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Synthesis and application in surface-enhanced Raman scattering property of fist-like platinum microparticles

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ABSTRACT

Platinum microparticles with fist-like shape were synthesized through the reduction of chloroplatinic acid (H_2PtCl_6) with absolute ethanol under hydrothermal atmosphere, whose diameters and lengths can be effectively controlled by varying H_2PtCl_6 concentration. Unlike previous methods for only synthesizing platinum nanoparticles of about 10 nm or even smaller, the use of the hydrothermal and surfactant-free system provides a shortcut strategy to prepare micron-sized platinum particles. Surface-enhanced Raman scattering (SERS) investigation demonstrated that the microfists have SERS activity and similar SERS enhancement to an electrochemically roughened Pt electrode. We believe that the Pt microfists should be not only an ideal model to understand and calculate the SERS enhancement mechanism of electrochemically roughened transitional metal but also may find practical applications for electronics, photonics, and microdevices.

1. Introduction

Platinum (Pt) materials have been intriguing scientists' tremendous interest because they play an important role in a wide variety of applications such as catalysis, fuel cell, electro-optical device, and many other areas [1]. It is well known that the properties of metal particles depend strongly on their composition, structure, size, and shape [2–5]. Therefore, it is a central theme of contemporary material chemistry to control the morphology (i.e., composition, structure, size, and shape) and further the ease of varying their unique physical and chemical properties. At present, Pt nanomaterials with sphere, wire, and other novel shapes have been easily fabricated [6–9]. However, micron-scale Pt materials, as a more extensively applied promising material because of its better properties and easier manipulating size [10], have still been prepared rarely. Nevertheless, Kikuchi et al. have successfully fabricated micron-scale Pt spheres through aluminum anodizing, laser irradiation, electroplating, and lifting off [11]. Regretfully, this method needs rather perplexing process and operation.

Surface-enhanced Raman scattering (SERS) has attracted widespread attention because of its extremely high surface sensitivity since Fleischmann, Hendra, and McQuillan for the first time reported a surface Raman spectrum from pyridine adsorbed on an electrochemically roughened silver electrode in 1974 [12]. Subsequently, Tian's group has been done a large quantity work to extend SERS from noble metals (e.g., Au, Ag, and Cu) to transition metals (e.g., Pt, Ru, Pd, Fe, Co, and Ni) [13]. It is well known that the SERS of a probe molecule on an electrochemically roughened electrode is due to its roughness surface. However, its structure, containing all sorts of nanometer-scale, submicron-scale, and micron-scale dimensions, is very complex and difficult to accurately quantify its surface area and surface roughness, which inevitably blocks understanding SERS enhancement mechanism. Therefore, it is of key importance to prepare a SERS substrate with a similar structure of electrochemically roughened electrode by a solution-phase synthesis route.

In the present work, we report a very simple strategy for the synthesis of Pt microparticles with fist-like shape. The microfists consist of coupled submicron-scale Pt particles while the surface of Pt submicrons possesses a lot of Pt nanoparticles of about 17 nm again. The Pt microfists were utilized to serve as SERS substrate and found that the microfists are a good SERS substrate and ideal SERS model for theory calculation.

2. Experimental

Chloroplatinic acid (H_2PtCl_6), ethanol (C_2H_5OH), pyridine (C_5H_5N), and potassium chloride (KCl) were obtained from Guangdong Guanghua Chemical Reagent Company. All above reagents were analytical grade and used without further purification. Aqueous-phase solutions were prepared with water purified in a Milli-Q system (>18.0 MΩ cm) and glassware used was washed with aqua regia and rinsed with ultrapure water prior to use.

In a typical synthesis, 1, 5, 10, and 30 mL of 10 mM H_2PtCl_6 absolute ethanol solutions were first added into four Teflon-lined stainless steel autoclaves, respectively. Then, 29, 25, and 20 mL absolute ethanol was

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introduced into the autoclaves containing 1, 5, and 10 mL solution. Finally, the four autoclaves were heated at 150 °C for 24 h, and the final products were obtained by repeatedly centrifuging and washing the mixtures with Milli-Q water and absolute ethanol several times while the samples were cooled to room temperature.

The separate mixtures were dispersed with 18 MΩ cm water and prepared as samples to afford TEM and SEM images. TEM and SEM grids were prepared by placing 1 μL of the mixtures on carbon-coated copper grids and drying them at room temperature. The sample for XRD measurement was prepared by placing a colloidal solution on the groove plane of quartz glass and letting it dry at room temperature. A 120 mL reaction mixture prepared using 10 mM H_2PtCl_6 was concentrated by centrifugation and was dispersed with 18 MΩ cm water to afford the colloidal solution. The SERS sample was prepared by mixing the equal volume of 0.03 M pyridine, 0.3 M KCl, and Pt colloidal solution concentrated with 30 mL reaction solution.

Transmission electron microscopy (TEM) was performed with a Hitachi H-7500 microscope operated at 80 kV. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were carried out with a field-emission microscope LEO 1530VP. X-ray diffraction (XRD) patterns were recorded on powder samples using a D/max-IIIA (Japan) X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15418 nm). UV–vis spectra were collected using a Hitachi U-3010 spectrophotometer. Surface-enhanced Raman scattering (SERS) spectra were obtained with a Labram Aramis Raman system (Horiba Jobin Yvon) operated with the excitation laser line at 632.8 nm.

3. Results and discussion

Fig. 1 shows TEM images of platinum particles prepared using different H_2PtCl_6 concentrations. With increasing H_2PtCl_6 concentrations of 0.3, 1.7, 3.3, and 10 mM, the diameters of the Pt particles gradually increase (0.28, 0.33, 0.74, and 1.16 μm, respectively). Moreover, the shapes of the Pt particles can be effectively controlled by varying H_2PtCl_6 concentrations. In the experiment using a relatively low H_2PtCl_6 concentration (0.3 mM), monodispersed and uniform Pt submicron particles can be obtained. When higher H_2PtCl_6 (>0.3 mM) is used, the fist-like Pt microparticles are easily formed, and their lengths gradually decrease with increasing H_2PtCl_6 concentrations.

Fig. 2A,B gives representative SEM images of fist-like platinum microparticles prepared using 3.3 and 10.0 mM H_2PtCl_6. Figs. 1B–D and 2A,B indicate that the submicron/micron-scale single Pt particles, fabricated using higher H_2PtCl_6 (>0.3 mM), trend to couple one another. Of particular interest here is the surface of the single submicron/micron particles that are filled with Pt nanoparticles of about 17 nm again. The structure of Pt microfists is rather similar with the surface of a roughened Pt electrode [14]. To verify the component of the samples thus produced, EDS measurement was performed. The Cu and C elements observed in the Fig. 2C are from the copper grid made for the SEM sample of Fig. 2B. Only Pt element in Fig. 2C indicates that the resulting microparticles are pure platinum.

XRD measurement was carried out for the as-fabricated product to further demonstrate the component of the sample because it can accurately assess the overall crystalline structure and phase purity of materials [15]. Fig. 3 shows XRD pattern taken from the sample prepared using 10.0 mM H_2PtCl_6. As seen in Fig. 3, the diffraction peaks at $2\theta = 39.8°$, 46.2°, 67.5°, 81.3°, and 85.7° can be indexed to (111), (200), (220), (311), and (222) planes of a pure face-centered cubic (fcc) structure of Pt (JCPDS: 04-0802, space group: Fm3m (225)). The XRD measurement indicates that the as-prepared sample is pure Pt and has a face-centered cubic structure.

The SERS activity of the Pt microfists was studied and pyridine (Py) was selected as a probe molecule. Fig. 4 gives Raman spectra of 1 M Py solution and 0.01 M Py adsorbed on the platinum microfists prepared using 10.0 mM H_2PtCl_6, respectively. The Raman spectrum peaks at ca. 1002, 1035, 1069, 1153, 1217, 1576, and 1594 cm^{-1} are characteristic modes of Py solution (curve a) [16]. For example, the bands at ca. 1002 and 1035 cm^{-1} correspond to the ring-breathing mode and the ring mode of pyridine molecules, respectively. It should be point out that the frequencies and relative intensities of the bands usually change

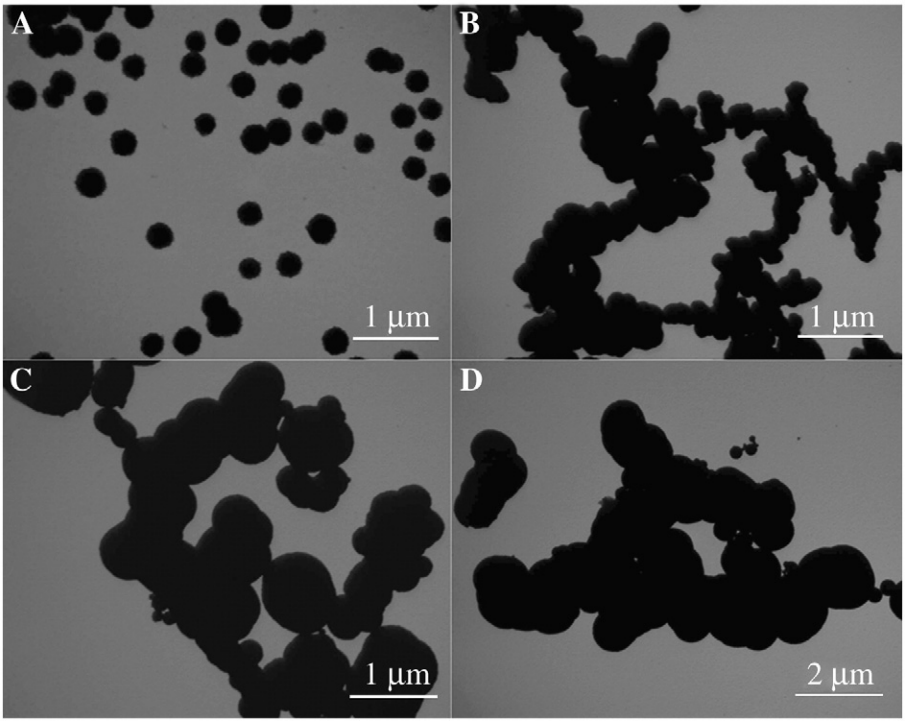

Fig. 1. TEM images of platinum particles prepared using different H_2PtCl_6 concentrations. (A) 0.3, (B) 1.7, (C) 3.3, and (D) 10.0 mM. Scale bar: (A, B, C) 1 μm and (D) 2 μm.