

Size control of polymer-stabilized ruthenium nanoparticles by polyol reduction

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A series of polymer-stabilized ruthenium nanoparticles with various dimensions are prepared by heating or refluxing a polyol solution of ruthenium(III) salts. The average diameters of Ru nanoparticles can be controlled in the range of 1.4–7.4 nm with relative standard deviations of less than 0.3 by changing the polyols, the reduction temperature and/or the amount of protective polymer. The larger ruthenium particles are obtained in the order of EG > DEG > TrEG, indicating that the slower reduction rate of Ru³⁺ ions is a decisive factor for obtaining larger particles. The ruthenium particle dimensions are dependent on the reduction temperature, nature of the media and the amount of protective polymer.

Introduction

Owing to the quantum size effect,¹ nanoscale metal particles are currently being developed for use as advanced materials with new electronic, optical, and magnetic properties as well as novel catalytic properties. As a bridge between homogeneous and heterogeneous catalysis, nanoscale metal, especially platinum group metal, particles have received renewed attention in catalysis.² Accordingly, an effective size control of the metal nanoparticles is important in order to investigate their novel catalytic properties. Among the platinum group metals, the preparation of Pt, Pd, Ir and Rh nanoparticles has been extensively studied. However, the preparation of ruthenium nanoclusters is scarcely reported.

Although the standard reduction potential of RuCl₃ to Ru(0) is relatively high ($\varphi^\circ = 0.3862$ V),³ we have not been able to obtain polymer-stabilized ruthenium clusters by simply refluxing an alcohol–water solution of RuCl₃ in a similar way to the preparation of Pt or Pd clusters described in the literature⁴ or even by reducing Ru(III) salts with hydroxylamine (NH₂OH) and/or hydrazine (NH₂NH₂). Bradley *et al.*⁵ reported that the H₂ dissociation of Ru(cod)(cot) (cod = cyclooctadiene; cot = cyclooctatriene) in organic media (*e.g.* THF) in the presence of nitrocellulose or cellulose acetate gave ruthenium nanoclusters. However, the experiment indicated that Ru(cod)(cot) was sensitive to air and needed careful protection, and unknown ruthenium compounds were still present. Bönemann and co-workers⁶ successfully synthesized tetraalkylammonium-stabilized ruthenium colloids *via* hydrotriorganoborate reduction, but they were characterized only by elemental analysis. We have reported that polyvinylpyrrolidone (PVP)-stabilized Ru nanoclusters (designated as PVP-Ru) were prepared by sodium borohydride reduction at room temperature in MeOH–H₂O solution.⁷ Different from PVP-stabilized platinum (PVP-Pt) and PVP-stabilized iridium (PVP-Ir) which were prepared by Hirai's method and were stable on standing for several months in solvents such as water, alcohols and acetic acid *etc.*, PVP-Ru was stable on standing for only several days in the above solvents. XPS characterization showed that there existed a small amount of boride associated with Ru and a large amount of borate adsorbed on the Ru surface.⁷ In fact, conventional supported or unsupported Ru catalysts are usually prepared by NaBH₄ reduction,^{8–10} and all contained

boron species. It had been found that boron species had an obvious influence on the performance of Ru catalysts.^{11,12} In addition, it was reported that dry Ru metal particles prepared by NaBH₄ reduction exploded in air.¹³ This phenomenon has also been observed in our experiments. NaBH₄ reduction is therefore not considered to be an ideal method for preparation of Ru clusters.

Recently, we reported that polymer-stabilized Ru clusters can be prepared by the reduction of RuCl₃ in ethylene glycol under microwave irradiation,¹⁴ the average diameters of the resulting Ru clusters are around 1.4 nm with a narrow size distribution. Miyazaki *et al.*¹⁵ also reported that Ru colloid was produced by the reduction of RuCl₃ in ethylene glycol, but the resultant Ru colloids were unprotected and tended to agglomerate even during the preparation. In the present study, employing several polyols such as ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TrEG) as reaction media, we successfully prepared a series of stable Ru colloids *via* conventional heating or refluxing of the polyol solutions of RuCl₃ in the presence of PVP. The particle dimensions varied with preparation conditions. The objective of this paper is to establish a practical method to effectively control the particle dimensions of ruthenium, which in effect helps us to investigate the relationship between catalytic properties and particle size.

Experimental

Materials

Ruthenium chloride hydrate (RuCl₃·*n*H₂O) was used as received. Polyvinylpyrrolidone (PVP, av. MW 40 000) was obtained from Fluka. Other AR grade organic solvents (*e.g.* polyols, acetone) were first dried with inorganic salts (*e.g.* CaSO₄), followed by distillation and/or vacuum distillation prior to use.

Preparation of PVP-stabilized ruthenium colloids in polyol media

Typically, in a 250 mL flask, PVP (0.8325 g, 7.5 × 10⁻³ mol) and RuCl₃·*n*H₂O (0.0371 g, 1.5 × 10⁻⁴ mol) were dissolved in polyol solvent (150 mL) under stirring to form a dark red

solution, which was then either heated to reflux or to a given temperature with vigorous stirring. In the early stages, the color of the solution changed from dark red to light yellow then turned to dark brown. On stirring for 3 h, a transparent dark brown homogeneous colloidal solution of Ru nanoclusters was obtained without any precipitate. Different Ru colloids can be obtained by variation of the molar ratio of PVP to $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, the reaction temperature and the polyol solvents used. Generally, as-prepared polyol dispersions of Ru clusters were precipitated using anhydrous acetone. The precipitates were washed with anhydrous acetone and dried under vacuum and then re-dispersed into methanol prior to characterization or reaction.

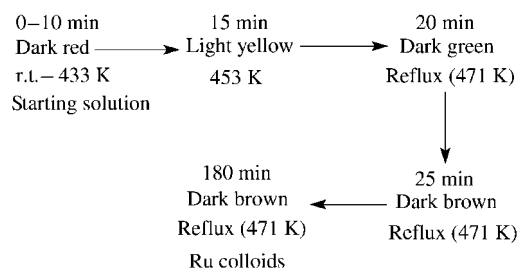
Measurements

UV-Vis spectra were recorded with a Unicam SP1750 UV-vis spectrophotometer. Transmission electron microscopy (TEM) photographs were taken with a Hitachi-9000 NAR apparatus. Samples for TEM were prepared by placing a drop of a colloidal dispersion of PVP-Ru onto a perforated carbon coated copper grid, followed by naturally evaporating the solvent. The mean particle diameter and standard deviation were calculated by counting ~ 250 particles from the enlarged photographs. X-Ray photoelectron spectra (XPS) were recorded on an ESCALAB 220I-XL (VG, Inc.) photoelectron spectrometer using monochromated Al-K α radiation under a vacuum of 2×10^{-8} Pa. Binding energy refers to C 1s (284.6 eV). XPS samples were prepared *via* immobilization of metallic colloids on Al_2O_3 . X-Ray powder diffraction (XRD) measurements were made with a Rigaku D/Max-3B diffractometer employing Cu-K α radiation.

Results and discussion

Formation of PVP-stabilized colloidal Ru clusters in polyol media

Metal nanoclusters are usually prepared by chemically or physically forming metal atoms in solution followed by an aggregation process of the metal atoms in the presence of protective agents such as polymers, surfactants or strong coordination ligands. PVP has been proven to be an effective protective agent.¹⁶ In order to prepare a stable metal cluster with a defined particle size and narrow distribution, suitable solvents and an effective method of controlling the metal particle size have to be used. In this work, glycols served both as a reducing agent and a solvent while PVP was selected as a protective agent. During the course of the preparation of ruthenium clusters we observed a succession of color changes in the reaction solution. As shown below (Scheme 1), the following changes were observed in the case of ethylene glycol as solvent:



Scheme 1

When the reaction solution was heated to 433 K, the color of the solution began to change. The color changes showed that Ru(III) salts (dark red) were reduced, step by step, to Ru(0)

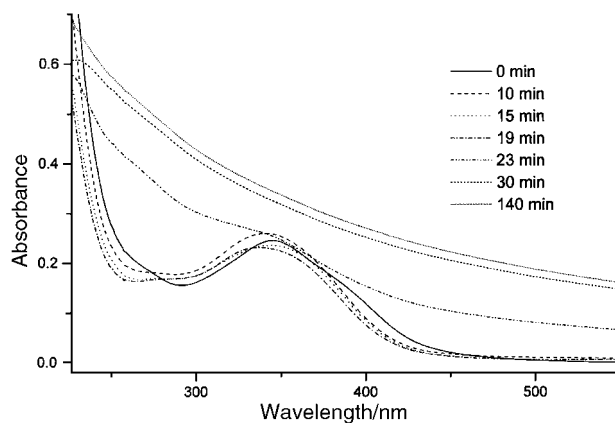


Fig. 1 UV-Vis absorption spectra during the formation of ruthenium clusters in the PVP-RuCl₃-EG system at different reaction stages.

(dark brown), this accords with what has been reported in the literature.¹⁷⁻²⁰ By refluxing or heating a polyol solution of RuCl_3 for 3 h, a transparent Ru colloidal dispersion was obtained without precipitates. The resultant Ru colloids are very stable in polyol media, no precipitate was observed after standing in air for at least six months.

The formation process for PVP-Ru (PVP/Ru=20) synthesized in ethylene glycol was monitored by UV-vis measurements as a representative example. As shown in Fig. 1, the original solution (before heating) shows a peak at 347 nm in its UV-vis spectrum. As the heating time is increased, the peak at 347 nm gradually decreases, shifting to higher frequency initially and totally disappearing after 25 min, indicating that Ru^{3+} has been completely reduced and that the Ru colloids were formed 25 minutes later as shown by the increasingly dispersed spectrum.

PVP-stabilized Ru colloids can be precipitated with anhydrous acetone, the resultant precipitates were washed with anhydrous acetone to thoroughly remove the polyol residues, followed by drying the precipitates under vacuum. The dry precipitates can be re-dispersed in solvents such as water and alcohols as well as in acetic acid *etc.* The re-dispersed PVP-Ru colloids are also very stable in the above solvents for at least several months. PVP-Ru colloids prepared by polyol reduction are obviously more stable than those prepared by NaBH_4 reduction, the latter are somewhat unstable, lasting for only several days in water or alcohol. UV-Vis measurements were employed to clarify the protecting action of PVP on Ru colloids in the presence or absence of $\text{Na}_2\text{B}_4\text{O}_7$. As shown in Fig. 2, compared to the peak for RuCl_3 solution, the mixed solution of

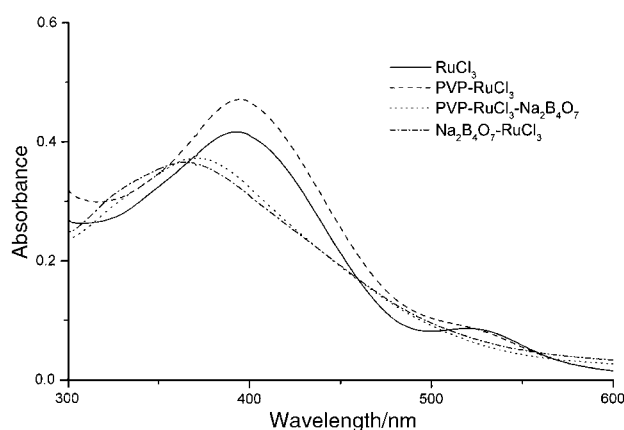


Fig. 2 UV-Vis spectra of RuCl_3 and mixed solutions of RuCl_3 with PVP and/or $\text{Na}_2\text{B}_4\text{O}_7$. (PVP/RuCl₃=10, B/Ru=2/1, $[\text{Ru}^{3+}] = 1.55 \times 10^{-4}$ M, ethanol solvent).

RuCl₃ and PVP shows a peak slightly shifted to higher wavelength with significant absorbance enhancement. This difference proves the coordination of N and/or O atoms from PVP to Ru³⁺, which in turn provides the protecting action of PVP to Ru metal clusters. However, the mixed solution of RuCl₃ and Na₂B₄O₇ shows a peak obviously shifted to lower wavelength which reveals that coordination of B₄O₇²⁻ to Ru³⁺ is stronger than that of PVP to Ru³⁺. Furthermore, XPS measurement showed that a large amount of borate adsorbed on the Ru particle surface.⁷ TEM observation of PVP-Ru prepared by NaBH₄ reduction exhibited a tendency for agglomeration of Ru clusters.²¹ On the basis of the above measurements, it can be rationalized that large amount of borate adsorbed on the surface of colloidal particles inhibits the coordination of PVP to Ru, thereby weakening the stabilizing action of PVP in PVP-Ru/B colloids. In addition, we presumed that the impurities (boride) present in the Ru particle surface might also influence the stability.

Influences of reduction temperature and solvents on the size of Ru nanoclusters

The particle size of Ru colloids prepared by the present method is closely dependent on the reduction temperature and the nature of the solvents. As shown in Table 1, narrowly distributed Ru clusters with mean diameters from 1.4–7.4 nm can be obtained by varying the solvents and the heating conditions. Representative TEM photographs and histograms are shown in Fig. 3. For ethylene glycol, the duration of the color change decreased with increasing reduction temperature, indicating that the reduction rate increases with increasing temperature. As a result, the particle sizes obtained decrease with increasing temperature whilst the relative standard deviations change little. Employing DEG or TrEG as reducing agent, the mean diameters of the resultant clusters are 2.9 nm and 1.8 nm, respectively. The particle size decreases in the order EG > DEG > TrEG under reflux, in reverse order of their increasing boiling points. From the time of the color change, it can be deduced that the reduction rate is closely dependent on the reaction temperature. For example, while Ru³⁺ ions were gradually reduced by EG over a long period, the reduction of Ru³⁺ occurred in a short time in the case of TrEG. Thus, the fast reduction of Ru³⁺ by the polyol with higher boiling point produced more Ru nuclei in a shorter period and, in turn, hindered the growth of Ru particles. In general, the reduction rate of Ru³⁺ ions increases with increasing reaction temperature. In addition, it was found in our experiments that different polyols have similar reduction abilities for Ru(III) ions based on the same time for the color change between EG and TrEG at the same temperature. Here, the employment of DEG and TrEG with higher boiling points as reducing agent really acts to elevate the reduction temperature, thereby accelerating the rate of reduction of Ru³⁺ ions. A faster reduction rate of Ru³⁺ ions is needed to generate smaller Ru particles with a narrow size distribution. This also conforms to the observation for the rapid synthesis of Ru nanoclusters by microwave irradiation.¹⁴ In other words, a lower reaction temperature results in a slower

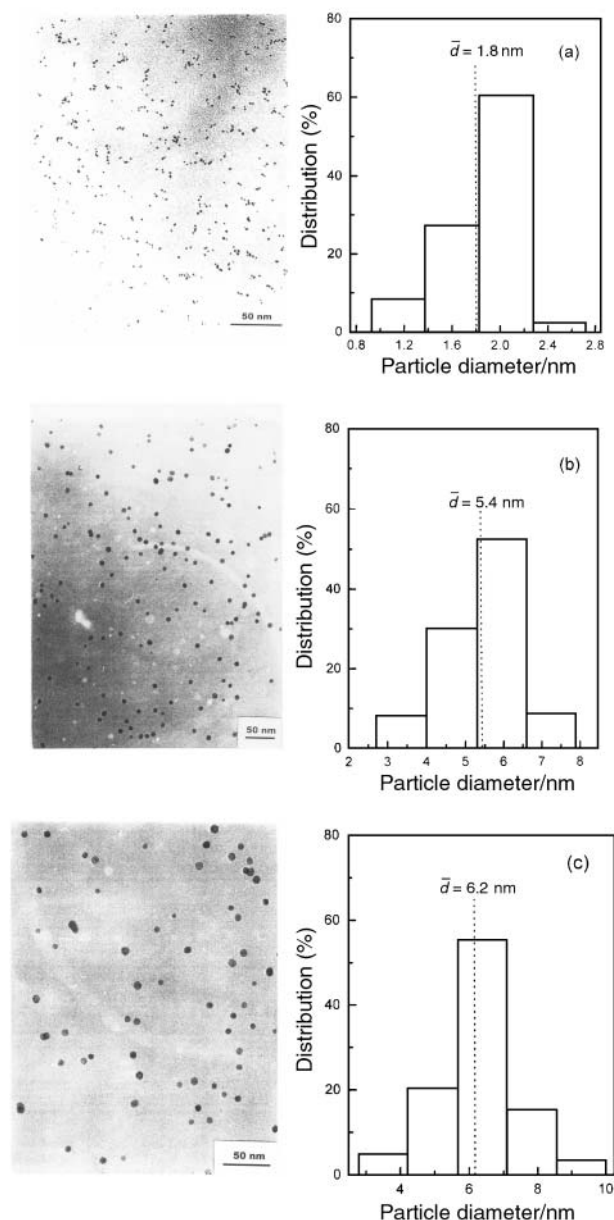


Fig. 3 TEM photographs (left) and the corresponding particle size distribution histograms (right) of PVP-stabilized ruthenium clusters. (a), (b) and (c) correspond to sample numbers 5, 3 and 2 in Table 1, respectively.

reduction rate and thus generates larger Ru particles. Such a size control method was also reported by Teranishi *et al.*^{22,23} in the preparation of Pt and Pd nanoparticles *via* refluxing alcohol–water solutions of [PtCl₆]²⁻ or [PdCl₄]²⁻. Based on above results, we deduced that the reduction rate of Ru(III) ions determined the particle size. An appropriate choice of polyol solvents is important in controlling the particle size.

Table 1 Synthesis conditions and dimensions of PVP-stabilized ruthenium metal clusters^a

Sample no.	Preparation conditions		Time for color change/min	Average diameter, <i>d</i> /nm	Standard deviation, <i>σ</i> /nm	Relative standard deviation, <i>σ</i> / <i>d</i>
	Solvent	Temperature/°C				
1	Ethylene glycol	160	90	7.4	2.20	0.30
2	Ethylene glycol	180	45	6.2	1.65	0.27
3	Ethylene glycol	Reflux, 198	15	5.4	1.16	0.22
4	Diethylene glycol	Reflux, 245	5	2.9	0.70	0.24
5	Triethylene glycol	Reflux, 285	2	1.8	0.45	0.25
6 ^b	Ethylene glycol	Microwave irradiation	0.5	1.4	0.22	0.16

^aThe molar ratios of RuCl₃ to PVP were 1:10. The concentration of RuCl₃ was 1.12 × 10⁻⁶ mol mL⁻¹. ^bData from ref. 14.

Table 2 Influence of the amount of PVP on the particle sizes of ruthenium colloids^a

Sample no.	mol PVP/mol RuCl ₃	Average diameter, <i>d</i> /nm	Standard deviation, σ /nm	Relative standard deviation, σ/d
Ru 1 ^b	1	5.7	1.57	0.28
Ru 2	5	5.8	1.45	0.25
Ru 3	10	5.4	1.16	0.21
Ru 4	20	5.1	1.14	0.22
Ru 5	50	3.8	0.86	0.23

^aSolvent: ethylene glycol, maintained at reflux for 3 h. ^bA certain amount of precipitates were observed in the colloid solution with PVP/Ru = 1.

Size control of Ru nanoparticles by variation of the amount of PVP

As shown in Table 2, the size of the PVP-Ru nanoparticles is influenced by the molar ratio of PVP to Ru. The coordination of N and O atoms of PVP to the surface metal atoms has been confirmed by FT-IR and XPS measurements.²² Moreover, the coordination of PVP to Ru(III) is also confirmed by UV-vis measurements as shown in Fig. 2. Accordingly, the amount of PVP added to the solution is expected to affect the reduction of Ru(III) and the growth process of Ru nanoparticles. A lower PVP/Ru molar ratio in EG gives larger Ru nanoparticles with a narrow size distribution, although the PVP/Ru ratio of 1 gave Ru precipitates. Similar results were obtained in the case of DEG and TrEG. With the decrease in the PVP/Ru ratio, the reduction of Ru(III) becomes easier. On the other hand, the growth of the particles proceeds faster due to the lack of protecting groups, thus leading to larger particle sizes. Although the variation of the molar ratio of PVP to Ru(III) certainly affected the concentration of Ru(III), thereby causing a change in the reduction rate, it is well established that the variation of temperature exerted a much stronger influence on the reduction rate than the concentration did.²⁴ Thus, we rationalized that the variation of the amount of PVP only resulted in a limited contribution to particle size control. Additionally, in Teranishi's work,^{22,23} the Pt or Pd nanoparticles

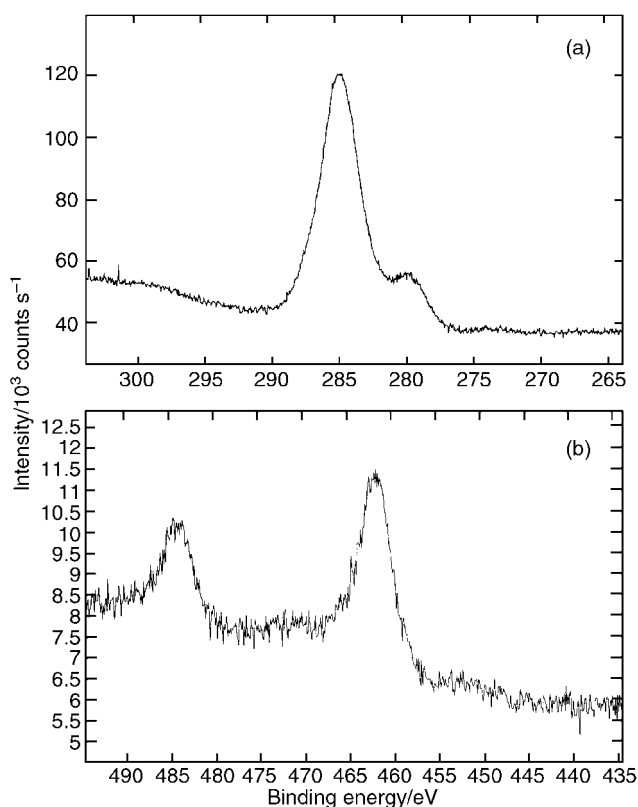


Fig. 4 XPS spectrograms for the ruthenium clusters: C 1s and Ru 3d_{5/2} (a), Ru 3p_{1/2} and Ru 3p_{3/2} (b).

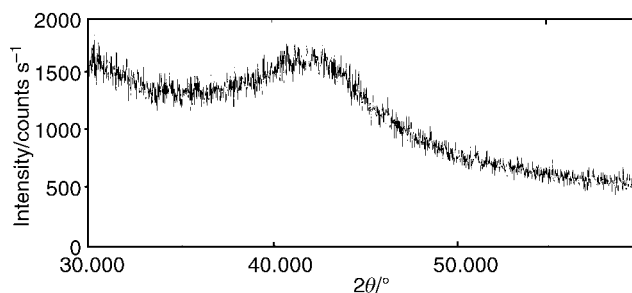


Fig. 5 X-Ray diffractogram for the ruthenium clusters (sample no. 5 in Table 1).

with average diameters larger than 3.3 nm could only be obtained by stepwise growth. Compared to [PtCl₆]²⁻ and [PdCl₆]²⁻, Ru³⁺ is less easily reduced in the presence of PVP. The successful preparation of larger Ru particles in one step is also attributed to the low reducibility of Ru³⁺.

Characterization of Ru nanoparticles

XPS measurement was employed to confirm the formation of ruthenium nanoparticles. As shown in Fig. 4, XPS spectra (Ru 3d_{5/2} at 280.2 eV, Ru 3p_{1/2} and Ru 3p_{3/2} at 484.1 eV and 462.0 eV, respectively) of PVP-Ru verified that the ruthenium particles were in a zero oxidation state in accordance with the literature.²⁵

The X-ray diffraction (XRD) pattern of the ruthenium clusters (no. 5 in Table 1) shows a single diffuse "peak" (Fig. 5). The diffraction angle of the peak is $2\theta = 42.8^\circ$, which is exactly consistent with the *d* value (2.11 Å) of ruthenium metal.²⁶ The crystal size of the ruthenium cluster (1.7 nm) calculated by the Scherrer formula is nicely close to the average diameter (1.8 nm) determined by TEM observation.

Conclusion

PVP-stabilized ruthenium nanoparticles with various dimensions have been prepared by polyol reduction in the presence of PVP. The particle size can be effectively controlled in the range of 1.4–7.4 nm by the variation of solvents, the reduction temperature and the amount of PVP used in the one-step reduction. The lower reduction rate of Ru³⁺ is an important factor in the production of larger particles.

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