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Urea assisted electrochemical synthesis of flower-like platinum arrays with high electrocatalytic activity

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ABSTRACT

In this paper, well-defined flower-like Pt arrays were prepared on the glassy carbon electrode by one-step electrodeposition at–0.3 V for 600 s in 0.5 M H_2SO_4 containing 5 mM H_2PtCl_6 and 150 mM urea. This method is simple, facile, and controllable, without using any template, seed or surfactant. The experimental parameters were investigated and found urea acted as a growth directing agent. The as-prepared Pt nanocrystals were preferentially growing along the (111) directions, which were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and energy dispersive X-ray (EDX). Moreover, the flower-like Pt nanoarrays exhibited a large effective surface area (EASA) and enhanced performance toward the oxidation of ethylene glycol and methanol in acid media, compared with Pt nanoparticles and commercial Pt black catalysts. This strategy can be extended to prepare other noble metal nanostructures as good electrocatalysts in fuel cells.

1. Introduction

In recent years, nano-sized noble metal materials have aroused tremendous attention because of their unique physical and chemical properties [1–4]. Particularly, platinum (Pt) nanostructures play an important role in the cutting-edge applications of advanced technology [5–8], owing to their shape- and size-dependent properties [1,9,10]. Thus, much work has been focused on manipulating their morphology and size by finely adjusting the experimental conditions [11–17].

Up to now, a number of Pt nanostructures were prepared [18], including multipods [5,11,13], wires [14,15,19], dendrites [1,12,20], cubes [10,11,21], rods [1,21], and flowers [22–25]. Thus-prepared Pt nanomaterials were demonstrated the improved catalytic activity for electrocatalytic oxidation of small organic molecules such as formic acid [1,26,27], methanol [20,28,29], ethanol [5,11,30], methanol [26], and glucose [12,31].

Several good examples have been reported. Hsieh et al. electrodeposited Pt nanoflowers on ITO substrates [5], which displayed the enhanced catalytic ability toward ethanol oxidation. Tiwari's group synthesized Pt nanoflowers with three-dimensional (3D) structures on silicon substrates by potentiostatic pulse plating [2], which showed the improved electrocatalytic activity toward methanol oxidation and the adsorbed CO-based species. Yin and coworkers prepared monomorphic single-crystalline Pt nanoflowers assisted by iodine ions [20]. Chen et al. constructed 3D Pt nanoflowers with high yield and good monodispersity supported on GO nanosheets [22]. Nevertheless, some of them involved complicated procedures and expensive raw material [1,23,25]. It is more desirable to develop a controllable, economical, and effective approach to synthesize Pt nanomaterials.

In this paper, a simple and facile method was developed for one-step electrodeposition of well-defined flower-like Pt nanoarrays on a glassy carbon electrode (GCE) at room temperature, where urea was used as a growth directing agent for the first time. This method did not need any seed, template, or surfactant. The electrocatalytic performances of the as-prepared Pt nanoarrays were investigated, using the oxidation of ethylene glycol (EG) and methanol in acid media as model systems.

2. Experimental

2.1. Chemicals

Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), ethylene glycol (EG), H_2SO_4, urea, NaOH, and commercial Pt black catalyst were purchased from Shanghai Aladdin Chemical Reagent Company (Shanghai, China)

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and used without further purification. All the aqueous solutions were prepared with twice-distilled water.

2.2. Preparation of flower-like Pt nanoarrays

Typically, Pt nannoflowers were prepared by a one-step electrodeposition on a GCE in the electrolyte containing 0.5 M H_2SO_4, 5 mM H_2PtCl_6 and 150 mM urea at–0.3 V for 600 s, followed by thoroughly washing with water and dried at room temperature. For comparison, Pt nanoparticles were prepared without urea, but using the same electrical charges, while other conditions were kept constant.

2.3. Characterization

X-ray diffraction (XRD) analysis was performed by a Bruker-D8-AXS diffractometer equipped with a Cu Ka source. Scanning electron microscopy (SEM) images were taken using a JEOL-JSM-6390LV field emission scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were carried out by a JEOL JEM-2100F system at 200 kV accelerating voltage. The TEM sample was prepared by depositing a drop of the dispersion of the diluted sample on a copper grid coated with carbon film and dried in air. Energy dispersive X-ray (EDX) spectroscopy was performed by X-ray energy dispersive spectrometer at 15 kV (JEOL, JSM-7500F).

Electrochemical experiments were conducted on a CHI 660D electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China) by using a conventional three-electrode cell, which included a saturated calomel electrode (SCE) as reference electrode, a platinum wire as counter electrode, and the bare or Pt deposits modified GCE as working electrode. N_2 was bubbled into all the electrolytes for 30 min before cyclic voltammetric experiments, if not stated otherwise.

3. Results and discussion

3.1. Characterization

Fig. 1 displays typical SEM and TEM images of the flower-like Pt arrays prepared under the standard conditions. Low-magnification SEM image (Fig. 1A) displays monodispersed Pt nanoflowers with well distribution and high density on the GCE surface. These Pt nanoflowers have the mean diameter of ca. 500 nm, which are assembled by many nanosheets with rough fringes and further reassembled to petals (Fig. 1B). The thickness of each nanosheet is ca. 50 nm. Similar observations are observed by the TEM image (Fig. 1C). Furthermore, HRTEM image (Fig. 1D) reveals the uniform interplanar spacing with a value of 0.23 nm, which is in agreement with the (111) lattice spacing of face-centered-cubic (fcc) Pt [10,20,32]. The corresponding SAED pattern reflects the polycrystallinity of the flower-like Pt nanoarrays (inset in Fig. 1C).

Fig. 2 shows the XRD patterns of the typical flower-like Pt arrays, where the characteristic diffraction peaks at 39.8°, 46.2°, 67.5°, 81.2°, and 85.7° are well matched with the (111), (200), (220), (311), and (222) planes of Pt (JCPDS card No. 65-2868), respectively. Meanwhile, no peaks of impurities are detected, suggesting high purity of the electrodeposited Pt nanoflowers, as again demonstrated by the EDX spectrum (Fig. 2B). Moreover, the diffraction peak of the (111) planes is stronger and sharper, compared with those of the (200), (220), (311), and (222) planes, revealing the preferential growth along the (111) directions.

In order to investigate the electrochemical behaviors of the flower-like Pt nanoarrays, the cyclic voltammograms (CVs) of the bare (Fig. 3, curve a) and flower-like Pt arrays (Fig. 3, curve b) modified electrodes are recorded in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1}. There are three distinguished H adsorption-desorption peaks at −0.30 V, −0.19 V, and −0.10 V for the flower-like Pt arrays, respectively. And the reduction peak of the flower-like Pt arrays is detected at 0.48 V. Further augmenting the potential, a wide plateau is observed, which is assigned to the oxidation of the Pt

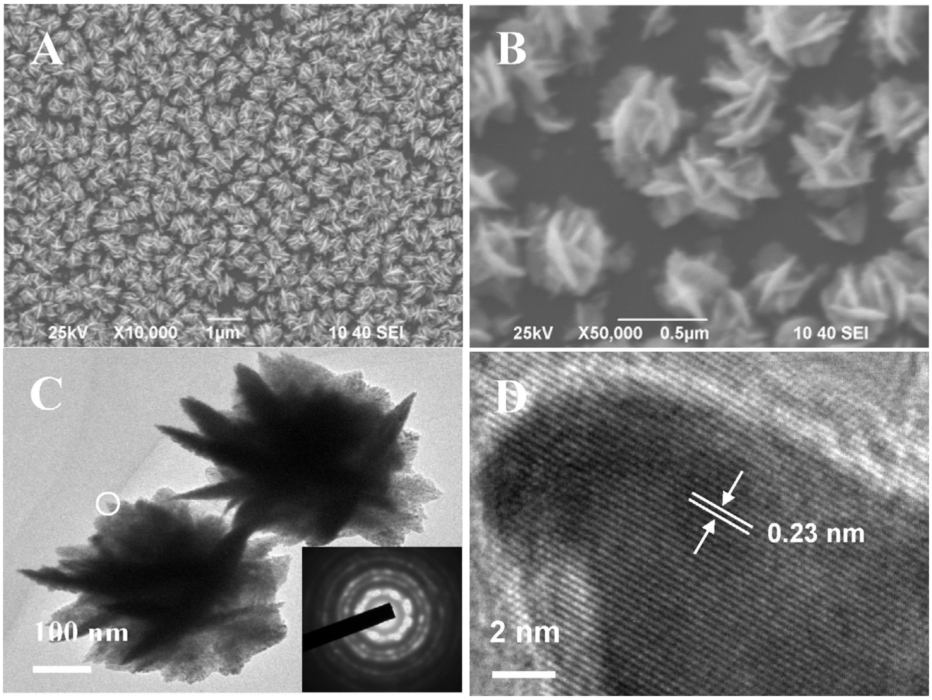

Fig. 1. Typical SEM images of the flower-like Pt arrays with low (A) and high (B) magnification. TEM image of the Pt nanoflowers (C). HRTEM image (D) of the tips from the marked sheet. Inset shows the corresponding SAED pattern.