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PtFe nanotubes/graphene hybrid: Facile synthesis and its electrochemical properties

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ABSTRACT

PtFe nanotubes are synthesized by galvanic exchange reactions using Co nanowires as template and reducing agent, followed by mixed with graphene to prepare PtFe nanotubes/graphene hybrid catalyst. The morphology and crystal structure of as-made hybrid are characterized by transmission electron microscope and X-ray diffraction. Its electro-catalytic properties toward methanol oxidation are investigated by cyclic voltammetry and chronoamperometry. The average diameter and wall thickness of the PtFe nanotubes supported on graphene are ca. 50 nm and 10 nm, respectively. As an electro-catalyst for methanol electro-oxidation, PtFe nanotubes/graphene catalyst displays higher specific activity and stability than commercial PtRu/C catalyst and PtFe nanoparticles/graphene catalyst.

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1. Introduction

A growing demand for efficient but low-cost renewable energy has sparked significant interest in the commercial development of fuel cell technology as a replacement for combustion-based energy sources [1]. Among different types of fuel cells, direct methanol fuel cell (DMFC) is an excellent power source due to its high energy-conversion efficiency and energy density, low operating temperature, low-to-zero pollutant emission, as well as the simple handling and processing of the fuel [2]. A key component in such DMFC is the anode, on which methanol is oxidized, to produce carbon dioxide, hydrogen

ions, and electrons. Platinum and its alloy have been studied as anode catalysts for many years. However, the durability of the electro-catalysts is still needed to improve before the commercialization of DMFC. Currently, DMFC anode catalyst is mainly Pt-based alloys supported on carbon black. The poor durability of these catalysts can be summarized as follows: 1) loss of platinum nanoparticles because of corrosion of the carbon support, and 2) dissolution and re-deposition of the platinum nanoparticles [3]. The carbon-corrosion problem can be alleviated by the use of a more corrosion-resistant catalyst support, such as graphitized-carbon materials, carbon nanotubes and graphene (G) etc. [4–6]. No effective solutions,

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however, exist for addressing the other problem. Thus, it is highly desirable to develop new routes for synthesizing novel electro-catalysts with high durability.

One-dimensional nanotubes can provide better opportunities for enhancing the electro-catalytic durability of the catalysts. This is because the nanotubes are less vulnerable than small nanoparticles to dissolution, Ostwald ripening, and aggregation during electro-catalytic processes due to their particular structure [3]. To date, various Pt-based alloy nanotubes have been synthesized, such as PtRu, PtPd, PtNi, PtCo, PtCu and PtNiP [7–12]. PtFe alloy has been proposed as both anode catalyst and cathode catalyst [13–16]. However, the report on synthesis of PtFe nanotubes is rare.

In this communication, we propose a simple method to synthesize PtFe nanotubes using galvanic displacement reaction for the first time. Sellmyer et al. reported synthesis of PtFe nanotubes using porous anodic aluminum oxide (AAO) membrane as template [17]. In their method, PtFe first electrodeposited into the pores of AAO template and then an etching step was carried out to remove AAO template using NaOH aqueous solution. The procedure is relatively complex and not environmentally-friendly. Moreover, the electrochemical properties of the nanotubes were not studied. On the contrary, in our present method, the AAO template and the procedure for etching the template are needless. The key to synthesis of PtFe nanotubes is using galvanic displacement reactions between Co nanowires and precursors of Pt and Fe. G has been proved to be an effective catalyst supports for DMFC due to their specific electronic conductivity and extremely high specific surface area [18–21]. To reduce the aggregation between PtFe nanotubes, the as-prepared PtFe nanotubes are mixed with G. The hybrid is denoted as PtFe nanotubes/G. This is the first report on the preparation and the use of PtFe nanotubes/G as catalyst for DMFC. Furthermore, as-prepared PtFe nanotubes/G catalyst shows higher specific activity and stability than commercial PtRu/C catalyst (Johnson Matthey, 20 wt.%).

2. Experimental

2.1. Materials

5 wt.% nafion solution, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, H_2SO_4 , methanol, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, trisodium citrate dihydrate, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were purchased from Sigma, Shenyang Keda reagent factory, Baiyin Liangyou Chemicals Co. Ltd., Tianjin Fuyu Special Chemicals Co. Ltd., Tianjin Tianhao Fine Chemicals Co. Ltd., Sichun Xilong Chemicals Co. Ltd., and Tianjin Basf Chemicals Co. Ltd., respectively. NaBH_4 and ethanol were purchased from China National Pharmaceutical Corp. All reagents were used as received without further purification. Deionized water (DI water) with resistance of approximately 18 M Ω cm was used throughout the experiment.

2.2. Synthesis of G

The procedures for synthesis of G are shown in our previous work [22]. An improvement is that the prepared G was dried in a vacuum freeze drier instead of the oven. The drying in low

temperature (below zero degree) can reduce the aggregation among G sheets.

2.3. Synthesis of PtFe nanotubes

To synthesize PtFe nanotubes, 20 ml of 12 mM CoCl_2 and 71 mg of trisodium citrate dihydrate which was used as capping agent were added to 200 g of DI water. The solution was purged with N_2 for 30 min, then a fresh NaBH_4 solution which contained 18.2 mg NaBH_4 and 10 g DI water was added dropwise into the above solution under vigorous stir, giving rise to a brown Co hydrosol. The Co hydrosol was aged for 0.5 h. Then, a mixture of 5 ml of 19.3 mM H_2PtCl_6 and 20 ml of 4.8 mM $\text{Fe}(\text{NO}_3)_3$ was added dropwise under vigorous stir. The color of the solution became black immediately and then turned to light pink. A black deposit was formed when the solution color turned to light pink, indicating the PtCl_6^{2-} and Fe^{3+} were reduced to Pt and Fe and PtFe nanotubes formed. The mixture was kept on stirring for 0.5 h to complete the reaction. To avoid the oxidation of the Co nanowires by atmospheric oxygen, high-purity nitrogen was bubbled through the solution during the above procedure. The deposit of PtFe nanotubes was washed by DI water for several times and dried in vacuum freeze drier.

2.4. Synthesis of PtFe nanotubes/G hybrid

To synthesize PtFe nanotubes/G hybrid, 30 mg of G was dispersed in 30 g of ethanol by ultrasonication. Then the obtained G dispersion was mixed with PtFe nanotubes by further ultrasonication. The product was collected by filtration, washed with DI water for several times, and dried in vacuum freeze drier.

2.5. Synthesis of PtFe nanoparticles/G hybrid

For comparison, PtFe nanoparticles/G hybrid was also prepared. In brief, 99.4 mg of trisodium citrate dihydrate, 5 ml of 19.3 mM H_2PtCl_6 , and 39 mg of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added to 200 g of DI water to form a solution by magnetic stir. Then a fresh NaBH_4 solution was added dropwise into the above solution under vigorous stirring. The procedures for mixing the above dispersion with G, collecting, washing and drying the prepared catalyst were the same as those in the synthesis of PtFe nanotubes/G hybrid.

2.6. Characterization

Transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy dispersive spectroscopic (EDS) elemental mapping measurements were performed on FEI Tecnai-G2-F30 microscope equipped with an EDAX X-ray detector. Structural investigation of the samples was performed by X-ray diffraction using $\text{Cu K}\alpha$ radiation (XRD, Panalytical X'Pert Pro). An IRIS Advantage ER/S inductively coupled plasma spectrometer (ICP, TJA) was used for all metal-determinations. The surface chemical species of PtFe nanotubes were examined on a Perkin-Elmer PHI-5702 multifunctional X-ray

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