

Factors affecting the size of polymer stabilized Pd nanoparticles

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A consistent and reproducible one-step method for the preparation of Pd nanoparticles of mean sizes varying from 1.5 to 15 nm with relative standard deviation of <0.5 is reported. We have shown that the particle size can be controlled by changing the concentrations of the stabilizing polymer (PVP) and precursor salt, the nature of the reducing agent, the reduction temperature, average molecular weight of the stabilizing polymer as well as the initial pH of the solution. Lower reducing temperature and higher pH lead to the formation of smaller particles. Different molecular weights of the PVP have no significant effect on the particle size. It is inferred that the relative nucleation and crystal growth rate are the decisive factors in determination of the particle size and dispersion. Interestingly, the larger Pd nanoparticles show well-defined morphology and shape, which has only recently been reported by us for this colloidal particle unsupported on solid surface.

Introduction

On account of the quantum confinement effect in particles with diameter of 1–10 nm, metallic and alloy nanoparticles have received renewed interest in recent years. A number of preparative methods for such materials involving chemical and electrochemical reduction, vapor deposition, photolysis, sonochemical and thermal decomposition as well as the recently reported microwave irradiation have been developed.^{1–7} It is important from a practical view point to synthesis well dispersed and stabilized nanoparticles by utilizing polymer, surfactant, ligand or solvent as stabilizing matrix.^{2,8,9} Several studies have been carried out to correlate the effects of particle size and size dispersity with their chemical and physical properties.^{10–12} For example, the reactivity and selectivity of the nanoparticles are strongly dependent on the particle size and the melting point of the nanoparticles is lower than that of the bulk metal. Although the particle size is the most obvious variable observed when the synthesis conditions are changed by the choice of the precursors, protective polymers and the reduction conditions, control of the size of the nanoparticles is still a significant challenge for their applications such as in catalysis. Nearly monodispersed nanoparticles with sizes ranging from 1–20 nm have been reported, with most of them assuming near spherical shape.^{13–15} Teranishi *et al.* have claimed that the PVP stabilized Pd, Pt and Pd/Ni nanoparticles larger than 3 nm cannot be established in a one-step reaction. Stepwise growth techniques^{16–18} have thus been devised. Natan *et al.* have reported the preparation of the larger Au nanoparticles ($d > 20$ nm) stabilized by sodium citrate through stepwise growth¹⁹ on smaller Au seeds. Preparation of larger Bi, Sn and In seeded with Au was claimed as a general synthetic method for monodispersed metallic nanoparticles.²⁰ The mechanism for the growth has also been discussed.

The purpose of the present study is to develop an effective one-step method for the preparation of well-controlled and uniform particle sizes of Pd nanoparticles by varying the synthesis conditions such as the reducing agent and the reducing temperature in the presence of stabilizing polyvinylpyrrolidone. The effect of the average molecular weight of the protective polymer on the particle size was also investigated. In this paper, we also report the effect of pH and reaction time on the mean size. The Pd nanoparticles synthesized in this study have a larger size and satisfactory size distribution.

Experimental

Materials

Palladium chloride (Merck, Germany), polyvinylpyrrolidone (PVP, average molecular weight, M_w , 10 000, 40 000 and 360 000, Sigma, St. Louis) and sodium hydroxide were used as purchased. Methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, ethylene glycol (EG), formaldehyde, *N,N*-dimethylformamide (DMF), 2-butoxyethanol and 2-methoxyethanol were analytical grade reagents and used without further purification.

Synthesis procedure of PVP stabilized Pd nanoparticles (PVP-Pd)

The PVP stabilized Pd nanoparticles were prepared according to the published method with some modifications.²¹ For example, a sample with molar ratio of PVP : Pd = 60 : 4 was prepared as follows: H_2PdCl_4 was first prepared by converting 0.0887 g of $PdCl_2$ (0.5 mmol) with 0.1 ml of concentrated HCl without evaporating off the excess HCl. The pre-prepared H_2PdCl_4 together with 0.8325 g of PVP (7.5 mmol) were added to a mixed solvent of 75 ml distilled water and 65 ml of reducing agent, followed by drop-wise addition of 10 ml of 0.1 M methanolic NaOH. In the case without addition of methanolic NaOH, 75 ml of reducing agent was used. The solution was refluxed (or heated at other temperatures) in a 250 ml round-bottomed flask with vigorous stirring for 3 h to obtain a dark-black homogeneous colloidal dispersion. Methanol, ethanol, *n*-propanol, propan-2-ol, *n*-butanol, butan-2-ol, ethylene glycol, formaldehyde, *N,N*-dimethylformamide, 2-butoxyethanol and 2-methoxyethanol were used as the reducing agents in this study.

Measurements

The particle size and morphology of the PVP-Pd nanoparticles were characterized using a Philips CM 120 TEM operated at 80 kV, while the crystalline structure was determined by HRTEM and electron diffraction on a JEOL-1020 electron microscope operated at 200 kV. The samples for TEM were prepared by placing a drop of the colloidal dispersion onto a copper grid followed by evaporating off the solvent under ambient conditions. The average particle size and size

distribution were measured from the enlarged micrographs of > 300 particles by using an image analysis software. The crystal structure of the PVP-Pd nanoparticles was also investigated by X-ray powder diffraction using a Siemens 5000 X-ray diffractometer with Cu-K α radiation. The PVP-Pd nanoparticle samples were dried under vacuum at room temperature prior to XRD measurement.

Results and discussion

On addition of a few drops of 0.1 M NaOH into a refluxing and well-stirred methanolic solution of H₂PdCl₄ in the presence of PVP, with a molar ratio of PVP : Pd = 60 : 4, the solution with an initial pH \sim 4 turned dark brown within 5 min, indicating the formation of Pd⁰ particles. An aliquot (1 ml) of the solution was taken at regular intervals and TEM micrographs for each of the samples were taken to determine the particle size of the Pd crystallites formed. A typical TEM image and size distribution histogram are shown in Fig. 1. The histogram shows that no particle smaller than 2.3 nm is observed. The TEM also shows that the larger particles formed have definite geometric shapes, including triangular, rhombohedral or square, pentagonal and hexagonal, some of which including the triangular crystals are plate-like.²² Well-defined geometric shapes of Pd nanoparticles without solid support have only recently been reported although different geometric shapes for Pt,²³ Cu,²⁴ Au²⁵ and Ag²⁶ have been reported before. A powder X-ray diffraction pattern of the Pd particles indicated that they have a face centred cubic (FCC) structure (Fig 2), similar to previous reports.¹⁶

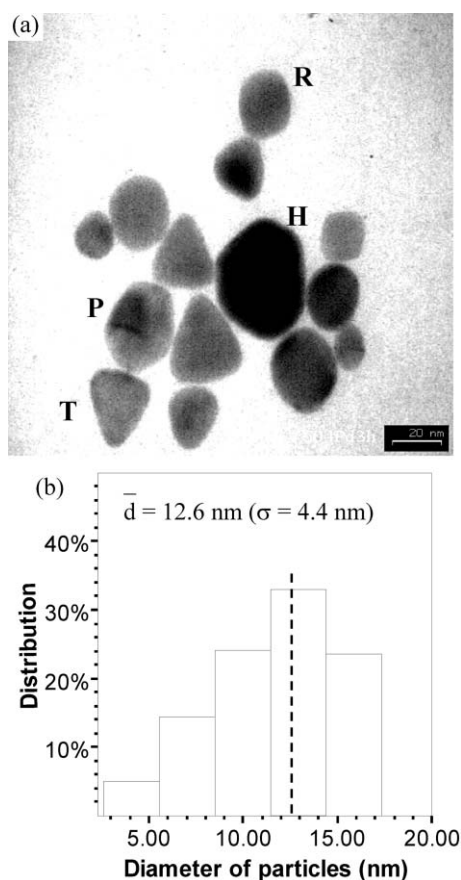


Fig. 1 TEM micrograph and corresponding particle size distribution histogram for molar ratio of PVP : Pd = 60 : 4 refluxed in CH₃OH–H₂O solution for 3 h (R: rhombohedral, H: hexagonal, P: pentagonal, T: triangular particles.) [Scale bar = 20 nm].

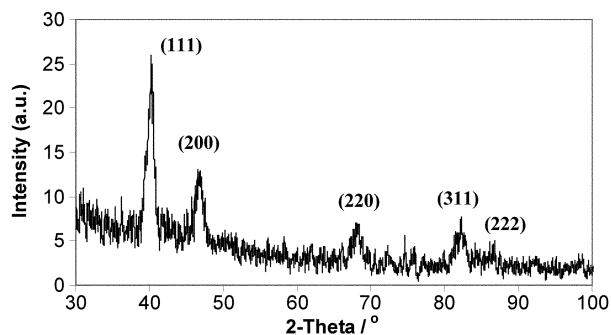


Fig. 2 XRD diffractogram of FCC structure PVP-Pd nanoparticles.

Crystal growth with time

A plot of the mean particle size as a function of time of this reaction shows that the particles have largely been formed at the early stage of the reduction. The subsequent slow increase in size persisted for about 3 h (Fig. 3). The mean size of the particles ranges from 11.3 nm to 13.9 nm with relative standard deviations between 0.26 to 0.36 from 15 min to 3 h. Very few small particles are seen in all samples. It is thus inferred that nucleation is largely completed before, or as soon as, crystal growth begins because otherwise a wider dispersion of the sizes including smaller particles would have been observed if nucleation continued along with crystal growth. The increase in particle size with time is due to the continued reduction and accumulation of the Pd⁰ onto the preformed crystals. The absence of particles with size < 2.3 nm and the growth of the larger particles may be due to the disintegration of the smaller particles or nuclei below a certain critical size which are thermodynamically unstable because of the large surface energy. The atoms from the disintegration then attach themselves to the larger particles that exceed the critical size, and this is in accordance to the crystal growth rule that larger particles grow at the expense of the smaller ones.²⁷

Effect of temperature

As shown in Table 1, the mean particle size decreases with decrease in temperature under otherwise the same conditions as shown in runs 5 and 6 with *n*-propanol, runs 7 and 8 with isopropanol (propan-2-ol) and runs 16 and 17 with methanol. This may be due to an increase in the nucleation rate and a concomitant decrease in the crystal growth rate as the temperature is decreased resulting in formation of a larger number of nuclei hence smaller particle size. This phenomenon is similar to crystal growth from solution and in recrystallization from melts whereby the number average solute cluster size is a nonlinear function of the temperature. An increase in temperature results in larger particles in both cases. In subsequent experiments, the reductions were carried out at

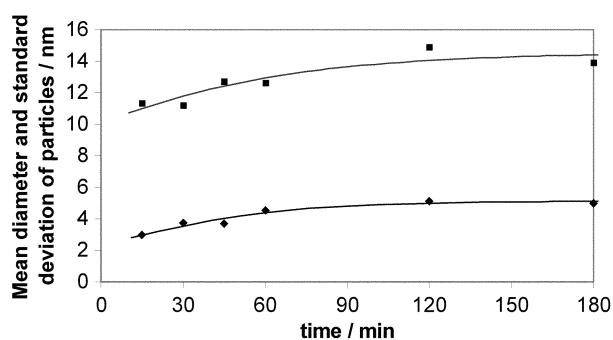


Fig. 3 Variation of mean diameter and standard deviation with time for molar ratio of PVP : Pd = 60 : 4 refluxed in CH₃OH–H₂O solution (■: mean diameter, ◆: standard deviation).

Table 1 Synthesis conditions, mean diameter (\bar{d}), standard deviation (σ) and relative standard deviation (σ_r) for PVP stabilized Pd nanoparticles

No.	Molar ratio of PVP : Pd	M_w of PVP	Reducing agent	Condition ^a	\bar{d} /nm	σ /nm	σ_r^b
1	80 : 4	40 000	CH ₃ OH	r 3 h	11.7	4.17	0.36
2	60 : 4	40 000	CH ₃ OH	r 3 h	12.6	4.35	0.34
3				r 3 h ^c	14.4	6.09	0.42
4			C ₂ H ₅ OH	r 3 h	4.8	3.51	0.73
5			<i>n</i> -C ₃ H ₇ OH	r 3 h	8.2	3.33	0.40
6				60 °C, 3 h	7.4	2.61	0.36
7			<i>i</i> -C ₃ H ₇ OH	r 3 h	8.7	3.30	0.38
8				50 °C, 3 h	7.1	1.89	0.27
9			<i>n</i> -C ₄ H ₉ OH	r 3 h	7.8	3.58	0.46
10			<i>i</i> -C ₄ H ₉ OH	r 3 h	5.5	3.27	0.59
11			2-MethoxyC ₂	r 3 h	3.3	0.93	0.28
12			2-ButoxyC ₂	r 3 h	6.3	2.25	0.36
13			HCHO	r 3 h	2.4	0.74	0.32
14			DMF	r 3 h	5.5	7.20	1.31
15			HOCH ₂ CH ₂ OH	r 3 h ^c	5.0	1.49	0.30
16		10 000	CH ₃ OH	r 3 h	8.7	6.95	0.80
17				50 °C, 3 h	5.8	7.30	1.27
18			<i>i</i> -C ₃ H ₇ OH	r 3 h	7.4	2.95	0.40
19		360 000	CH ₃ OH	r 3 h	10.3	3.44	0.34
20			<i>i</i> -C ₃ H ₇ OH	r 3 h	8.7	3.36	0.39
21	20 : 4	40 000	CH ₃ OH	r 3 h	15.6	6.18	0.40
22	40 : 4				13.7	6.43	0.47
23	40 : 3				7.4	2.84	0.38
24	40 : 2				5.7	5.12	0.89
25	40 : 1				1.5	0.42	0.28

^ar 3 h refluxed for 3 hour under air. ^bRelative standard deviation ($\sigma_r = \sigma/\bar{d}$). ^cWithout 0.1 M NaOH-CH₃OH.

the refluxing temperature of the medium and samples were taken after 3 h.

Effect of stabilizing polymer

Stabilizing polymer molecules, PVP, are adsorbed on the particles surfaces preventing their aggregation. Thus a higher concentration of PVP should lead to smaller particles. This is confirmed from our results plotted in the second half of Fig. 4 which shows a steady but small decrease in mean particle size as the ratio of polymer to Pd ratio is increased.

The effect of molecular weight of PVP on the particles size of Pd and Pt has been investigated before.^{17,28} For Pd, increase in molecular weight increases slightly the mean particle size, while it had no significant effect on Pt particle size. We thus further investigated the stabilizing effect of the average molecular weight of PVP using three PVPs with M_w of 10 000, 40 000 and 360 000. For samples prepared with isopropanol as the

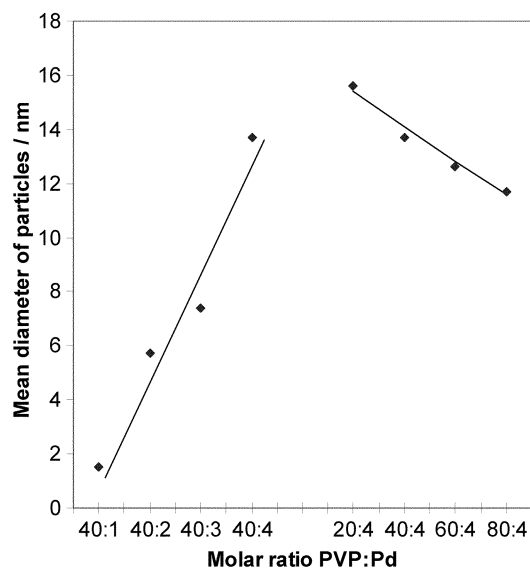


Fig. 4 Effect of PVP and Pd precursor salt concentration on the mean diameter of Pd nanoparticles refluxed in CH₃OH-H₂O solution for 3 h.

reducing agent at a ratio of PVP : Pd = 60 : 4, the particle sizes were 7.4, 8.7 and 8.7 nm respectively. The stabilizing efficiency of the polymer with different M_w is not significantly different, except a slightly smaller size was obtained with the lowest M_w polymer perhaps due to the presence of a larger number of polymer molecules.

Effect of pH

Palladium ions can exist in the oxidation state of 2+ or 4+ and have variable coordination numbers. It is thus expected that the reduction rate of the complex ions will depend on the conditions including the pH of the solution during reduction. The result showed that as the pH of the precursor solution was increased from 2 to 10.2, the mean size of the particles formed decreased nonlinearly from 14.4 to 1.5 nm as shown in Fig. 5. It is thus possible to control the mean particle size by controlling the initial pH of the solution. When the solution becomes more alkaline, the reduction becomes faster as indicated by the rate of the colour change from pale yellow to dark brown. For the reduction with citrate, it was reported that the pH must be >3.²⁹ However, in our system, we are able to effect the reduction at pH = 2 or higher.

Effect of concentration of Pd salt

It has been reported that to synthesize Pd nanoparticles with size > 3.0 nm, a stepwise procedure has to be adopted and it

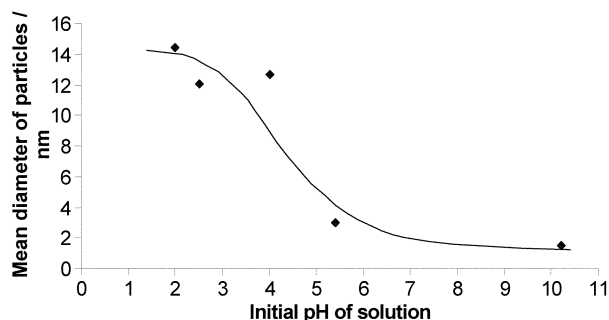


Fig. 5 Effect of initial pH of the solution on the mean diameter of Pd nanoparticles refluxed in CH₃OH-H₂O solution for 3 h.

was stated specifically in the same papers that larger particles are not obtainable by a one step synthesis.^{16,17} We thus performed a series of four experiments by increasing the precursor salt concentration but keeping all other parameters constant. The results are graphically presented in Fig. 4. It is clearly seen that the mean particle size increases from 1.5 nm (relative standard deviation, $\sigma_r = 0.28$) for the lowest precursor concentration of 0.833 M to 13.7 nm ($\sigma_r = 0.47$) for the sample prepared with four times the lowest concentration. The increase in mean size with the precursor concentration is nearly linear. For the increase in mean size of a spherical particle from d_1 to d_2 , the amount of metal atom required is proportional to $d_2^3 - d_1^3$. Alternatively, every doubling of the amount of atom reduced will only result in an increase in size by a factor of 1.26, or if the particles were plate-like, in which the thickness did not increase substantially, the mean size shall only be increased by a factor of 1.41 and not by ~ 2 as observed. The observation can thus be rationalized only if the number of particles has been decreased substantially on increasing the concentration of the precursor. This is reasonable in that as the concentration of the precursor was increased, the rate of reduction is increased leading to an increase of the crystal growth rate on the nuclei that were initially formed, which inhibits further nucleation, concomitantly smaller particles disintegrate and re-attach themselves to the larger particles as in Ostwald ripening. A smaller number of larger particles thus results.

Effect of reducing agent

Palladium ions can be reduced by a large number of reducing agents of diverse activity. The mean sizes of Pd nanoparticles were determined using different reducing agents, mainly alcohols, under similar conditions, at pH ~ 4 and a concentration of the reducing agent of 50%, the refluxing temperatures vary slightly with the agent used. The results obtained are shown in Table 1. The mean size, which ranges from 2.4 to 12.6 nm with narrow dispersion in all cases, in increasing order is as follows:

HCHO < CH₃OCH₂CH₂OH < C₂H₅OH \approx HOCH₂CH₂OH \approx DMF \approx 2-C₄H₉OH < 2-C₄H₉OCH₂CH₂OH < n-C₄H₉OH < n-C₃H₇OH \approx i-C₃H₇OH < CH₃OH.

Apparently this is approximately in the order of their decreasing reducing activities.

Conclusion

It has been claimed that nanoscale colloidal particles with mean size > 3 nm cannot be obtained by a one-step synthesis method as it is restricted by the low precursor concentration. Thus the seeding or stepwise method has been widely applied for the synthesis of larger particles. However, a convenient and simple one-step method has been developed in the present study to control the size of PVP stabilized Pd nanoparticles via chemical reduction by varying the reducing agent, the reducing temperature and the pH. For the formation of the larger

particles, the nucleation proceeds for a short period. It was then overtaken by the crystal growth process. The larger particles thus obtained have well-defined geometric shapes and have FCC structure as in bulk Pd.

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