

Rapid Communication

## SYNTHESIS OF POLYMER-STABILIZED RUTHENIUM COLLOIDS BY LOW BOILING POINT ALCOHOL REDUCTION\*

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**Abstract** Stable and well-dispersed poly(*N*-vinyl-2-pyrrolidone) (PVP)-stabilized ruthenium colloidal clusters were prepared via the reduction of ruthenium(III) chloride by refluxing with low boiling point alcohols. Investigation of the size of Ru colloids by transmission electron microscopy (TEM) indicated that the average diameters could be controlled in the range of 1.2–1.6 nm with relative standard deviations of less than 0.33 by changing the molar ratio of PVP to Ru. The X-ray photoelectron spectroscopy (XPS) characterization verified the formation of elemental ruthenium colloids.

**Keywords** Polymer-stabilized colloid, Poly(*N*-vinyl-2-pyrrolidone), Ruthenium, Alcohol reduction

### INTRODUCTION

Nanosized metal colloids and clusters have been attracting renewed attention for their unique chemical and physical properties which differ from those of both the single metal atom and the bulk metal<sup>[1–3]</sup>. Ruthenium has been known to show fascinating activity as a catalyst<sup>[4–6]</sup>. Among the platinum group metals, the preparation of ruthenium colloids is comparatively difficult and has been scarcely studied. It was reported that polymer-stabilized ruthenium colloids could not be obtained by simply refluxing an alcohol-water solution of RuCl<sub>3</sub><sup>[7, 8]</sup>, in spite of the standard reduction potential of RuCl<sub>3</sub> to Ru(0) being relatively high ( $\varphi^\circ = 0.3862$  V)<sup>[9]</sup>. Thus, several strategies, such as, sodium borohydride reduction<sup>[10]</sup>, organoboride reduction<sup>[11]</sup> and polyol reduction<sup>[12]</sup> have been explored. In the present communication, we found that, in the presence of PVP, ruthenium colloids can be produced from RuCl<sub>3</sub> alcohol solutions after a prolonged refluxing. TEM observation and XPS measurement illustrated the formation of ruthenium nanoclusters.

### EXPERIMENTAL

#### Materials

Ruthenium chloride hydrate (RuCl<sub>3</sub>·*n*H<sub>2</sub>O, Ru content ≥ 37%) was used as received from Kunming Institute of Novel Metals. Polyvinylpyrrolidone (PVP, av.  $M_w = 40,000$ ) was obtained from Fluka. *n*-Butanol, *iso*-butanol, *n*-propanol, and ethanol were supplied by Beijing Chemical Corporation. Argon gas (Ar) with a purity of 99.99% was supplied by Beijing Gases Factory. *n*-Butanol was purified according to the method in the literature<sup>[13]</sup>.

#### Synthesis of PVP-Stabilized Ruthenium Colloids

In a 100 mL round-bottomed flask, PVP (0.5828 g,  $5.25 \times 10^{-3}$  mol) and RuCl<sub>3</sub> (0.1434 g,  $5.25 \times 10^{-4}$  mol) were dissolved in *n*-butanol (70 mL) under stirring to form a dark red solution, which was then heated to reflux. After the mixture was refluxed for a certain period of time, the color of the solution changed from dark red to orange

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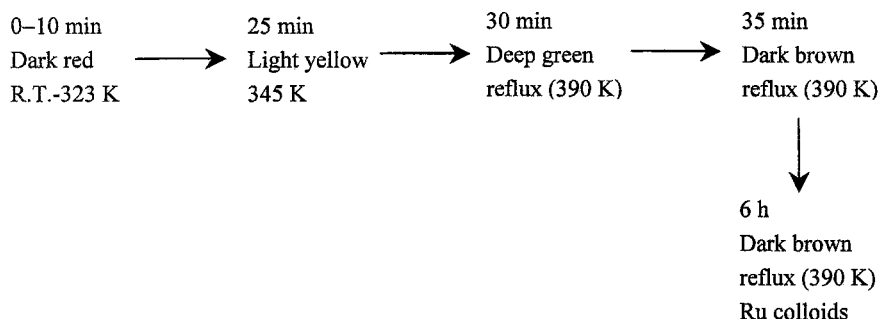
and then turned to deep green, finally to dark brown. By refluxing an alcohol solution of  $\text{RuCl}_3$  for 6 h, a homogenous Ru colloid dispersion was obtained without precipitates. Different Ru colloids with various dimensions can be prepared by varying of the molar ratio of PVP to  $\text{RuCl}_3$ .

### Characterization

Transmission electron microscopic (TEM) microphotographs were taken by using a Hitachi-9000 NAR electron microscope. Particle diameters and standard deviations were calculated by counting approximately 300 particles from the enlarged photographs. X-Ray photoelectron spectra (XPS) were recorded on an ESCA LAB 220I-XL (VG, Inc.) photoelectron spectrometer using monochromated  $\text{Al-K}\alpha$  radiation under a vacuum of  $2 \times 10^{-8}$  Pa. All binding energy values were referred to carbon ( $\text{C}_{1s}$  = 284.6 eV). XPS samples were prepared by simply drying the Ru colloidal dispersion via rotatory evaporation at 310K.

## RESULTS AND DISCUSSION

In the previous research, it was widely acknowledged that Ru nanoparticles could not be obtained by simply heating or refluxing the corresponding metal salts in a low boiling point alcohol solution. Presently we found that after a prolonged refluxing, Ru colloids could be prepared from a  $\text{RuCl}_3$  butanol solution in the presence of PVP. During the formation of Ru nanoclusters, butanol serves not only as a solvent, but also acts as a reducing agent. A series of PVP-stabilized Ru nanoparticles were synthesized by heating the solvent at its boiling point and they were stable for at least half a year. As shown in Scheme 1, a succession of color changes was observed in the reaction solution during the course of the preparation of ruthenium nanoclusters.



**Scheme 1** Color changes of the reaction solution during the course of the ruthenium nanocluster preparation

Table 1 lists the various parameters of corresponding PVP-stabilized Ru colloids prepared under different conditions. Representative TEM microphotographs and histograms are also given in Fig. 1. Average diameters ( $d$ ) and standard deviations ( $\sigma$ ) were calculated from the enlarged TEM photos of colloidal particles with different sizes. As shown in Table 1, both the solvent purification (refer to experiments no. 3 and 4) and the protection by argon during the course of reduction (refer to experiments no. 3 and 5) have little effect on the colloid dispersity.

Furthermore, it can be seen from Table 1, that the average diameters of the colloidal particles decreases with increasing molar ratio of PVP (refer to monomeric unit) to  $\text{RuCl}_3$ , indicating that the size of the PVP-stabilized Ru nanoparticles is influenced by the amount of the stabilizing polymer — PVP. When the molar ratio of PVP:Ru was 50:1, the particle size was the smallest (1.2 nm), with the decrease in the ratio of PVP:Ru to 10:1, the particle dimension increased to 1.6 nm. However, the relative standard deviation even became smaller with the lower molar ratio of stabilizing polymer to metal. These results imply that the ruthenium colloids thus synthesized will have an excellent stability. It is consistent with the fact that no precipitate can be observed in the colloid dispersion over a period of 1/2 year on standing at room temperature.

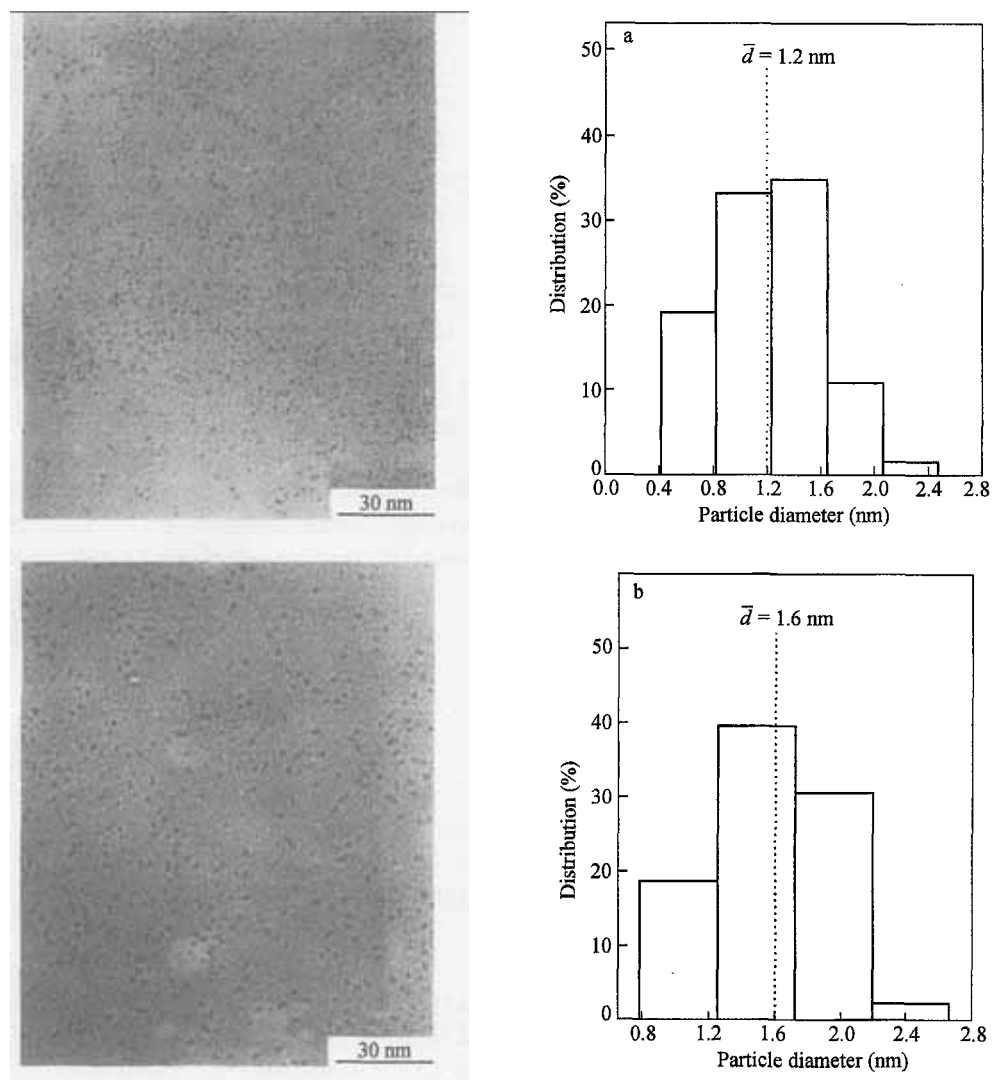


**Fig. 1** TEM photographs (left) and the corresponding particle size distribution histograms (right) of PVP-stabilized ruthenium nanoclusters (a) and (b) correspond to sample numbers 1 and 4 in Table 1, respectively

**Table 1.** Synthesis conditions and dimensions of PVP-stabilized ruthenium colloids<sup>a</sup>

| Experiment no. | Preparation conditions          |                      |                      | Av. diameter $\bar{d}$ (nm) | Std. deviation $\sigma$ (nm) | Relative std. deviation, $\sigma/\bar{d}$ |
|----------------|---------------------------------|----------------------|----------------------|-----------------------------|------------------------------|-------------------------------------------|
|                | PVP/RuCl <sub>3</sub> (mol/mol) | Solvent purification | Argon gas protection |                             |                              |                                           |
| 1              | 50                              | Yes                  | Yes                  | 1.2                         | 0.40                         | 0.33                                      |
| 2              | 20                              | No                   | Yes                  | 1.3                         | 0.34                         | 0.28                                      |
| 3              | 10                              | Yes                  | Yes                  | 1.8                         | 0.45                         | 0.26                                      |
| 4              | 10                              | No                   | Yes                  | 1.6                         | 0.43                         | 0.26                                      |
| 5              | 10                              | Yes                  | No                   | 1.5                         | 0.39                         | 0.26                                      |

<sup>a</sup> Solvent: *n*-butanol, boiling point: 117.3°C. The concentration of RuCl<sub>3</sub> was  $7.5 \times 10^{-3}$  mol • L<sup>-1</sup>

To confirm the formation of metallic ruthenium nanoclusters, XPS was employed to determine the oxidation state of ruthenium (Fig. 2). The binding energy of Ru 3d<sub>5/2</sub> (280.0 eV), Ru 3p<sub>1/2</sub> (483.8 eV) and Ru 3p<sub>3/2</sub>

(461.2 eV) in the clusters were concordant with those of bulk ruthenium metal<sup>[14]</sup>.

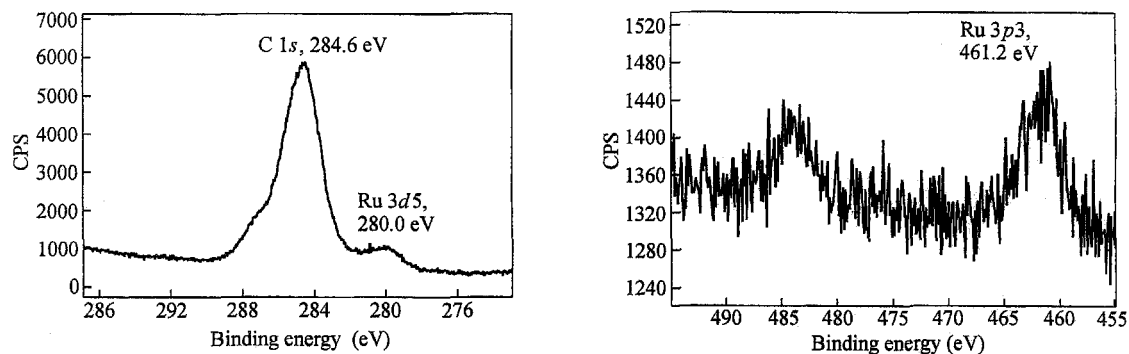


Fig. 2 XPS spectrograms for the ruthenium nanoclusters

Ruthenium nanoclusters can even be synthesized by the reduction of  $\text{RuCl}_3$  in other low boiling point alcohols, such as *iso*-butanol, *n*-propanol and ethanol, the average particle diameters are 1.7 nm, 1.8 nm and 2.5 nm, respectively. XPS and UV-Visible measurements proved that complete reduction of Ru(III) to Ru(0) was realized in preparation. Further research is now in progress.

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