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Synthesis and Characterizations of Hollow Spheres of Platinum Nanoparticles Using Se@Pt as Precursor

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Hollow spheres of platinum nanoparticles with an average diameter of 50-200 nm have been prepared by spheres of Se@Pt reaction with aqueous hydrazine. The products were characterized by X-ray powder diffraction, transmission electron microscopy, X-ray photoelectron spectra and and UV-visible absorption spectroscopy. The sizes of the nanoparticles of platinum were estimated by Debye-Scherrer formula according to XRD spectrum.

Keywords: Hollow spheres, Nanoparticles, Sol-gel, Fish gelatin, Platinum.

INTRODUCTION

Hollow spheres of nanometer to micrometer dimensions are pursued with great interest because of possible technical applications in optics[1], photonic catalysis[2,3], lithium ion batteries[4], medicine release[5] and targeted drug delivery[6]. Platinum plays an important role in a wide variety of applications. For examples, it serves as an excellent catalyst for CO/NOx oxidation in catalytic converters, production of nitric acid, refining of petroleum, and many organic reactions such as hydrogenations[7]. It is also a critical component of the fuel cell technology, where platinum acts as the most effective electrocatalyst for the oxygen reduction reaction and fuel (including hydrogen, methanol, ethanol and formic acid) oxidation reaction[8]. In the synthesis of platinum nanoparticles, control over the shape and size has been one of the important and challenging tasks[9]. Many studies on the methods for the preparation of platinum nanoparticles were reported, such as controlled chemical reduction[10,11], electrochemical synthesis[12], irradiation method[13], thermal decomposition process[14,15] and bio-directed synthesis[16]. In this paper we report a method to synthesize spheres of Se@Pt by a very simple reaction of Na_2SeO_3, $H_2PtCl_6{\cdot}6H_2O$ and $(NH_2OH)_2{\cdot}H_2SO_4$ in the presence of fish gelatin. Hollow spheres of platinum nanoparticles have been prepared by spheres of Se@Pt reaction with aqueous hydrazine. The hollow spheres of platinum were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS) and UV-visible absorption spectroscopy.

EXPERIMENTAL

All the reagents used in the experiment were of the analytical purity. Na_2SeO_3, $H_2PtCl_6{\cdot}6H_2O$, NaOH, $(NH_2OH)_2{\cdot}H_2SO_4$, C_2H_5OH, aqueous hydrazine and in the presence of fish gelatin were purchased from Shanghai Chemical Reagent Factory (China). Doubly distilled water was used throughout.

Powder XRD patterns were recorded on a Shimadzu X-ray diffractometer XD-3A (CuK_α radiation, λ = 0.15418 nm). TEM was performed using a JEOL-JEM 200CX instrument. The samples used for TEM observations were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 10 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. XPS were recorded on ESCALAB MKΠ instrument. A UV-3100 photospectrometer was used to record the UV-visible absorption spectra of the as-prepared platinum nanoparticles.

Standard procedure for the preparation of hollow spheres of platinum nanoparticles: Preparation of spheres of Se@Pt. 0.01 mol L^{-1} Na_2SeO_3 solution and 0.1 mol L^{-1} $(NH_2OH)_2{\cdot}H_2SO_4$ solutions were prepared respectively, in which 5 % in the presence of fish gelatin. 20 mL of 0.01 mol L^{-1} Na_2SeO_3 solutions and same volume of 0.1 mol L^{-1} $(NH_2OH)_2{\cdot}H_2SO_4$ solutions were added quickly with stirring for 0.5 h under agitation at 10 °C. Then, the 20 mL of 0.02 mol L^{-1} $H_2PtCl_6{\cdot}6H_2O$ solution was carried in the system of reaction. The mixture solution was stirred at 400 rpm at 25 °C for 8 h. The precipitates of as-prepared were separated by centrifugation from the solution. The reactor obtained was

washed thoroughly with doubly distilled water and vacuum dried at room temperature overnight.

Synthesis of hollow spheres of platinum nanoparticles: The precipitates of as-prepared spheres of Se@Pt were reacted with 50 mL of aqueous hydrazine solutions at 80 °C for 10 h. The platinum nanocrystals obtained were washed thoroughly with doubly distilled water and vacuum dried at room temperature overnight.

RESULTS AND DISCUSSION

XRD study: An XRD pattern of hollow spheres of platinum was given in Fig. 1. The XRD spectrum contains five peaks that are clearly distinguishable. All of them can be perfectly indexed to crystalline platinum, not only in peak position, but also in their relative intensity. The peak positions are in good agreement with those for platinum powder obtained from the International Center of Diffraction Data card (ICDD, formerly JCPDS, 04-0802). The size of the subunits of the polycrystalline platinum particles was calculated to be about 3 nm according to half-width of the diffraction peaks using Debye-Scherer equation.

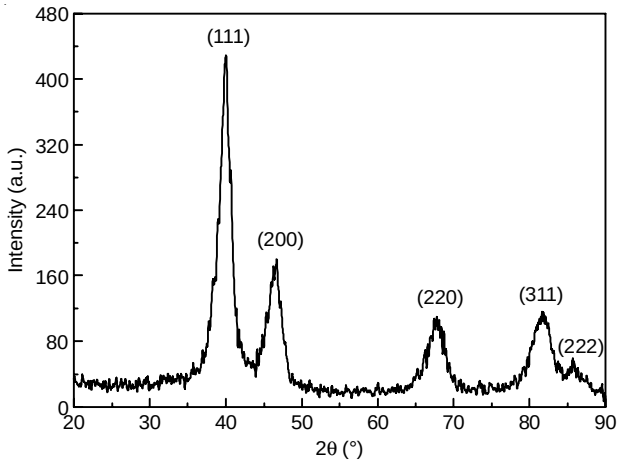

Fig. 1. XRD patterns of the hollow spheres of platinum nanoparticles

TEM measurements: The morphology of the as-prepared Se@Pt and platinum was studied by TEM. The spherical structures of the Se@Pt were observed in Fig. 2a. The spherical hollow structures of the product of platinum were obtained (Fig. 2b). As was seen in the TEM picture of hollow sphere of platinum, the spherical surface was an aggregation of many small nanoparticles. The hollow spheres of platinum with the dimensions of about 50-200 nm can be observed in Fig. 2b.

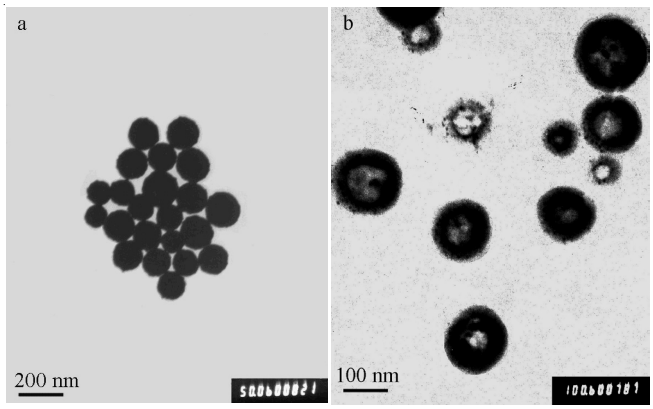

Fig. 2. TEM micrographs of (a) spheres of Se@Pt; (b) the hollow spheres of platinum

XPS measurements: The wide XPS picture of the product is shown in Fig. 3. The high-resolution XPS spectrum for the Pt_{4f} region of the as-prepared platinum nanoparticles is shown in Fig. 4. The peaks at 71.1 and 74.4 eV, which was corrected with reference to C_{1s} (284.6 eV), corresponding to the binding energy of $Pt^{7/2}{}_{4f}$ and $Pt^{5/2}{}_{4f}$ are in good agreement with the data observed for Pt[17]. Thus, the XPS results prove that the sample is composed of platinum. This result is in good agreement with XRD result.

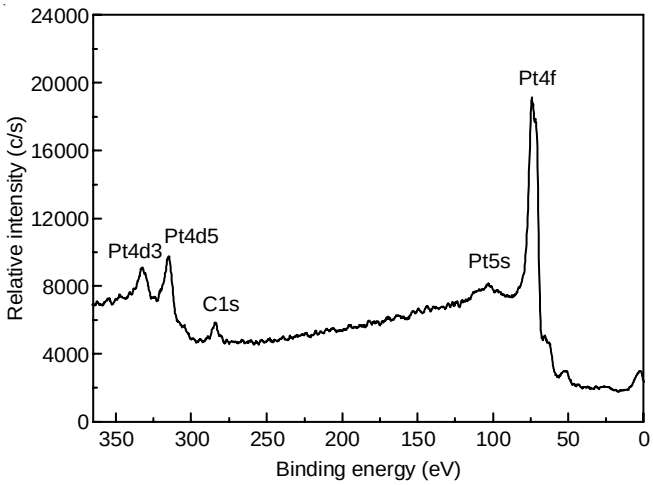

Fig. 3. Wide X-ray photoelectron spectrum of the as-prepared hollow spheres of platinum nanoparticles

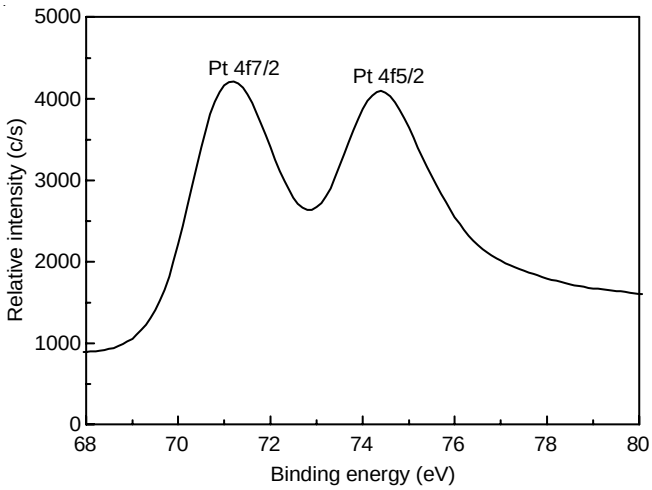

Fig. 4. High-resolution XPS spectrum taken for the Pt_{4f} region of the as-prepared hollow spheres of platinum nanoparticles

Optical properties: The as-prepared sample were well dispersed in ethanol to form a transparent solution by ultrasonic vibration for 10 min. UV-visible absorption spectrum of the Se shows one absorption peak at 410 nm in Fig. 5a. As shown in Fig. 5b, c, the absorption peak of the as-prepared Se@Pt and hollow sphere of platinum at 210 nm, respectively.

Proposed reaction path: Based on the investigation on the formation of hollow spheres, the possible mechanism may be summarized as below:

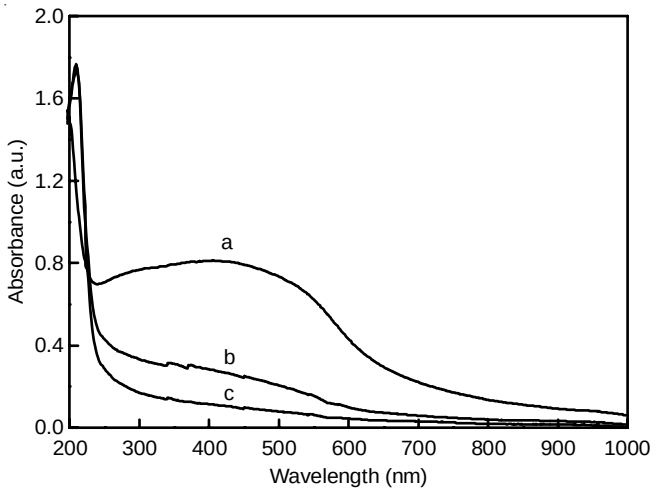

Fig. 5. UV-visible absorption spectra of (a) Se; (b) spheres of Se@Pt; (c) as-prepared platinum

$$Na_2SeO_3 + 2(NH_2OH)_2 \cdot H_2SO_4 + 2NaOH \longrightarrow Se + 2N_2 + 2Na_2SO_4 + 9H_2O$$

$$H_2PtCl_6 + 2(NH_2OH)_2 \cdot H_2SO_4 + 10NaOH \longrightarrow Pt + 2N_2 + 2Na_2SO_4 + 6NaCl + 14H_2O$$

$$2Se + NH_2NH_2 + 4NaOH \longrightarrow 2Na_2Se + N_2 + 4H_2O$$

In the experiment, we employed hydroxylamine sulfate as reducing agents. The reducing ability of hydroxylamine hydrosulfate increased as the pH value of the reaction solution was increased. The pH value was adjusted to 9-10 using NaOH in the course of the reaction. The fish gelatin acts as an inhibitor of the direct reaction and coagulation of the produced nanoparticles. We employed Se@Pt spheres as the precursory solid (TEM micrograph of the Se@Pt spheres is shows in Fig. 2a). Then, the hollow spheres of platinum nanoparticles were prepared by Se was dissolved into aqueous hydrazine solutions. The controllable synthesis routes for hollow spheres of platinum nanoparticles as shown in Fig. 6.

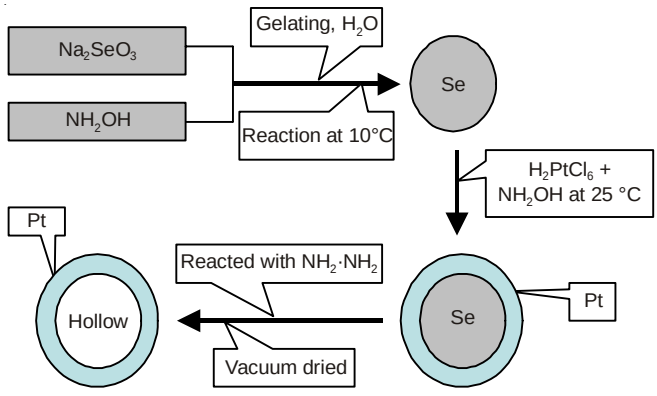

Fig. 6. Basic process for preparation of hollow spheres of platinum

Conclusion

Hollow spheres of platinum nanoparticles with an average diameter of 50-200 nm have been prepared by spheres of Se@Pt reaction with aqueous hydrazine. The reaction path of hollow spheres platinum was proposed. It is expected that the method can be extended to prepare hollow spheres of other metals.

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