

Facile Synthesis Methods of Ag and Ru Powder

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Abstract—In this work, both Ag and Ru powders with high purity and good crystallinity were successfully synthesized. Both methods are facile and high yield. As for Ag powder, the best condition to synthesize monodispersed Ag powder is discussed. The Ru powder synthesis process is divided into two parts: Reaction in aqueous phase and calcination in hydrogen ambient.

Index Terms—silver, ruthenium, synthesis, wet-chemical, calcinations

I. INTRODUCTION

As noble metal, silver (Ag) has received many attentions because of its high melting point, good electrical/thermo conductivity, good chemical stability and catalytic activity etc. Synthesis of Ag powder has always been a good research point. There are many chemical reduction agents such as methanol [1], organic amine [2], hydroboron [3] and sodium hypophosphite [4] etc. chosen to synthesize Ag though wet-chemical method.

Also as an important member of the group of platinum metals, ruthenium has been known to show very unique and interesting activities as a catalyst [5]. Several approaches to the preparation of metal Ru nanoparticles have been reported, such as chemical reduction [6], and thermal decomposition [7].

In this work, both Ag and Ru powders with high purity and good crystallinity were successfully synthesized. Both methods are facile and high yield.

II. EXPERIMENT METHODS

A. Chemicals and Materials

Silver nitrate (AgNO_3 , reagent-grade) and Ruthenium (III) chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, reagent-grade) were purchased from Sino-platinum Co., Ltd., ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, reagent-grade), glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, reagent grade), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot n\text{H}_2\text{O}$, 85%, reagent-grade), ammonium hydroxide ($\text{NH}_3 \cdot n\text{H}_2\text{O}$, reagent-grade), sodium carbonate (Na_2CO_3 , reagent-grade), nitrate acid (HNO_3 , 65%), Arabic gum ($\text{C}_{10}\text{H}_{18}\text{O}_9$, reagent-grade), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.5%,) were all purchased from Sinopharm Chemical Reagent Co., Ltd. The water used in the experiment was taken from Milli-Q purification system.

B. Synthesis and Characterization of Silver Powder

Arabic gum powder (gum to AgNO_3 mass ratio 4wt% and 10wt%) was dispersed in 200ml water to make the base solution in 1000ml beaker and the pH was adjusted to ~1-3 by the HNO_3 . The AgNO_3 was dispersed in 250ml water to make various concentrations of solutions (1M, 0.8M, 0.4M and 0.08M). Similar to AgNO_3 , 250ml ascorbic acid (also called Vitamin C or VC) solution was made at various concentrations (0.8M, 0.4M and 0.08M). The two solutions were simultaneously dropwise added into base solution. The base solution was under magnetic stirring in room temperature (25 °C). After the drop, the solution was stirred for another 30min to make sure the reaction was completed. The sediment was washed by water and ethanol for several times and dried in 50 °C oven in air. Characterization of the powders was achieved by X-ray diffraction XRD, Model PW 3040/60; PANALYTICAL B.V, Almelo, the Netherlands) operating at 40kV/40mA with nickel-filtered $\text{Cu K}\alpha$ radiation. Particle and substrate morphologies and Energy Dispersive X-Ray Spectrometer (EDX) were observed via scanning electron microscopy (SEM, JSM-6510A; JEOL, Tokyo, Japan) operated at 10kV.

C. Synthesis and Characterization of Ruthenium

1) Glucose Case

Gum powder (3wt% mass ratio to RuCl_3) was added into 150ml RuCl_3 base solution (0.1M). 50ml 0.4M ammonium hydroxide was drop wise added into the base solution which under magnetic stirring and temperature is 80 °C. After the drop, the reduction solution (100ml, 0.075M glucose, mixed with 1ml ammonium hydroxide) was slowly dropwise added into base solution. After the reaction was completed, the sediment was washed by water and ethanol for several times, and air dried in 50 °C oven. The as-made powder was then characterized by X-ray diffraction (XRD, Model PW 3040/60; PANALYTICAL B.V, Almelo, the Netherlands) operating at 40kV/40mA with nickel-filtered $\text{Cu K}\alpha$ radiation. Particle and substrate morphologies and Energy Dispersive X-Ray Spectrometer (EDX) were observed via scanning electron microscopy (SEM, JSM-6510A; JEOL, Tokyo, Japan) operated at 10kV. And after the characterization, the powder was calcined under 600 °C in hydrogen furnace for 2h. The calcined powder was also characterized by the aforesaid equipments.

2) Hydrazine Hydrate Case

Gum powder (3wt% mass ratio to RuCl_3) was added into 50ml RuCl_3 base solution (0.1M). 50ml 0.15M Na_2CO_3 was dropwise added into the base solution which under magnetic stirring and temperature is 60 °C. After the drop, the reduction solution (100ml, 0.15M hydrazine hydrate) was slowly dropwise added into base solution. After the reaction was completed, the sediment was washed by water and ethanol for several times, and dried in 50 °C oven in air. The as-made powder was then characterized by X-ray diffraction XRD, Model PW 3040/60; PANALYTICAL B.V, Almelo, the Netherlands) operating at 40kV/40mA with nickel-filtered $\text{Cu K}\alpha$ radiation. Particle and substrate morphologies were observed via scanning electron microscopy (SEM, JSM-6510A; JEOL, Tokyo, Japan) operated at 10kV. And after the characterization, the powder was calcined under 600 °C in hydrogen furnace for 2h. The calcined powder was also characterized by the former methods.

III. RESULTS AND DISCUSSION

A. Silver Powder

As shown in Fig. 1, the morphology evolution of Ag crystals with reducing AgNO_3 concentration is significant. From Fig. 1a-d, the particle size increased from ~200nm up to ~1 μm . The increasing particle size is mainly attributed to the decreasing of Ag^+ concentration. Based on LaMer and co-workers module [8], the crystal nucleation and growth are highly depended on metal atom concentration. If the concentration is sufficient higher than the critical supersaturation, the nucleation will dominate the process. Continuously consumption of Ag atoms will pull the system back to crystal growth process. The high concentration of Ag^+ will provide a sufficient high reduction rate thus generates excessive Ag atoms to sustain the system in nucleation region. Although the dispersing agent is introduced in the system, the fast-formed small crystals cannot be well separated as shown in Fig. 1a-d; the aggregation of Ag NCs is obvious. Further increase gum mass ratio to AgNO_3 to 10wt%, the Ag NCs can be well separated in Fig. 1e and Fig. 1f. The role of gum as dispersing agent can be summed as follows: After the attachment of oxygen atoms to Ag atoms in solution, the hydrophilic group of gum can provide a better dispensability of Ag crystals in solution. Moreover, the steric hindrance of gum can physically prevent the NCs aggregation. Thus with the sufficient amount of gum, the Ag crystals can be well separated.

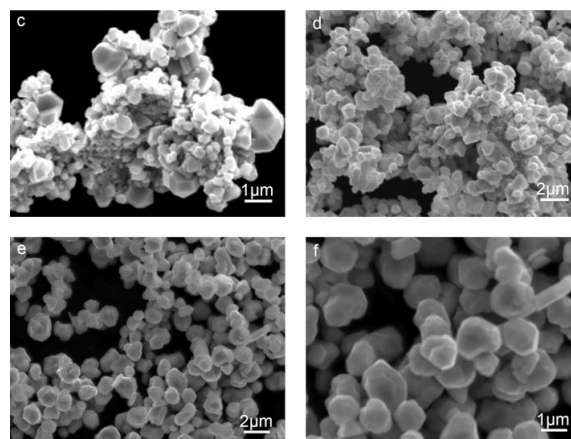
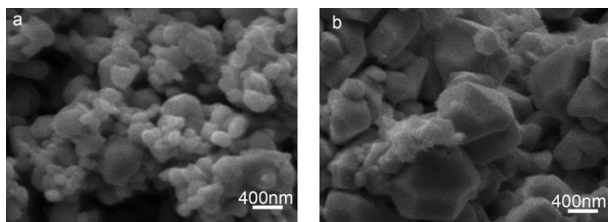


Figure 1. SEM images of Ag powders made under different conditions: (a) 1M AgNO_3 , 0.8M VC; (b) 0.8M AgNO_3 , 0.8M VC; (c) 0.4M AgNO_3 , 0.4M VC; (d) 0.1M AgNO_3 , 0.1M VC and (e), (f) 0.1M AgNO_3 , 0.1M VC. The gum added in (a)-(d) is 4wt% mass ratio to AgNO_3 , 10wt% in (e) and (f).

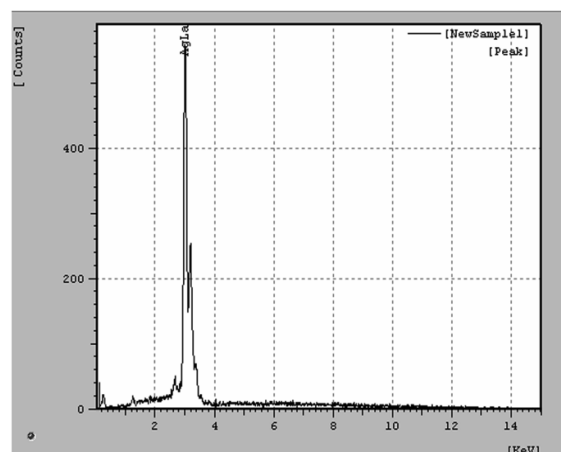


Figure 2. EDX spectroscopy of Ag powder of Fig. 1e

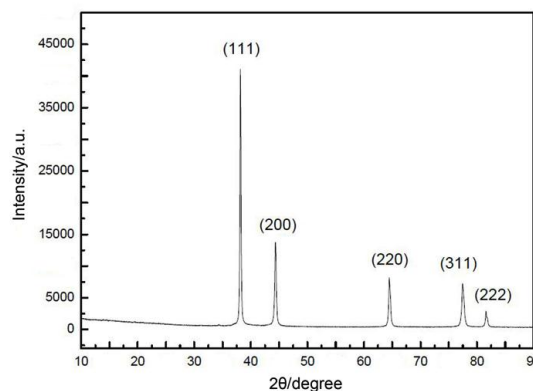


Figure 3. XRD patterns of Ag powder in Fig. 1e

Fig. 2 is the EDX spectroscopy of Ag powder in Fig. 1e. Clear and sharp peaks reveal the high purity of Ag NCs. Also, as shown in Fig. 3, the XRD patterns can be well indexed to Ag (JCPDS Card NO. 89-3722) indicating the high purity and good crystallinity of the sample.

B. Ruthenium Powder

Two different synthesis routes were introduced to produce pure Ru powder. It is noticed that unlike Ag case, the reduction environment is basic. There are not many differences between morphology of as-made particles of these purchase methods. Relatively small particle size and obvious aggregation can be found in each sample (Fig. 4a and Fig. c). But after the analysis of XRD patterns (Fig. 6), the as-made powders were found amorphous. This proves that with the serials reactions in aqueous phase, the Ru^+ was not reduced to Ru^0 , but formed a new compound, which is easy to separate from solution. Then to achieve fully reduction of Ru^+ , the powder was calcined under 60 °C for 2h in hydrogen furnace. Following the XRD analysis, the XRD peaks can be well indexed to Ru (JCPDS Card NO. 6-0663) indicating that the Ru powder was pure phase. However, as the temperature of calcining process is too high, the dispersing agent designed for aqueous reaction is totally burned out. The particle is badly aggregated (Fig.4b and d) and the large particles can hardly be separated by grind in mortar. The further analysis by EDX spectroscopy indicates the high purity of Ru powder (Fig. 5). According to the data, there are rarely obvious differences between two methods. Considering the toxic of hydrazine hydrate the glucose is better for reduction.

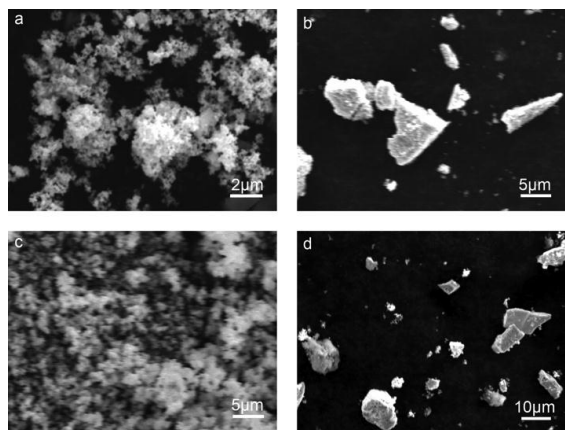


Figure 4. SEM images of ruthenium powder. (a) is glucose case powder before calcined, (c) is hydrazine hydrate case powder, (b) and (d) are images of powders after calcined respectively

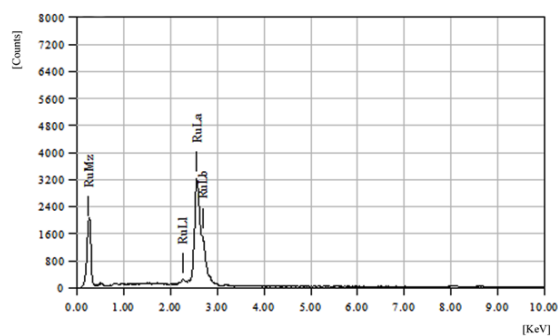


Figure 5. EDX spectroscopy of Ru powder of Fig. 4b

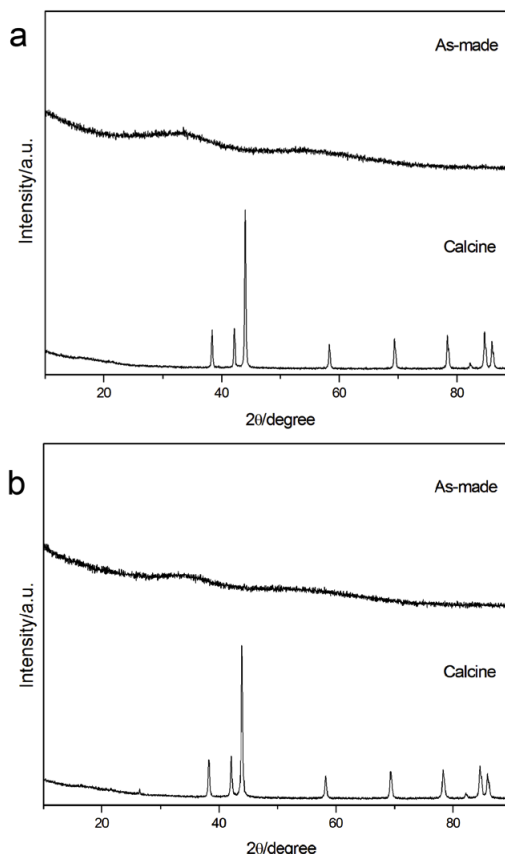


Figure 6. XRD patterns of (a) Ru powder in glucose case, (b) Hydrazine hydrate case

IV. CONCLUSION

In this work, both high purity and good crystallinity Ag and Ru powders were successfully synthesized. Both methods are facile and high yield. As for Ag powder, the best condition to synthesize monodispersed Ag powder was found. And the role of gum was discussed as the dispersing agent. The Ru powder synthesis process is divided into two parts: reaction in aqueous phase and calcination in hydrogen ambient. It is noticed that after the calcination, the particle aggregation was more seriously. To overcome this deficiency, further milling is necessary if smaller size particle is required.

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