



Water-Dispersible Ru(0) Nanorods With High Aspect Ratio: Microwave Synthesis, Characterization, Formation Mechanism and Catalytic Activity

SHUGE PENG*, XINJIE FAN, XIAOFEI LIU and JUN ZHANG

Key Laboratory of Polymer and Nanomaterials, College of Chemical Engineering and Pharmacy, Henan University of Science and Technology, 471003, Luoyang, P.R. China

*Corresponding author: Fax: +86 379 64232193; Tel: +86 379 64216956; E-mail: sgpeng@mail.haust.edu.cn

(Received: 12 January 2012;

Accepted: 9 November 2012)

AJC-12391

Water-dispersible Ru(0) nanorods with high aspect ratio have been successfully prepared by alcohol reduction using microwave heating. For the alcohol reduction, *n*-propanol was used as solvent and reducer and poly(N-vinyl-2-pyrrolidone) were used as stabilizer. The effects of the reactant concentrations on the morphology and size of the Ru(0) nanorods were discussed. The catalytic activity of water-dispersible Ru(0) nanorods was also investigated in hydrogen generation from the hydrolysis of sodium borohydride. The structure and morphology of the prepared samples were characterized by transmission electron microscopy, X-ray photoelectron spectrum, Fourier transform infrared spectrum (FT-IR) and elemental analysis (ICP-AES). A possible formation mechanism for the Ru(0) nanorods based on the experimental results was also proposed. The water-dispersible Ru(0) nanorods provided a lower apparent activation energy ($E_a = 33.4 \pm 1$ kJ/mol) than bulk Ru(0) metal and other reported Ru-based supported catalysts for the hydrolysis of NaBH₄.

Key Words: Ru(0) nanorods, Microwave heating, Alcohol reduction, Hydrogen generation.

INTRODUCTION

One-dimensional (1D) metallic nanostructures such as wires, rods, belts and tubes have been the focus of intensive research owing to their unique applications in electronics, photography, information storage, photonics, sensing, imaging, medicine, as well as novel chemical and catalytic properties¹. As an important member of the group of platinum metals, Ru nanostructures with well-defined dimensions represent a particular class of interesting nanomaterials to synthesize and study because of their unique and interesting activities as the catalyst²⁻⁴. In the case of catalysis, it is well-established that the activity of a metal nanocrystal can be enhanced by reducing its size⁵. The selectivity, however, is most sensitive to the packing of atoms on the surface or the exposed faces of a nanocrystal⁶. To utilize efficiently the metal nanocrystals, shape control of Ru nanostructure is the key.

However, much effort has been mainly focused on developing diverse methods to obtain size controllable Ru nanoparticles. Few researches are reported on the special morphologies of Ru nanostructures. Compared with extensive experimental studies on the synthesis of other noble metals nanorods, such as Ag, Au, Pt and Pd^{7,8}, little work has been made for the synthesis of Ru nanorods. By analogy with their study for Ag or other novel metals, similar anisotropic

nanostructures of Ru(0) should be created. Unfortunately, these methods looks like not to be applied to synthesize of Ru(0) nanorods. The main reason might due to the particular physico-chemical properties of Ru compare to the other novel metals. So far, the study on the morphology control of Ru(0) nanoclusters still remains a preparative challenge.

So far, only Harpeness *et al.*⁹, reported the preparation of rod-like Ru(0) nanostructure with the low aspect ratio of only 1.6. The Ru(0) nanorods with high aspect ratio have not been prepared. In the present study, we have attempted to synthesize Ru(0) nanorods with high aspect ratio by a microwave irradiation method in a one-pot. It was found that the diameter and length of Ru(0) nanorods could be controlled by changing the reaction concentration. To the best of our knowledge, this is the first synthesis of Ru(0) nanorods by a microwave irradiation method.

EXPERIMENTAL

Ruthenium chloride hydrate (RuCl₃·*n*H₂O, Ru content ≥ 37 %) was from Kunming Institute of Novel Metals. Poly(N-vinyl-2-pyrrolidone) (PVP, *m.w.* = 40,000) was obtained from Fluka. All the other reagents in the experiments were analytical pure grade and were used as received.

Preparation of Ru(0) nanorods: The typical preparation of Ru(0) nanorods as following: 0.8325 g of poly(N-vinyl-2-

pyrrolidone) (PVP) (2.5×10^{-2} mol, as monomeric unit) and 0.1961 g of RuCl_3 (2.5×10^{-3} mol) were dissolved by 50 mL of *n*-propanol in a 250 mL round-bottomed flask at room temperature under magnetic stirring and finally formed a dark red solution. Then the solution was irradiated to reflux by a modified domestic microwave oven (800 W, 2.45 GHz) with a refluxing apparatus. After the mixture was refluxed for a certain period of time, the colour of the solution changed from dark red to deep purple. In all the experiments the microwave oven was employed at 100 % power. The resulting product could be collected by centrifugation at 10000 rpm/min for 5 min and washed three times using ethanol, then dried 10 h under vacuum at 50 °C.

The diameter and length of Ru(0) nanorods could be controlled by changing the reaction concentration. The concentrations of Ru^{3+} were 0.75×10^{-3} , 2.5×10^{-3} and 15×10^{-3} mol/L at a fixed Ru^{3+} /PVP molar ratio of 10 in our experiments, corresponding to sample 1, 2 and 3, respectively.

Catalytic activity tests: The catalytic activity of PVP-stabilized Ru(0) nanorods was determined by measuring the amount of hydrogen generation from the hydrolysis of sodium borohydride solution using the modified water-displacement method¹⁰. A three-necked flask containing a Teflon-coated stir bar sodium borohydride was placed on a magnetic stirrer. Then, a graduated glass tube filled with water was connected to the three-necked flask to measure the volume of the hydrogen gas evolved in the reaction. Next, a certain concentration Ru(0) nanorods colloids were injected rapidly into the three-necked flask by glass syringe. Immediately the catalytic hydrolysis reaction of NaBH_4 was triggered. The starting point of the catalytic reaction was defined as the time when the catalyst was added to the flask. The volume of hydrogen evolved was measured by recording the displacement of water level at constant pressure. During the measurement, the solution temperature was measured and carefully controlled within ± 0.2 °C.

Characterization techniques of Ru(0) nanorods:

Transmission electron microscope (TEM) images were measured on a JEOL JSM-200 CX X-ray photoelectron spectrum (XPS) was obtained on an ESCA LAB 220I-XL photoelectron spectrometer using monochromated AlK_{α} radiation. All binding energy values were referred to carbon ($\text{C}_{1s} = 284.6$ eV). Infrared spectrum (IR) were carried out on a Thermo Nicolet Fourier Transform Spectrum using a KBr disk method. The content of Ru in the catalysts was determined on an HK-2000 ICP-AES.

RESULTS AND DISCUSSION

Characterization of Ru(0) nanorods: Fig. 1(a-c) shows TEM photographs of the PVP-stabilized Ru nanoclusters obtained at three different Ru^{3+} concentrations and a fixed Ru^{3+} /PVP molar ratio of 10. At the lowest Ru^{3+} concentration of 0.75×10^{-3} mol/L, a spherical particles with diameters of about 10-15 nm were produced [Fig. 1(a)]. When the Ru^{3+} concentration increased to 2.5×10^{-3} mol/L [Fig. 1(b)], it appeared that one-dimensional nanorod structure was obtained. At the Ru^{3+} concentration of 15×10^{-3} mol/L [Fig. 1(c)], larger nanorods with diameters of 20-40 nm and lengths of 100-600

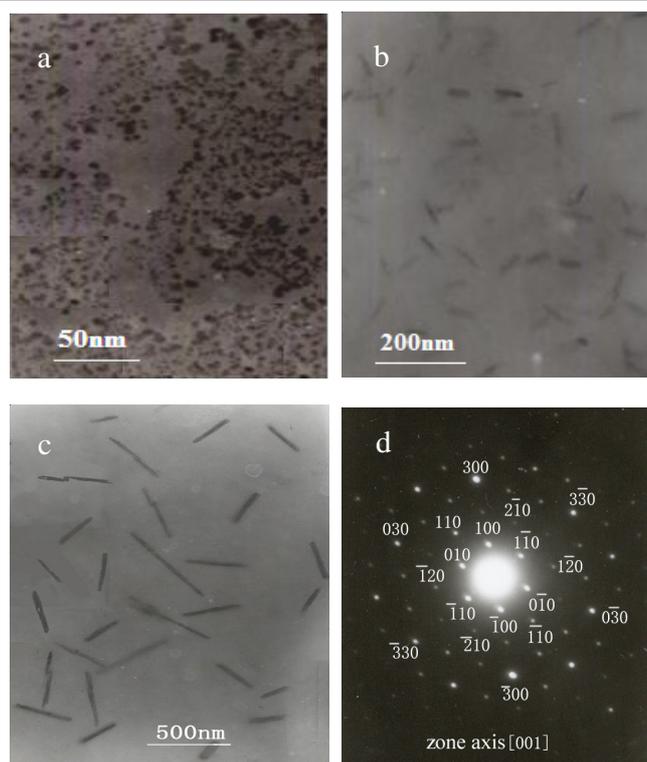


Fig. 1. TEM photographs of Ru(0) nanorods obtained by microwave heating method. The concentration of Ru^{3+} were (a) 0.75×10^{-3} mol/L, (b) 2.5×10^{-3} mol/L and (c) 15×10^{-3} mol/L at a fixed Ru^{3+} /PVP molar ratio of 10. (d) Electron diffraction pattern of PVP-stabilized Ru(0) nanorods shown in panel (c)

nm were observed. The aspect ratio of nanorods ranged between 5 and 40. These results indicated that the diameter and length of nanorods were greatly increased with increasing the Ru^{3+} concentration when Ru^{3+} /PVP molar ratio was fixed at 10. To investigate the crystal structure of nanorods, the electron diffraction pattern was also conducted. A typical result obtained for the nanorods in Fig. 1(c) is shown in Fig. 1 (d). The electron diffraction pattern of nanorods presented the single crystal diffraction design. The measuring d-spacings of (100) and (110) planes were 2.34 and 1.36 Å, respectively. All the other diffraction spots could be indexed as shown in Fig. 1(d) when the electron beam direction (zone axis) was [001], which was consistent well with the standard Ru metal data file (JCPDS Card: 06-0663)¹¹. In addition, ED pattern of nanorods showed the characteristics of hexagonal compact (*h c p*) structure, which was consistent with the structure of Ru metal, one of a few transition metals that crystallize only in a hexagonal compact structure.

To further confirm the formation of metallic Ru(0) nanostructures, XPS measurements were employed to determine the oxidation state of PVP-stabilized Ru nanorods. The results are shown in Fig. 2. The binding energies at 280.0, 483.8 and 461.2 eV in the PVP-coated Ru nanostructures (sample 3) were attributed to the binding energy of Ru $3d_{5/2}$, Ru $3p_{1/2}$ and Ru $3p_{3/2}$, respectively, which were consistent with those of Ru metal¹². Combined with the results of TEM, EDS and XPS, it could be clearly seen that Ru(0) nanorods had been successfully prepared by alcohol reduction using microwave heating.

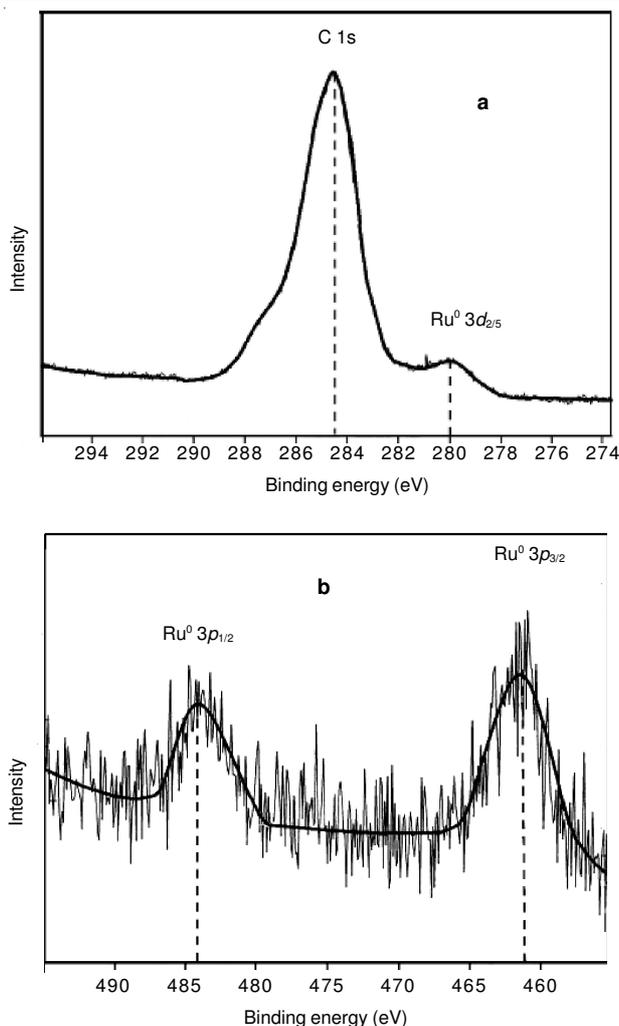


Fig. 2. XPS spectra of PVP-stabilized Ru(0) nanorods. The four vertical lines indicate the peak positions of the binding energies of C1s and Ru 3d_{5/2} (a) and Ru 3p_{1/2} and Ru 3p_{3/2}(b)

The combination between ruthenium and poly(N-vinyl-2-pyrrolidone) was investigated by FT-IR spectroscopic measurement, as shown in Fig. 3. In comparison with the FT-IR spectrum of PVP, the absorption band at 2960, 1660, 1280 and 1070 cm⁻¹ were assigned to the vibration models of C-H, C-O, N-OH and C-N, respectively, indicating PVP had been present on the surface of Ru and served as a capping agent. Furthermore, comparative FT-IR spectra of the PVP-stabilized Ru(0) nanorods and PVP indicated that the bonding mode of PVP on the nanoclusters surface was due to the carbonyl group coordinated to the Ru atoms on the nanoclusters surface¹³.

Elemental analysis showed that the Ru content in samples 1, 2 and 3 were almost 8.8 wt. %, close to the initial Ru content in solution: 9.1 wt. %.

Formation mechanism of Ru(0) nanorods: The formation of anisotropic Ru nanorods probably started by the following reactions according to reduction mechanism of metallic ions in alcohol reduction proposed by Fievet *et al.*¹⁴:

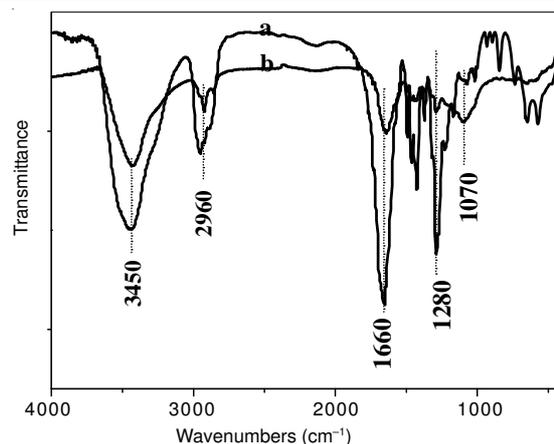
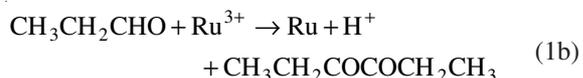


Fig. 3. FT-IR spectra of PVP (a) and PVP-stabilized Ru(0) nanorods (b) prepared by microwave heating method

As a result of the above reduction process, nucleation and growth processes of Ru nanoparticles obeyed the ostwald-ripening theory. Poly(N-vinyl-2-pyrrolidone) acted as a kinetically controller of the growth rates of different crystalline faces through adsorption and desorption. The PVP adsorbed on specific crystalline surfaces could significantly decrease their growth rates and led to a highly anisotropic growth¹⁵. With the assistance of PVP, some of the large nanoparticles were grown into anisotropic rod-shaped structure. In the oil-bath heating, shuttle-like Ru nanostructures with aspect ratios below 5 were dominantly produced¹². Generally speaking, microwave heating contributes to the nucleation and growth of metal nanostructures. Ru nanorods under microwave heating must be induced by bursting nucleation due to rapid and homogeneous dielectric heating, which could not be achieved by oil-bath heating.

Catalytic activity: The effect of the temperature on the catalytic activity was investigated by varying temperatures in the range of 10-30 °C starting with the substrate concentration of 150 mM NaBH₄ and catalyst concentration of 0.75 mM Ru(0) nanorods (sample 3), as shown in Fig. 4. The values of hydrogen generation rate were determined from the linear portions of the H₂ volume *versus* time plots at five different temperatures. As the solution temperature increased, the hydrogen generation rate increased. According to the Arrhenius equation, the relationship of the reaction rate and the activation energy could be expressed as the followings:

$$\ln r = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln k_0$$

where k_0 is the pre-exponential parameter, E_a the activation energy of the reaction, R the gas constant (8.314 J mol⁻¹ K⁻¹) and T is the reaction temperature. The inset shows the Arrhenius plot, $\ln r$ *versus* the reciprocal absolute temperature (1/T). According to the slope of the fitted line (-4.02), the apparent activation energy for the hydrolysis of NaBH₄ catalyzed by Ru(0) nanorods could be calculated as 33.4 ± 1 kJ/mol based on the Arrhenius relationship. Activation energies for the hydrolysis reaction of sodium borohydride solution catalyzed by other Ru-based catalysts are listed in Table-1 for comparison. Apart from the activation energy found by Özkar and Zahmakiran¹⁶ with acetate stabilized Ru(0) nanoclusters,

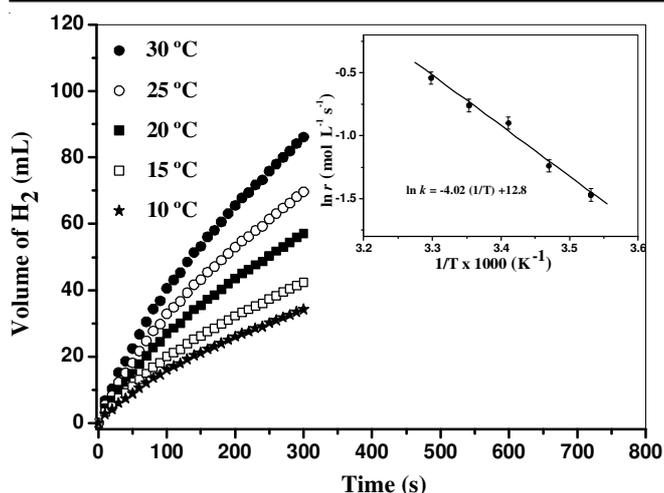


Fig. 4. Volume of hydrogen *versus* time plot depending on the temperature, and the Arrhenius plot, $\ln r$ *versus* the reciprocal absolute temperature $1/T$ (the inset) for the hydrolysis of NaBH_4 (150 mM) catalyzed by Ru(0) nanorods at various temperatures in the range of 10–30 °C. The error bars on the plot reflect an around $\pm 5\%$ measurement error of the hydrogen generation rate

TABLE-1
ACTIVATION ENERGY FOR VARIOUS RU-BASED
CATALYST SYSTEMS USED FOR THE
HYDROLYSIS OF SODIUM BOROHYDRIDE

Catalyst	Activation energy (kJ mol^{-1})	Reference
Ru(0) nanorods	33.4	This work
Ru(0) nanoclusters	28.5	16
Ru/LiCoO ₂	68.5	17
Ru/IRA-400	56	18
Ru/IRA-120	50	19
Ru-promoted sulphated Zr	76	20
Ru/C	66.9	21
Ru/Graphite	61.1	22

the Ru(0) nanorods stabilized by PVP provided the lowest activation energy for the hydrolysis of sodium borohydride. The high catalytic activities of Ru(0) nanorods for hydrogen generation from NaBH_4 hydrolysis might due to the good dispersion in water and the weak coordination between PVP and Ru(0) metal.

Conclusion

In summary, Ru(0) nanorods stabilized by PVP with high aspect ratio were obtained in a one pot under microwave irradiation for the first time. The obtained products showed the

single crystalline structure of *hcp* Ru(0) metal and typical one-dimensional nanorod structure. The diameter and length of nanorods could be varied by changing the concentrations of the Ru^{3+} and PVP. The kinetics of the hydrolysis of NaBH_4 catalyzed by water-dispersible PVP-stabilized Ru(0) nanorods revealed that Ru(0) nanorods were highly active catalyst even at room temperatures, providing lower apparent activation energy ($E_a = 33.4 \pm 1 \text{ kJ/mol}$) than bulk Ru(0) metal and other reported Ru-based supported catalysts for the hydrolysis of NaBH_4 .

ACKNOWLEDGEMENTS

This work was financially supported by National Natural Science Foundation of China (No. 21101058).

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