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One-step electrochemically co-deposited Pt nanoparticles/polyaniline composites with raspberry structures for methanol electro-oxidation

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ABSTRACT

In this work, the raspberry-like Pt nanoparticles/polyaniline complexes (PNPC) has been fabricated for methanol electro-oxidation. The PNPC were electrochemically deposited by one-step from solutions simultaneously containing aniline and potassium tetrachloroplatinate. Morphological and structural characterizations demonstrated that the Pt particles with diameters between 2 and 5 nm were like frambold of raspberry in polyaniline film. The electrochemical catalytic performance of PNPC was evaluated by cyclic voltammograms and chronoamperometric method. Electrochemical experiment results have amply confirmed that the PNPC have superior electrocatalytic oxidation performance and superior catalytic tolerance to carbonaceous species accumulation toward methanol oxidation. These results indicated that PNPC as catalysts carrier may have prosperous application for fuel cell technology.

1. Introduction

Polyaniline (PANI) as a conductive polymer has the advantages of low synthesis cost, good environmental stability, reversible redox property and good conductivity [1–4]. PANI materials have been applied to many fields, such as catalysis [5], sensor [6–10], electrical devices [11–15].

In PANI membranes, introduction of noble metal species would not only take advantage of the noble metal species catalytic activity, but also improve the electronic and chemical properties of the polymer [16–20]. Pt nanoparticles/PANI complexes (PANI-Pt) have been demonstrated excellent electro-catalytic activity toward the oxidation of organic small molecules, such as hydrogen peroxide [21], methanol [22–25], glycerol [26], hydrogen [27] and formic acid [28].

The simple synthetic method, cost-effectiveness, novel structure and good catalytic activity are likely to emerge as focal points in the field of electro-catalysts. The raspberry-like composite have applied in super-hydrophobic surface [29,30], drug delivery [31], super-hydrophilic coatings [32], self-cleaning coatings [33], etc. Different methods such as template method [34] and in situ polymerization technique [35,36] have been applied to prepare the raspberry-like composite particles. However, the electrochemical synthesis method has the advantage of without using a large number of toxic reagents and expensive instruments. Also, the electrochemical synthesis method is easy to control the morphology and size of nanoparticles.

In this paper, we synthesized raspberry-like Pt nanoparticles/polyaniline complexes by one-step. So the good conductivity of PANI and the favorable catalytic activity of Pt particles with diameters between 2 and 5 nm could be fully utilized. When the particle diameter was between 2 and 5 nm, the material has better catalytic activity [37–40]. X-ray photoelectron spectroscopy (XPS), scan electronic microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), transition electronic microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were used to characterize the complexes. Electrochemical experiment results showed that the raspberry-like Pt nanoparticles/polyaniline complexes had good catalytic activity and catalytic tolerance to methanol oxidation.

2. Experimental

Electrochemical synthesis and electro-catalytic oxidation experiments were performed at CHI 660E electrochemistry workstation (ChenHua Instruments Co., China) with a standard three-electrode electrochemical cell. A glassy carbon electrode (GCE), Ag/AgCl (3 M KCl solution) and Pt wire were employed respectively as the working electrode, reference electrode and the counter electrode. The GCE was polished separately with 0.3 μm and 0.05 μm alumina powder to obtain a smooth surface, then ultrasonic cleaning with ethanol and ultrapure water respectively. The potential was measured in the potassium ferrocyanide/potassium ferricyanide solution. We calculated ΔE of redox

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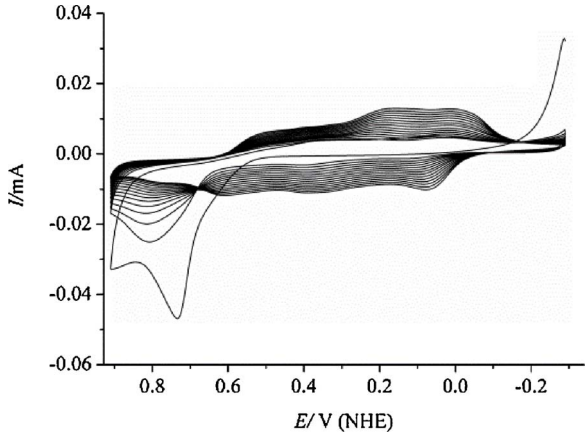

Fig. 1. The CVs in 0.1 M aniline +1.0 M $HClO_4$ + 0.005 M potassium tetrachloroplatinate argon saturated aqueous solution.

peak vs the normal hydrogen electrode (NHE) and modified the potential in the experiment solution.

The chemicals used in the experiments include aniline (Aniline is used after distillation under reduced pressure), Perchloric acid (super pure grade), potassium tetrachloroplatinate (Aldrich, 99.9%), potassium ferrocyanide (analytical pure grade), methanol (analytical pure grade), commercial Pt/C catalysts (Sigma-Aldrich, Pt 10 wt.% loading) and ultrapure water (Preparation of ultrapure water by a Milli-Q instrument, 18.2 MΩ).

The PANI film were grown by electrochemical deposition in 1.0 M $HClO_4$ + 0.1 M aniline argon saturated aqueous solution. The potential range was between −0.29 and 0.91 V with 10 mV/s sweep speed. Electro-deposition of polyaniline was performed after 15 cyclic voltammograms. The Pt nanoparticles/polyaniline complexes were prepared electrochemically on GCE from 1.0 M $HClO_4$ + 0.1 M aniline + 0.005 M potassium tetrachloroplatinate argon saturated aqueous solution at the same potential range, scan rate and cycle number.

5 mg of commercial Pt/C catalysts was used to modulate into a paste for the Fabrication electrode. 5 μL of Nafion and 200 μL of ethanol were uniformly mixed in an ultrasonic bath for 1 h. 4 μL of the paste was uniformly covered on a GCE with 0.07 cm^2 area. Then this GCE dried for 10 h at 50 °C to act as working electrode. This working electrode was used to measure after active scanning.

The amount of platinum was measured by an iCAP Q inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific). XPS spectra was recorded on an ESCALAB 250Xi spectrometer (Thermo Scientific). FTIR spectra were performed on a Brucker VERTEX80 spectrometer. Microstructure of materials was characterized by S4800 with energy dispersive X-ray spectroscopy (EDX) scan electronic microscopy (Hitachi), JEM 2100 transition electronic microscopy (JEOL) and high resolution transmission electron microscopy (JEOL).

The experiment temperature is at 25 °C.

3. Results and discussion

The cyclic voltammograms (CVs) of the PNPC growth were shown in Fig. 1. The redox current increased gradually with increasing number of cycles. The current of redox peak (near 0.05 V) and redox peak (near 0.55 V) decreased in CVs of PNPC relative to PANI films [15] because of the formation of platinum particles. There was a new pair of redox peaks (near 0.55 V) according to reduction of platinum. The results indicated that Pt nanoparticles and polyaniline film were co-deposited in the cyclic voltammetry process.

The synthesis of the raspberry-like Pt nanoparticles/polyaniline complexes were schematically illustrated in Fig. 2.

The typical SEM image of PNPC (Fig. 3A and B) illustrated that the diameters of PNPC particles was about 40–60 nm and many small particles with diameters several nanometers attached on PNPC particle surface. The amount of platinum was measured by ICP-MS and it is 161 μg cm^{-2} for PNPC, 172 μg cm^{-2} for Pt/C on working electrode.

The TEM image of PNPC (Fig. 4A) illustrated that particle was about 40–60 nm in diameter and was made up of small particles with diameters between 2 and 5 nm. The Pt particles attached on PANI surface because the nitrogen atom of amine in PANI interacts with Pt atom [41,42]. The Pt particles with diameters several nanometers were like frambold of raspberry which was illustrated in Fig. 2. The 0.23 nm spacing lattice fringes in the nanograins were clearly observed from

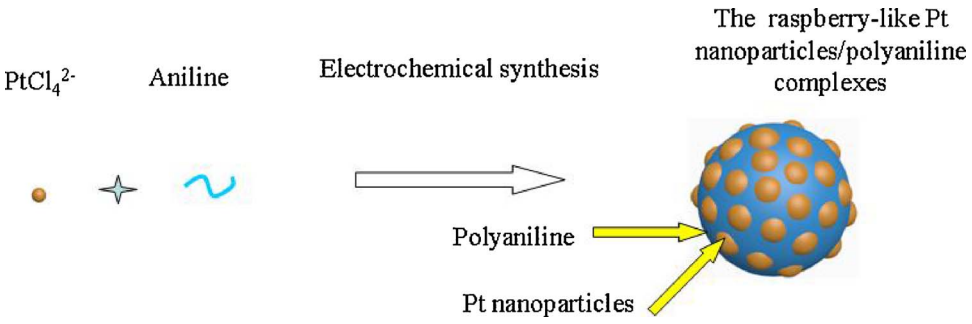

Fig. 2. Diagram of the synthesis of PNPC.

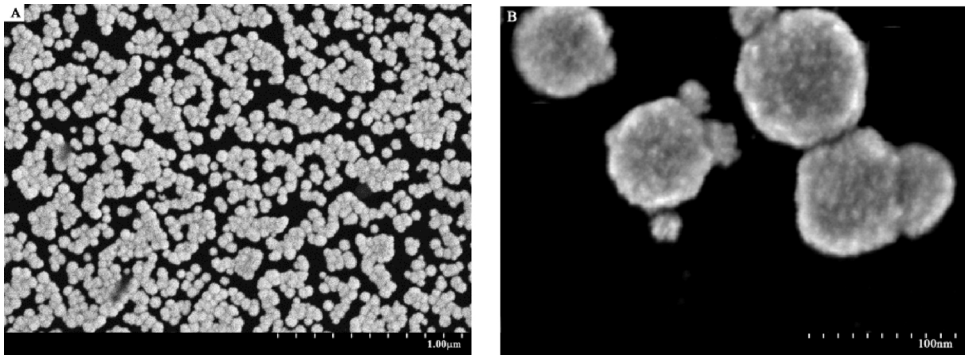

Fig. 3. SEM images of PNPC at different magnification (A) and (B).