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Short communication

A new kind of highly active hollow flower-like NiPdPt nanoparticles supported by multiwalled-carbon nanotubes toward ethanol electrooxidation

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HIGHLIGHTS

- Carbon-supported hollow flower-like NiPdPt has been synthesized.
- Ni nanoparticles are used as the sacrificial template to obtain NiPdPt.
- NiPdPt are well assembled on carbon nanotubes through electrostatic interaction.
- The as-prepared catalysts exhibit excellent electrocatalytic activity.

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ABSTRACT

Hollow flower-like NiPdPt nanoparticles (NPs) are prepared through galvanic replacement between Ni nanoparticles and noble metal salts. Multiwalled-carbon nanotubes (MWCNTs) can be used to support the as synthesized hollow flower-like NiPdPt NPs through electrostatic self-assembly. The structure and composition are analyzed by transmission electron microscope, X-ray diffraction and inductively coupled plasma optical emission spectrometer. Electrochemical catalytic measurement results prove that the as synthesized MWCNTs supported NiPdPt NPs present excellent catalytic activity toward ethanol electrooxidation in alkaline solution.

1. Introduction

In recent years, fuel cells have been receiving increasing attentions taking the advantages of its high efficiency and cleanness [1]. Direct ethanol fuel cells (DEFCs) are attracting special attention owing to its wide application nowadays, such as power sources for portable electronic devices and fuel-cell vehicles etc [2]. Comparing with other direct fuel cells, DEFCs present many obvious advantages. First, ethanol can be easily obtained in large quantities from chemical industry and fermentation of biomass. Second, ethanol has a lower toxicity while provides a higher energy density compared to its counterparts such as methanol and formic acid. Moreover, DEFCs conducting in alkaline media have some other obvious advantages such as improved kinetics for low-overvoltage ethanol oxidation and reduced risk of corrosion of the materials for high durability [3–5]. However, a significant challenge in the development of DEFCs technology is the urgent need for highly active catalysts for the ethanol oxidation reaction which takes place at the negative electrode [6].

Pd-based catalysts have been proven to be promising candidates for DEFCs due to its good catalytic activity and relatively low cost

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[5,7]. Many previous studies validate that the shape, size and composition of nanoparticles, have a significant effect on its catalytic activity [8,9]. Rationally design of bimetallic or multi-metallic nanostructures has been one of the hottest and attractive research topics for improving its catalytic activity and utilization efficiency of noble metals [10–12]. Until now, a variety of Pd-based materials have been synthesized for DEFCs, such as TiO_2 nanotubes supported-Pd [13], carbon-supported PdM (M = Au and Sn) nanocatalysts [14], carbon-supported PdSn binary catalysts [15] and Pd–Ni electrocatalysts [16,17], water-dispersible hybrid Au–Pd nanoparticles [18], carbon-supported Pd–Ag [19], Pt/Pd bimetallic nanotubes [2] and PdM (M = Pt, Au) bimetallic alloy nanowires etc [20]. Among these materials, PtPd materials draw particular attention by virtue of their outstanding catalytic activity derived from the presence of the powerful catalytic components of Pt and Pd [21].

As a special structure, metallic hollow nanospheres exhibit higher catalytic activity with the advantages of low density, saving materials, and reduction of costs compared with their solid counterparts [22–24]. Despite of some methods have already been developed for the synthesis of metallic hollow structure, it remains a great challenge to develop a one-pot and general route for the preparation of metallic hollow nanostructures. Hard templates methods still remain the most powerful and versatile way to prepare metallic hollow nanostructure. Among those cases, Co and Ag nanoparticles are two of the most often used sacrificial templates to obtain noble metallic hollow structure. However, Ag templates are not favorable from the point view of economy due to its relatively high price. What's more, employing Ag templates always lead to the AgCl precipitates and thus the further removal procedures [25,26]. Co templates are more economic comparing with Ag templates. However, it exhibits strong magnetic force, which may lead to adhesion and even aggregation of metallic hollow structure [27]. Compared with that, Ni as a non-noble metal, is more economical than Ag templates. Meanwhile, it has a weaker magnetic force than Co templates. What's more, the presence of Ni in Pd and Pt were found to be very favorable for the improvement of catalytic performance, due to the synergistic effect between small amount of Ni and Pt/Pd, which can greatly enhance the catalytic activity and stability of the catalyst [6].

In this work, we successfully developed a method to synthesize multiwalled-carbon nanotubes supported NiPdPt nanoparticles (MWCNTs-NiPdPt) by the galvanic replacement, employing Ni nanoparticles as the sacrificial templates. The obtained MWCNTs-NiPdPt were characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), inductively coupled plasma optical emission spectrometer (ICP-OES). The catalytic activity and stability of the prepared catalysts were investigated by cyclic voltammetry and chronoamperometry methods in alkaline media.

2. Experimental

2.1. Materials

Multiwalled-carbon nanotubes were purchased from Shenzhen Nanotech Port Company (China) and purified by refluxing in 3 mol L^{-1} nitric acid for 24 h. Vulcan XC-72 carbon was bought from Shanghai Ouman Chemical Corp (Shanghai, China). Nafion ethanol solution (5 wt.%) was obtained from Aldrich. Commercial ETK-Pd/C was purchased from Alfa Aesar. Sodium tetrachloropalladate (II), potassium chloroplatinate and trisodium citrate were obtained from Beijing Chemical Corp (China). All chemicals used were of analytical grade and used without further purification. Milli-Q ultrapure water (Millipore, ≥18.2 MΩ cm) was used throughout the experiments.

2.2. Synthesis of hollow flower-like NiPdPt nanoparticles

To synthesize the sacrificial Ni nanoparticles, 0.8 mL 0.1 mol L^{-1} $NiCl_2$ was added into 50 mL deionized water, followed by adding 1 mL 0.2 mol L^{-1} trisodium citrate as the stabilizers. The mixed solution was purged with N_2 for 30 min, then 6 mL aqueous solution containing 5 mg $NaBH_4$ was added dropwise under vigorous stirring. After several minutes, 300 μL 0.0558 mol L^{-1} Na_2PdCl_4 and 870 μL 0.0193 mol L^{-1} K_2PtCl_6 together with water were mixed to a total volume of 7 mL, and sequentially added to the reaction solution slowly. For comparison, the different mole ratio of NiPdPt were also prepared, just by changing the volume of Na_2PdCl_4 to 450 μL, 300 μL and the volume of K_2PtCl_6 to 430 μL, 2.6 mL respectively. The final products were centrifuged and washed with water several times, and dissolved in water for further use.

2.3. Preparation of MWCNTs-NiPdPt catalysts

4 mg of the as treated MWCNTs were dissolved in 6 mL water. To the solution, 100 μL poly(diallyldimethylammonium chloride) (PDDA) (25%) were added and sonicated for 3 h. The solution was then centrifuged and washed with water to remove the excessive PDDA. Subsequently, the MWCNTs were dissolved in 6 mL water, then mixed with half of the above prepared hollow flower-like NiPdPt nanoparticles and stirred overnight. Finally, the products were centrifuged and concentrated for further structural, composition and electrochemical characterizations. The Vulcan XC-72 carbon-supported $NiPd_{20}Pt_{23}$ was prepared by mixing carbon and $NiPd_{20}Pt_{23}$ together and sonicated for 15 min, then stirred overnight. The final products were centrifuged and concentrated.

2.4. Material structure and composition characterizations

The morphology and structure of the as prepared catalysts were analyzed with a HITACHI H-600 Analytical TEM with an accelerating voltage of 100 kV. The exact composition of MWCNTs-NiPdPt was determined by ICP-OES (X Series 2, Thermo Scientific USA). XRD pattern of MWCNTs-NiPdPt was performed on a D8 ADVANCE (BRUKER, Germany) diffractometer using Cu-Kα radiation with a Ni filter ($\lambda = 0.154059$ nm at 30 kV and 15 mA).

2.5. Electrochemical catalytic test toward ethanol electrooxidation

For electrochemical catalytic test, a glassy carbon electrode (GCE) with a diameter of 2.5 μm was employed as working electrode. A platinum wire was used as the counter electrode with Ag/AgCl electrode as the reference electrode respectively. The voltage applied has been converted to the voltage referenced to normal hydrogen electrode (NHE). Before each experiment, the GCE was polished carefully with 1.0, 0.3, and 0.05 μm alumina powder and rinsed with deionized water, followed by sonication in ethanol and Milli-Q ultrapure water successively. Then, the electrode was dried under nitrogen. For electrooxidation of ethanol test, 5 μL of commercial ETK-Pd/C or MWCNTs-NiPdPt catalysts solution (0.5 mg mL^{-1} of metal) was dropped on the surface of the GC electrode and dried with an infrared lamp carefully. Then, 5 μL of Nafion (0.5%) was coated on the surface of the above material modified GCE and dried before electrochemical experiments. All the electrochemical tests were carried out on a CHI 832B electrochemical workstation, Chenhua Instruments Corp (Shanghai, China).