sizes.

Generally, the primary reaction in an alcohol reduction process involves the reduction of the precursor by a polymeric solvent at the boiling point of the solvent, at which temperature the metal ions are transformed into metal atoms. Subsequent nucleation and growth of these reduced metal species in the solution phase provides the metal nanoparticles. In the majority of cases, to allow control over the size of the particles, a polymeric stabilizer is added. In a typical process, ethylene glycol is the solvent and PVP plays the dual roles of polymer stabilizer and reducing agent [13]. Previously, we employed PVP and sodium carbonate to synthesize quasi-silver nanoparticles having diameters of ca. 30 nm through the chemical reduction of silver nitrate [14]. We found that both the Na<sub>2</sub>CO<sub>3</sub>-to-Ag molar ratio and the concentration of PVP affected the reduction rate of Ag<sup>+</sup> ions, which determined the Ag particle size. It was also found that the mechanism through which PVP mediated the formation of these Ag nanoparticles involved three steps: (1) the formation of coordinative bonds between PVP and Ag<sup>+</sup> ions, (2) PVP-promoted nucleation, which tended to produce small Ag particles, and (3) steric shielding of the Ag nanoparticles surfaces through physical and chemical bonding to PVP, which inhibited particle-particle contact and, thus, the agglomeration of particles.

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In this study, we wished to obtain a high concentration of Pt as a colloidal dispersion; thus, we prepared Pt nanoparticles in the presence of the PVP as a stabilizing agent. To enhance the reduction of Pt (IV) species, we used NaOH and Na<sub>2</sub>CO<sub>3</sub> as reducing agents. We characterized the resulting colloidal particles using transmission electron microscopy (TEM) and a UV-visible spectrophotometer. In this paper, we discuss the effect of several reaction parameters, such as concentration and molecular weight of PVP and reducing agent-to-H<sub>2</sub>PtCl<sub>6</sub> molar ratio, on the sizes of the resulting Pt nanoparticles. In addition, we propose a mechanism for the preparation process of Pt nanoparticles.

## Experimental procedure

### Materials

All chemicals used in this investigation were reagent grade materials. Hydrogen hexachloroplatinate (IV) hydrate (H<sub>2</sub>PtCl<sub>6</sub> · nH<sub>2</sub>O n = 5.7, Junsei chemical Co.) was used as a Pt ion source. Polyvinylpyrrolidone (PVP, Kojima Chemical Co.) having molecular weights of 10,000, 29,000 and 40,000, were used as nucleation-prompting agent and stabilizer of the Pt nanoparticles. Sodium hydroxide (99.0%, NaOH, Samchun Pure Chemical Co.) and sodium carbonate (99.0%, Na<sub>2</sub>CO<sub>3</sub>, Samchun Pure Chemical Co.) were used to reduce the Pt ions. The ethanol (Yakuri Pure Chemicals Co.) was used as the reducing agent for Pt ions. The de-ionized water used in this study was double ionized by Eco-RO & UP (Mirae Scientific Technology Co.), having 18.2 MΩ electrical resistivity.

### Preparation of platinum nanoparticles

The colloidal Pt particles were synthesized through reduction in a 200 ml three-neck round flask equipped with a magnetic stirrer bar and a reflux condenser. The composition of each experimental condition mixture is indicated in Table 1. Briefly, the Pt ion solution (45 mMol in deionized water, 13.3 ml) was added under mild stirring to an ethanol/water (50 : 50 wt%) solution containing PVP. After complete mixing, an alkaline solution of either NaHCO<sub>3</sub> or NaOH was then added to

promote the reduction reaction. Pt nanoparticles were formed through the reduction of the Pt ions by PVP under a nitrogen atmosphere when the solution was heated to a given temperature. In a typical process, the reaction was conducted for 24 h at the boiling point of the mixture. The Pt concentration was fixed at 0.1% (w/v) throughout these experiments. After the conclusion of the reaction, a dark brown solution was obtained; it was cooled to room temperature to prevent any further structural change of the Pt nanoparticles.

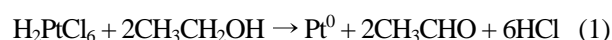
### Characterization

To investigate the formation and the morphological properties of the Pt nanoparticles, transmission electron microscopy (TEM, Jeol-model JEM-2000EX II) was used. Pt particles for observation under the microscope were prepared by placing a drop of the colloidal Pt dispersion onto a standard microscope grid (400-mesh) coated with a carbon film. The size distribution and average particle size of the colloidal Pt and the standard deviation of the particle population were determined from image analyses of the micrographs of these particles.

UV-visible absorption spectra of the colloidal Pt dispersions in ethanol/water (50 : 50 wt.%) were measured using a Shimadzu UV-1650PC double-beam spectrophotometer. All of the samples for the measurements of the UV-visible spectra were diluted except for the samples used to investigate the changes of the UV-visible spectra during the nanoparticle formation.

## Results & discussion

The colloidal Pt nanoparticles were reduced by both ethanol and the reducing agent. The equation for the reduction mechanism by ethanol is described as follows [15]:



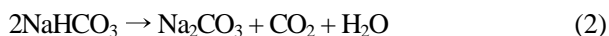
Alcohol reduction is based on a redox reaction between a metallic precursor and the solvent; the rate of reduction of the metal ions at the reflux temperature is greatly influenced by the difference between the oxidation

Table 1. Experimental conditions employed for the preparation of platinum nanoparticle.

Sample	Molecular weight of PVP	PVP concentration (PVP-to-Pt molar ratio)	Reducing agent	Reducing agent-to-Pt molar ratio	Average size [nm]
1	10,000	0.38 M	NaOH	1.96 M	2.0
2	10,000	0.38 M	NaOH	3.92 M	4.0
3	10,000	0.38 M	NaOH	5.89 M	3.8
4	10,000	0.38 M	NaHCO <sub>3</sub>	1.96 M	1.2
5	10,000	0.38 M	NaHCO <sub>3</sub>	3.92 M	2.1
6	10,000	0.38 M	NaHCO <sub>3</sub>	5.89 M	-
7	29,000	0.38 M	NaOH	3.92 M	2.2
8	40,000	0.38 M	NaOH	3.92 M	2.1
9	10,000	0.28 M	NaOH	3.92 M	-
10	10,000	0.47 M	NaOH	3.92 M	3.9

potential of the alcohol and the reduction potential of the metal species. Under ambient conditions, there is a long induction period until sufficient Pt atoms have accumulated as nucleation sites. The reduction period is shortened through heating and increasing the pH of the solution; under such conditions, the agglomeration of atoms may become rate limiting.

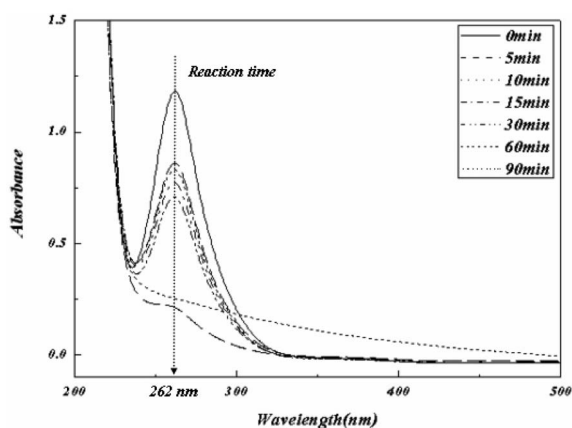
When  $\text{NaHCO}_3$  is used to promote the reduction, it undergoes decomposition as follows [16]:



$\text{NaHCO}_3$  is decomposed into  $\text{Na}_2\text{CO}_3$ ,  $\text{CO}_2$  and water at temperature above ca.  $50^\circ\text{C}$ . After the  $\text{NaHCO}_3$  creates the carbonate ion, the Pt ion would first combine with carbonate ion. As the carbonate ion is hydrolyzed to produce some hydroxyl ions by thermal energy, it starts to reduce Pt ions into Pt particles.

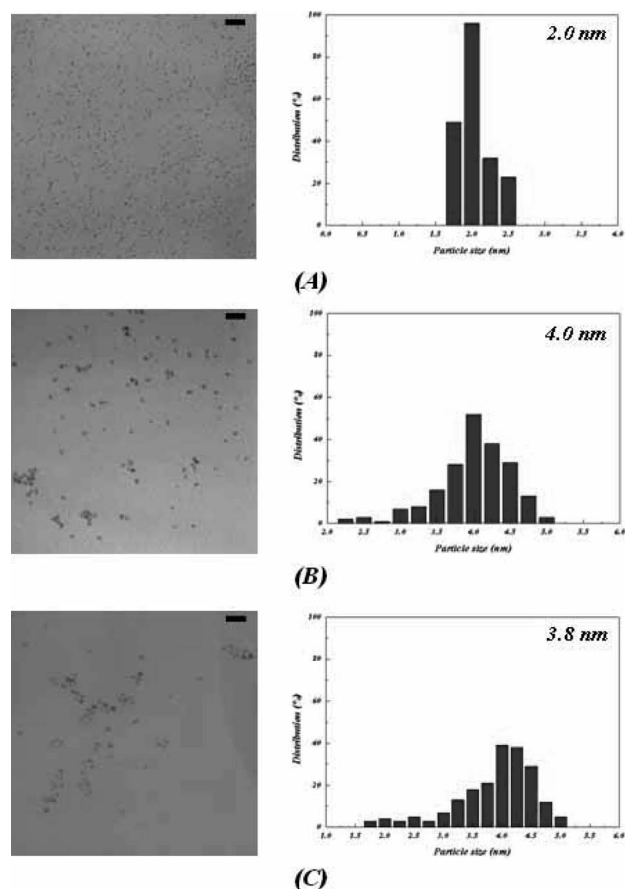
When  $\text{NaOH}$  was added to promote the reduction of Pt ions, the precursor solution quickly turned from pale yellow to a dark color and then gradually became dark brown as the reaction reached completion, similar to the behavior observed when  $\text{NaHCO}_3$  was added. The dark color most likely indicates that the Pt ions were gradually reduced to form fine Pt particles. We used UV-visible spectroscopy to monitor this reduction process through measurement of the time required to complete the evolution of the color of the solution. The solution of hydrogen hexachloroplatinate in ethanol/water was pale yellow; it exhibited a peak at 262 nm in its UV-visible spectrum, reflecting the presence of  $[\text{PtCl}_6]^{2-}$  ions (Figure 1). As the reaction time increased, the intensity of the peak at 262 nm decreased, disappeared within 90 minutes, indicating that the complete reduction of  $[\text{PtCl}_6]^{2-}$  ions according to equations 1 and 2. These UV-visible spectra, which are consistent with the results reported by Duff et al., suggest the formation of Pt nanoparticles [11].

In a previous study, we found that the concentration of the reducing agent greatly influenced the sizes of

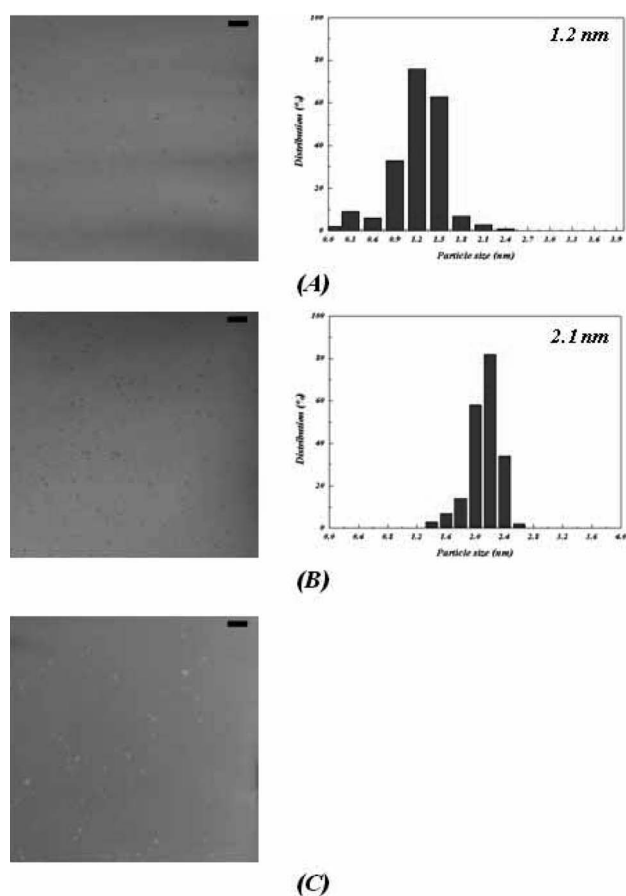


**Fig. 1.** UV-visible spectra of colloidal platinum at various times during the reaction.

PVP-Ag nanoparticles [14]. For the Pt nanoparticles, we sought an appropriate reducing agent and an optimal concentration of it in an attempt to control the rate of reduction of  $[\text{PtCl}_6]^{2-}$  to  $\text{Pt}^0$  and, hence, the particle size. Figs. 2 and 3 display the effect of the reducing agent on the formation of Pt nanoparticles when the reducing agent-to-Pt molar ratio was varied from 3.92 to 7.85. When we reduced Pt ions in the presence of PVP at a reducing agent-to-Pt molar ratio (R) of 1.96, we obtained monodispersed Pt nanoparticles having an average particle size of 2.0 nm. In general, an increase in the concentration of the reducing agent increases the rate of reduction of metal ions, leading to the formation of smaller metal particles in a low concentration of colloidal metal [17]. This phenomenon suggests that the reduction of  $[\text{PtCl}_6]^{2-}$  by the reducing agent produces more Pt nuclei within a shorter period, and that nucleation and growth are separate processes; i.e., a fast rate of reduction of  $[\text{PtCl}_6]^{2-}$  is needed to generate small Pt particles having a narrow size distribution. Figs. 2 and 3 indicate, however, that an increase in the concentration of the reducing agent increased the sizes of the Pt particles. It is possible that the long period of growth of the nuclei led to larger particles because of



**Fig. 2.** TEM images and size distributions of platinum particles prepared in the presence of various amounts of sodium hydroxide (A: sample 1, B: sample 2, C: sample 3, Scale bar: 20 nm).



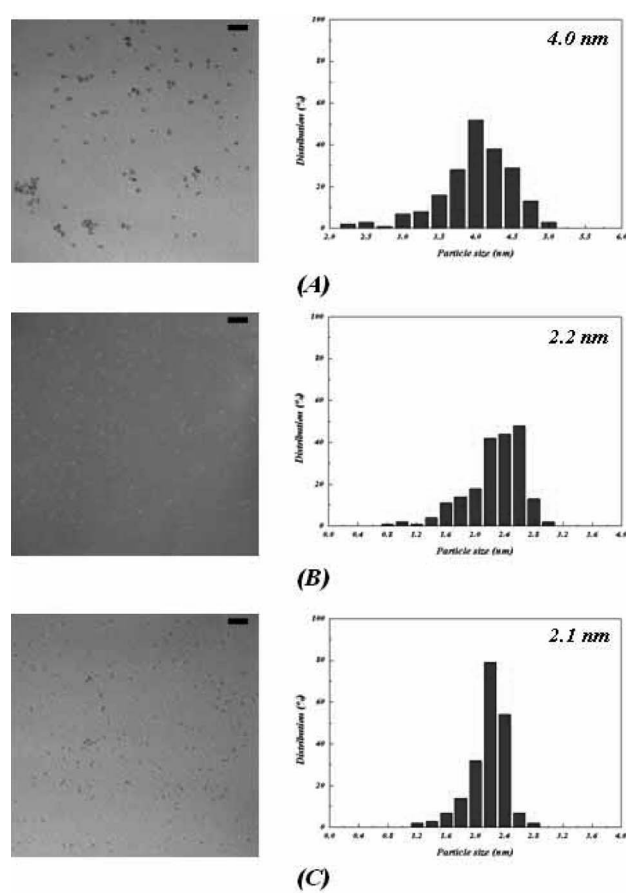
**Fig. 3.** TEM images and size distributions of platinum particles prepared in the presence of various amounts of sodium bicarbonate (A: sample 4, B: sample 5, C: sample 6, Scale bar: 20 nm).

the supply of a large amount of reduced species-atoms and microclusters-caused by the high precursor concentrations. This reaction proceeds through the following process:

1.  $[\text{PtCl}_6]^{2-}$  ions become Pt atoms through reaction with the reducing agent.
2. Aggregation of atoms occurs to form Pt nuclei.
3. A long period growth of Pt nuclei to form Pt nanoparticles by reduced species, atom and microclusters.

For the same reason, upon increasing the value of R to 3.92 and 5.89, the average sizes of the resulting Pt nanoparticles increased to 4.0 and 3.8 nm, respectively. At low values of R (under 1.96), the reduction often did not proceed. Consequently, 1.96 was the optimum value of R at which we obtained the smallest particles in the present reaction system, incorporating Pt at a concentration of 1,000 ppm and PVP at a concentration of 0.38 Mol. On the other hand, although the use of  $\text{NaHCO}_3$  gave smaller particles than did  $\text{NaOH}$ , we observed agglomeration of platinum particles and a lower rate of reduction in the former case.

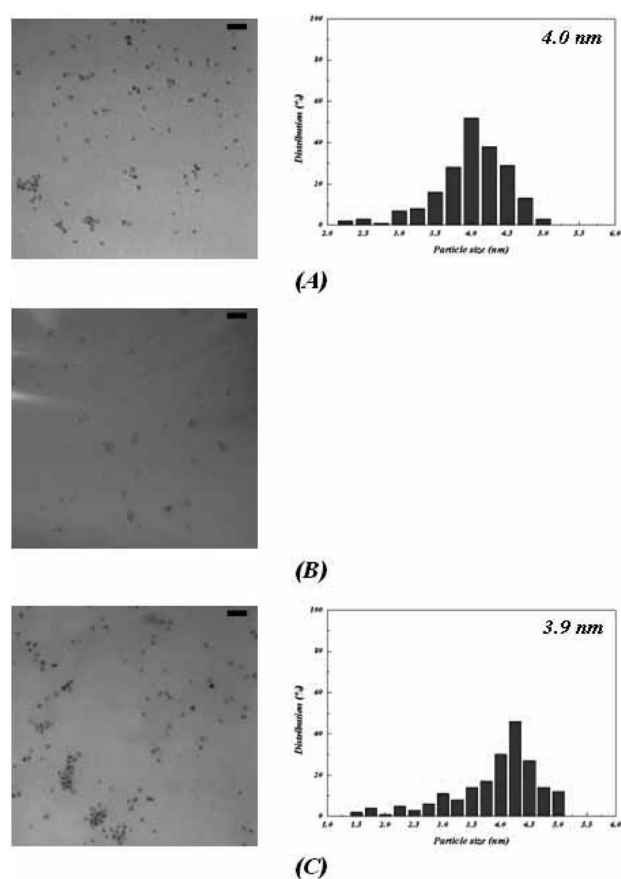
Fig. 4 displays TEM images and size distributions of the Pt nanoparticles prepared using PVP polymers of different molecular weights ( $M_w = 10,000, 29,000,$  and



**Fig. 4.** TEM images and size distributions of platinum particles Prepared in the presence of PVP polymer of different molecular weights (A: sample 2, B: sample 7, C: sample 8, Scale bar: 20 nm).

40,000). When using the short-chain PVP ( $M_w = 10,000$ ), we produced spherical nanoparticles having an average size of 4.0 nm. On the other hand, the longer-chain PVP polymers ( $M_w = 29,000$  and 40,000) gave smaller spherical nanoparticles (average sizes: 2.2 and 2.1 nm, respectively). The PVP-to-Pt molar ratio plays an important role in determining the particle size. We suggest that PVP polymer having higher molecular weights provide smaller, more stable Pt nanoparticles because of their stronger capping effects and higher degrees of steric hindrance resulting from their longer chain lengths.

To investigate the effect of the PVP concentration, we fixed the molecular weight of the PVP additive at 10,000 and monitored its concentration at 0.28, 0.38, and 0.47 M (samples 9, 2, and 10, respectively; Table 1). Fig. 5 displays TEM images and size distributions of the Pt nanoparticles prepared at these three PVP concentrations; the particle sizes increased upon increasing the concentration of PVP, and the Pt nanoparticles had an obvious tendency to form with spherical shapes. When PVP was present at a PVP-to-Pt molar ratio of 0.28, we observed aggregates consisting of small Pt nanoparticles (diameters: ca. 1.2 nm; Fig. 5 (B)). This finding indicates that the number of protecting groups of PVP was insufficient to preventing them from



**Fig. 5.** TEM images and size distributions of platinum particles Prepared in the presence of different PVP concentrations (A: sample 2, B: sample 9, C: sample 10, Scale bar: 20 nm).

aggregating. Therefore, PVP concentrations higher than 0.38 are required to form polymer-capped Pt nanoparticles. Because PVP has a hydrophobic backbone and hydrophilic pendent groups, its backbone forms a hydrophobic domain, which surrounds the Pt nanoparticles, while its pendent groups interact with the solvent (ethanol). It is this steric effect of the PVP polymer on the surface of the Pt particles that prevents them from aggregating [18]. The stability of the Pt nanoparticles in samples 2 and 10 was reflected by their lack of precipitation after storage in solution for 3 months.

### Conclusions

We have prepared Pt nanoparticles through chemical reduction of a Pt precursor in the presence of PVP as a capping agent and reducing agent. When PVP having a molecular weight of 10,000 was added at a PVP-to-Pt molar ratio of 0.38, we obtained well-dispersed Pt nanoparticles. Increasing the PVP concentration had only a stabilizing effect; indeed, at a PVP-to-Pt molar ratio of 0.28 Mol, we observed an aggregate consisting of small

nanoparticles.

The nature of the reducing agent and its concentration both affected the rate of reduction of the  $[\text{PtCl}_6]^{2-}$  ions, which determined the particle size. The rate of reduction when employing NaOH was faster than that in the case using  $\text{NaHCO}_3$ ; at values of the NaOH-to-Pt molar ratio of 1.96 and 3.92, the PVP polymer having a molecular weight of 10,000 provided the best protection, producing Pt colloids having sizes of ca. 2.0 and 4.0 nm, respectively, with almost no agglomeration. Thus, in this paper we propose a simple and efficient method for the synthesis of Pt nanoparticles at a relatively high concentration in an ethanol/water (50 : 50 wt%) solution. We hope that this method will be useful for the large-scale production of Pt nanoparticles.

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