A Rational Low-Temperature Approach to the Synthesis of Gladiate Ruthenium Nanoparticles

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Herein, a rational low-temperature approach has been successfully developed to prepare gladiate Ru nanoparticles with a pure hexagonal phase, which were confirmed by XRD, XPS, and TEM results. The reason for the formation of gladiate particles was also discussed.

In recent years, nanoscale noble metal particles have been the subject of much intensive research due to their fundamental significance for addressing some basic issues of the quantum size effect derived from the dramatic reduction of the number of free electrons[1] as well as their potential applications as advanced materials with intriguing chemical, electronic, magnetic, optical, thermal, and catalytic properties.[2] A great effort has been directed to preparing noble metal nanoparticles by many methods such as chemical reduction,[3] UV photolysis,[4] thermal decomposition,[5] metal vapor deposition,[6] electrochemical reduction,[7] sonochemhemical decomposition,[8] microwave irradiation,[9] rapid expansion of supercritical fluid solutions (RESS)[10] and the recently reported solvothermal route.[11]

Herein, we selected metal ruthenium as the focus of this effort because this material exhibits excellent catalytic properties for many chemical reactions.[12] It is well known that catalytic activity and selectivity are dependent on the particle size and shape of the metal nanoparticles. Therefore, the synthesis of ruthenium with well-controlled shape and size could be critical for its applications. We have developed a low-temperature controlled hydrothermal approach[13] to synthesize ruthenium nanoparticles. The chemical reaction we employed for the synthesis can be formulated as:

$$4RuCl_3 + 3N_2H_4 \rightarrow 4Ru + 3N_2 + 12HCl$$

In a typical procedure, analytically pure $RuCl_3 \cdot xH_2O$ (0.5 g) and slightly excessive amount of hydrazine were put in distilled water at room temperature to form a dark-brown solution. The mixture was stirred strongly for about 0.5 h and then transferred to a Teflon-lined stainless steel autoclave, which was filled with distilled water up to 95% of the total volume and maintained at 120 °C for 12 h. After the reaction was completed, a grayish-black precipitate was filtered off, washed with absolute ethanol and then dried under vacuum. Finally, the sample was collected for characterization.

The filtrate was strongly acidic, which was checked by a pH indicator paper ($pH = 1$–2) and indicated that $RuCl_3$ was reduced to elemental ruthenium in one-pot reaction. Conclusive evidence for the formation of Ru metal comes from X-ray diffraction (XRD) data. The XRD measurement was performed on a Rigaku D/max-rA X-ray diffractometer with Ni-filtered graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). All the diffraction peaks of the XRD pattern shown in Figure 1 can be readily indexed to a pure hexagonal phase of Ru metal. Refined lattice parameters $a = 2.706 \pm 0.002$ Å and $c = 4.268 \pm 0.004$ Å are extracted from the XRD data, which are in good agreement with those of Ru metal reported in the JCPDS diffraction file ($a = 2.7058$ Å and $c = 4.2619$ Å).[14] No impurity peaks have been found in the experimental range. This XRD pattern indicates that the reduction of Ru^{3+} is complete under current synthetic conditions; consequently, pure Ru metal was obtained. From the widths of the XRD peaks, the average crystalline size of the product is determined to be 25.4 nm according to the Scherrer formula.[15] Further evidence for the composition of the product can be derived from X-ray photoelectron spectra (XPS). The XPS was recorded on an ESCALab MKII X-ray photoelectron spectrometer with Mg Kα X-ray as the excitation source. The results obtained in the XPS analysis were corrected by referencing the C 1s line to 248.6 eV. A little oxygen was detected by XPS, which may come from adsorbed H_2O on the surface of the particles. The binding energy of Ru $3d_{5/2}$ is 280.6 eV, which is slightly larger than that in bulk Ru metal (280.1 eV). This can be attributed to the small metal clusters of Ru.[16]

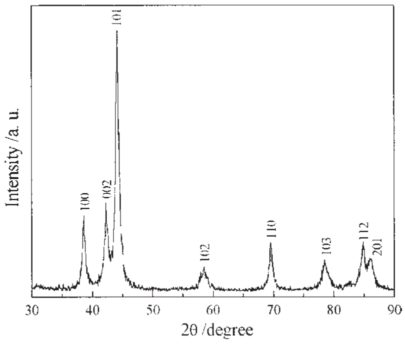

Figure 1. XRD pattern of the sample obtained by hydrothermal treatment.

The morphology of the sample was studied by transmission electron microscopy (TEM), which was carried out on a Hitachi Model H-800 transmission electron microscope with an accelerating voltage of 200 kV. A typical TEM image of the sample is shown in Figure 2. It can be seen that the metal particles are agglomerated. The particle size of the agglomerated clusters is in the range of 70–130 nm, which is larger than the result calculated from the Scherrer equation. Interestingly, these particles are gladiate. In order to study the reason for the formation of the gladiate structure, we have carefully investigated this approach. Very recently, ruthenium nanoparticles were synthesized by using the reaction between $RuCl_3$ and C_2H_5OH (or CH_3OH) at 175 °C for 24 h.[11] Generally speaking, the oxidizing ability of $RuCl_3$ is relatively weak. Therefore, in this letter, we chose hydrazine, which is of stronger reducibility than that of alcohol, as the reducing agent in order to decrease the reaction temperature.

However, the reaction between $RuCl_3$ and hydrazine can not proceed when just stirring without heating. During the hydrothermal treatment, the reaction proceeds. This strongly exothermic reaction ($\Delta H^0 = -1337.6\,\text{kJ/mol}$)[17] leads to the formation of temperature gradient of hydrothermal solution, then will induce the formation of gladiate particles. However, for open system, only irregular particles were observed if this reaction mixture was refluxed in an oil bath at the same temperature, the TEM image of which is shown in Figure 3. From the image, we can not find any gladiate particle. In addition, other researchers also observed the phenomenon that the morphology obtained in closed system was different from that obtained in open system.[18]

Figure 2. TEM image of the gladiate product obtained by hydrothermal approach.

Figure 3. TEM image of the as-prepared Ru particles in open system.

In summary, we have successfully synthesized gladiate Ru nanoparticles via a rational low-temperature approach. The product was characterized by XRD, XPS, and TEM. Finally, the reason for the formation of gladiate particles was also discussed.

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