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Controlled synthesis of novel octapod platinum nanocrystals under microwave irradiation

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ABSTRACT

Microwave was employed in the shape-controlled synthesis of Pt nanoparticles. Novel octapod Pt nanocrystals enclosed with (1 1 1) facets were readily synthesized with H_2PtCl_6 as a precursor, tetraethylene glycol (TEG) as both a solvent and a reducing agent, polyvinylpyrrolidone (PVP) as a stabilizer in the presence of an appropriate amount of KI under microwave irradiation for 140 s. The as-prepared Pt nanocrystals displayed a unique octapod nanostructure with five little mastoids in each concave center and exhibited higher electrocatalytic activity than commercial Pt black in the electro-oxidations of methanol and formic acid. The results demonstrated that the use of KI was crucial to the formation of Pt octapods. KI determined the formation of the novel octapod Pt nanocrystals by tuning up the reduction kinetics and adsorbing on the surfaces of growing Pt nanoparticles. The optimum molar ratio of H_2PtCl_6/KI/PVP was 1/30/45.

1. Introduction

In recent years, well-defined noble metal nanocrystals with concave faces or multipods have attracted much attention owing to their sharp corners, edges, surface cavities as well as their high-index facets, which demonstrate an enhancement of catalytic performance in terms of activity and selectivity [1]. The controlled synthesis of those conventional shapes enclosed by flat or convex faces has advanced remarkably such as nanorods [2,3], nanowires [4], hexagonal nanosheets [5], nanocubes [6–8], tetrahedral [9,10], octahedral [11], icosahedra [12–14], tetrahexahedra [15,16]. Compared to the controlled synthesis of these nanocrystals with flat or convex shapes, however, the synthesis of metallic nanocrystals with well-defined concave or multipod structures has still been at an initial stage. A few wet-chemical procedures have been developed for the controlled synthesis of concave surface or multipod nanostructures. Up to now, various concave or multipod polyhedral nanocrystals of noble metals have been obtained such as concave tetrahedron, concave cube as well as tetrapod, hexapod, octapod, trisoctahedron made of Ag, Au, Pt, Pd or Rh [17–30]. In case of platinum, it has attracted much interest due to its extraordinary catalytic properties. It has been widely used as the primary catalysts for reducing pollutants from automobiles, hydrogenation of methane, direct methanol fuel cell reaction as well as CO/NO_x oxidation in some industrial processes [31–37]. Recently, though several process for the synthesis of Pt concave nanocubes and octapods have been developed [23–25], it still remains a significant challenge to prepare concave or multipod Pt nanostructures in large scale by a simple method because of their high surface energy.

Microwave dielectric heating has been extensively applied to the synthesis of metallic nanostructures due to its advantages compared with conventional heating, such as prompt start up, uniform and fast heating, and low cost [8,14,38]. Herein microwave irradiation was employed in shape-controlled synthesis of Pt nanoparticles and novel multipod Pt nanocrystals were successfully obtained using H_2PtCl_6 as a precursor, tetraethylene glycol (TEG) as both a reducing agent and a solvent, polyvinylpyrrolidone (PVP) as a stabilizer in the presence of appropriate amount of KI. The synthesis parameters were also investigated. The catalytic property of the as-prepared Pt octapods was examined by electrocatalytic oxidation of methanol and formic acid.

2. Experimental

2.1. Materials

Hexachloroplatinic acid (H_2PtCl_6), PVP (average molecular weight, M_w = 30,000, Fluka Chemicals), TEG (Acros Chemicals),

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potassium iodide (KI, Shanghai Chemicals Co., China) and other chemicals were all of analytical grade and used without further purification.

2.2. Methods

In a typical synthesis, 100 mg of KI and 100 mg of PVP were dissolved in 9.5 mL of TEG to form a light-yellow solution with rigorous stirring in a 50-mL round-bottomed flask in water bath at 60 °C. Then, 0.5 mL of 0.04 mol L^{-1} H_2PtCl_6 solution in TEG was added. The final concentration of H_2PtCl_6 was 2 mmol L^{-1} and the molar ratio of H_2PtCl_6/KI/PVP was 1/30/45. After stirring for 30 min, the resulting transparent light-brown solution was then put into a modified domestic microwave oven (Galanz, 1000W) and heated for 140 s with 100% output of the power. The brownish black colloid was obtained and then left naturally to room temperature. The resultant black homogeneous Pt colloid was precipitated by acetone, separated by centrifugation and further purified by ethanol. Under the same conditions, the same reaction process was conducted using KBr or KCl instead of KI with the same concentration. In addition, the reaction was also conducted with the molar ratio of H_2PtCl_6/KI/PVP was 1/6/45 or 1/50/45, respectively.

2.3. Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken on a FEI Tecnai G^2 20 transmission electron microscopy operated at 200 kV. The sample for TEM observation was prepared by placing a drop of the colloidal dispersion onto a copper grid coated with a perforated carbon film, followed by evaporating the solvent at ambient temperature. The average particle size and the distribution were determined from the enlarged micrographs on the basis of the measurement of about 200 particles. Diffractograms of HRTEM were obtained by fast Fourier transformation (FFT). Scanning electron microscopy (SEM) images were taken on a SU8010 field-emission scanning electron microscope operated at 50 kV. X-ray powder diffraction (XRD) measurement was performed on a Bruker D8 Advance X-ray diffractometer employing Cu-$K\alpha$ radiation with 40 kV and 50 mA. X-ray photoelectron spectroscopy (XPS) was conducted on a VG Multilab 2000 X-ray photoelectron spectrometer using Mg $K\alpha$ radiation under a vacuum of 8×10^{-7} Pa. All binding energy values were determined with reference to carbon C_{1s} = 284.6 eV.

2.4. Electrochemical measurements

Cyclic voltammetry (CV) and CO stripping experiments were conducted using a CHI660E electrochemical workstation which was interfaced for data acquisition and analysis. All experiments were carried out at room temperature (25 °C). Pt-modified working electrodes were fabricated by depositing ethanol dispersion of purified octapod Pt nanocrystals onto a glassy carbon electrode followed by natural drying. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and counter electrode, respectively. For the electrooxidation of formic acid, the cyclic voltammograms were recorded at a sweep rate of 50 mV/s in 0.5 M H_2SO_4 + 0.5 M HCOOH. For the electrooxidation of ethanol, the cyclic voltammgrams were recorded at a sweep rate of 50 mV/s in 0.1 M $HClO_4$ + 0.1 M CH_3OH. Before cyclic voltammetry measurements, 2 cycles of potential sweeps between −0.25 V and 1.2 V were applied to clean the Pt surface in situ.

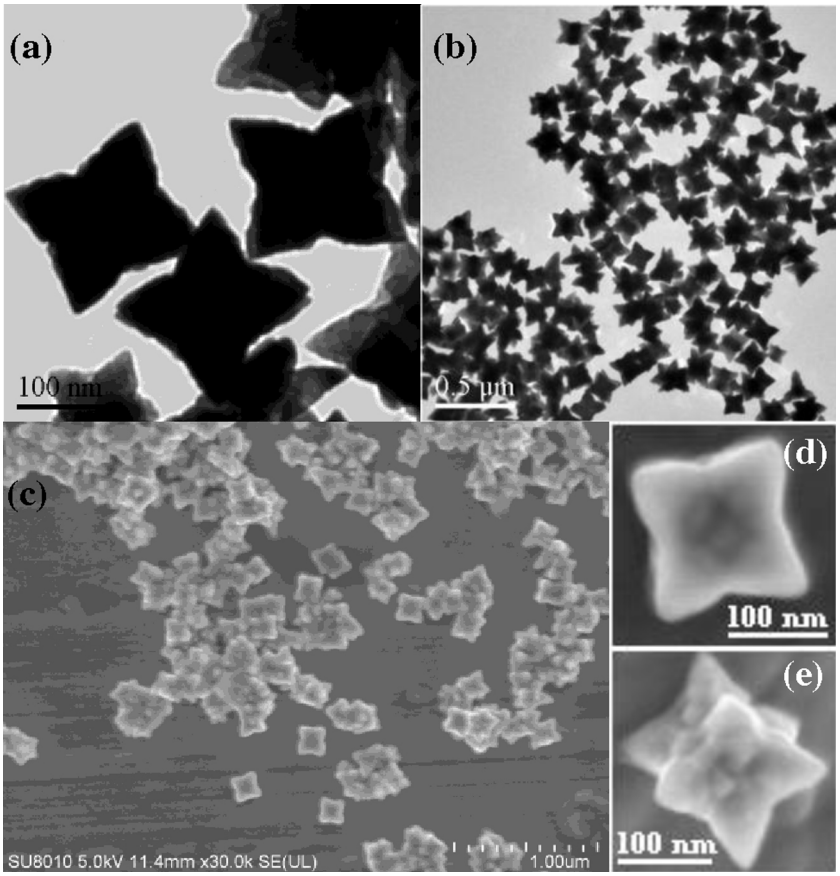

Fig. 1. TEM and SEM images of the as-prepared Pt octapods. (a and b) Typical TEM images; (c) typical SEM images; (d and e) SEM images of a single particle. [H_2PtCl_6] = 2 mmol L^{-1}; H_2PtCl_6/KI/PVP was 1/30/45 (molar ratio).