



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijhe

Hydrogen co-reduction synthesis of PdPtNi alloy nanoparticles on carbon nanotubes as enhanced catalyst for formic acid electrooxidation

Jun-Ming Zhang, Rui-Xiang Wang, Rui-Jiao Nong, Yang Li, Xiao-Jie Zhang, Pan-Yu Zhang, You-Jun Fan*

Guangxi Key Laboratory of Low Carbon Energy Materials, College of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, China

ARTICLE INFO

Article history:

Received 3 January 2016

Received in revised form

18 May 2016

Accepted 21 May 2016

Available online xxx

Keywords:

Direct formic acid fuel cell

PdPtNi

Alloy nanoparticles

Multi-walled carbon nanotubes

Anode catalyst

ABSTRACT

A novel electrocatalyst of PdPtNi ternary alloy nanoparticles supported on multi-walled carbon nanotubes (MWCNTs) for formic acid oxidation (FAO) reaction is synthesized by a simple hydrogen co-reduction process. The as-synthesized catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS). It is found that highly dispersed PdPtNi alloy nanoparticles of ca. 2.56 nm are homogeneously deposited on the MWCNT surface, and the alloying with Pt and Ni alters the electronic structure of Pd atoms with the downshift of Pd d-band center. Studies of cyclic voltammetry and chronoamperometry indicate that the electrocatalytic activity and durability of the PdPtNi/MWCNT for FAO are significantly enhanced as compared with the PdPt/MWCNT and commercial Pd/C catalysts. This study implies that the prepared PdPtNi/MWCNT composite is a promising anode electrocatalyst of direct formic acid fuel cells.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Direct formic acid fuel cell (DFAFC) has been considered as a promising energy conversion device for portable power applications due to its high theoretical open circuit potential (1.45 V), low toxicity of liquid fuel and low crossover flux through the Nafion membrane [1–4]. However, one of the major challenges for the practical applications of DFAFC is the lack of highly active electrocatalysts with low cost and long-term stability [3,5]. It is well known that formic acid oxidation (FAO) on Pd catalyst occurs mainly through the direct dehydrogenation pathway instead of the indirect

dehydration pathway on Pt catalyst [6,7]. Many studies have shown that the Pd-based catalysts have higher electrocatalytic performances for FAO than the Pt-based catalysts [8,9]. Unfortunately, during the electrochemical process in acid medium, Pd atoms on the catalyst surface are more easily removed as compared to Pt, which results in a low lifetime of Pd catalyst [10]. In order to solve this problem, considerable efforts have been devoted to exploit the Pd-based catalysts with high electrocatalytic activity and durability by alloying with a second metal or even a third metal, such as PdPt [5,10], PdAu [11], PdAg [12], PdCu [13,14], PdNi [15–17], PdSn [18,19], PdPb [20], PdCuSn [21] and PdPtCu [22] catalysts. For example, Xu et al. synthesized a nonporous

* Corresponding author.

E-mail address: youjunfan@mailbox.gxnu.edu.cn (Y.-J. Fan).

<http://dx.doi.org/10.1016/j.ijhydene.2016.05.198>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

PdPt alloy with enhanced FAO electrocatalytic activity and durability through the dealloying of Al from PdPtAl alloys [10]. Lu et al. reported the one-step wet chemical synthesis of bimetallic PdAg alloy nanowires, which exhibited superior electrocatalytic activity and stability towards FAO [12]. Zhu et al. synthesized a multi-walled carbon nanotubes (MWCNTs) supported PdCuSn (molar ratio 1:1:1) catalyst with excellent FAO activity by the NaBH_4 chemical reduction process [21]. More recently, Jiang et al. prepared a carbon supported Pd–Pt–Cu trimetallic nanocatalyst with higher FAO electrocatalytic performance via the one-pot liquid-phase chemical reduction route [22]. It is found that the trimetallic Pd-based nanoalloys are more flexible than the corresponding bimetallic alloys in tuning the composition and electronic properties of catalytic surfaces. Moreover, the fabrication of Pd-based ternary nanoalloys is also beneficial to maximize the utilization of Pd in the catalysts as well as to enhance their electrocatalytic properties. Consequently, it is of great importance to design a trimetallic Pd-based alloy with low cost and high performance as an electrocatalyst for FAO.

Although alloying of Pd with either Pt or Ni is an efficient way to enhance the electrocatalytic performance, to our knowledge, the studies on the synthesis of a trimetallic PdPtNi catalyst by co-alloying of Pt and Ni together with Pd have not yet been reported. On the other hand, compared with the bimetallic alloys, the synthesis of the effective trimetallic alloy catalysts is still challenging. In the previous studies, the Pd-based ternary catalysts were generally prepared by the impregnation method with NaBH_4 or polyol as reducing agent [21,22]. In this work, we report a simple and effective hydrogen co-reduction approach to synthesize highly dispersed PdPtNi alloy nanoparticles supported on MWCNTs for the FAO reaction. The physical features of as-obtained catalysts were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS). The electrocatalytic properties of the PdPtNi/MWCNT catalyst were evaluated by cyclic voltammetry (CV) and chronoamperometry (CA) methods, and the results were compared with those from the PdPt/MWCNT and commercial Pd/C catalysts. The results demonstrate that the prepared PdPtNi/MWCNT catalyst has much smaller particle size and better dispersion of catalytic nanoparticles, and its electrocatalytic activity and durability toward FAO is significantly superior to the PdPt/MWCNT and commercial Pd/C catalysts.

Experimental

Chemicals and materials

The raw MWCNTs with a diameter of 40–60 nm and a length of 5–15 μm were supplied from Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China). $\text{Pd}(\text{NO}_3)_2$, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, formic acid, nitric acid, sulfuric acid and anhydrous ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). A 5 wt% Nafion solution was purchased from Sigma–Aldrich, and the commercial Pd/C catalyst (10% Pd loading) was provided from Alfa Aesar. All of the chemical

reagents are of analytical grade and used without any further purification. All of the solutions throughout the experiments were prepared with tridistilled water.

Synthesis of catalysts

The raw MWCNTs were at first functionalized by a conventional acid oxidation treatment to increase the surface activity and dispersibility of MWCNTs. Typically, 100 mg of raw MWCNTs were added to 200 mL of a mixture of concentrated H_2SO_4 and HNO_3 (volume ratio 3:1) and then ultrasonically treated for 4 h, washed repeatedly with tridistilled water several times to a neutral pH. The resulting functionalized MWCNTs were collected by centrifugation and dried under vacuum at 60 °C for 12 h to a constant weight. 10 mg acid-treated MWCNTs were dispersed in 10 mL anhydrous ethanol by ultrasonic treatment for 1 h. Subsequently, 191 μL 0.0564 M $\text{Pd}(\text{NO}_3)_2$, 28.5 μL 0.0193 M H_2PtCl_6 and 238 μL 0.0630 M $\text{Ni}(\text{NO}_3)_2$ aqueous solutions were injected into the above suspension, respectively. The mixture was ultrasonically treated to allow the complete evaporation of the solvents, and then the solid mixture was kept at 80 °C in a oven for 12 h. Finally, the resultant solid powder was subjected to a thermal treatment at 300 °C under a constant N_2 and 10% H_2 flow for 3 h in a tube furnace. The obtained catalyst product was denoted as PdPtNi/MWCNTs. As a comparison, the PdPt nanoparticles supported on MWCNTs (PdPt/MWCNTs) with 20% metal loading and same atomic ratio of Pd:Pt were also prepared using the similar procedure as described above.

Physicochemical characterization

The crystalline structures of as-prepared catalysts were examined by Powder X-ray diffraction (XRD) on an X-ray diffractometer (Rigaku D/MAX 2500 v/pc, Japan) using a Cu $K\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$). The particle size and morphology analysis of the samples were investigated by high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100) with an accelerating voltage of 200 kV. Energy dispersion X-ray (EDX) spectroscopy analysis was performed on the same TEM apparatus (JEOL JEM-2100). High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images and element analysis mapping were obtained by a FEI Tecnai-F30 microscope. The surface information of the catalysts were measured by X-ray photoelectron spectroscopy (XPS), which was carried out on a Thermo Scientific ESCALAB 250Xi system using Al $K\alpha$ radiation, and all of the electron binding energy values were corrected by referencing the C 1s peak at 284.6 eV from adventitious carbon. To measure the noble metal contents of the catalysts, an inductively coupled plasma-optical emission spectrophotometer (ICP-OES, Thermo Electron IRIS Intrepid II XSP, USA) was employed. In this work, the Pd content of the PdPtNi/MWCNT and PdPt/MWCNT catalysts was determined to be 9.89% and 17.79%, respectively. The ICP-OES analysis also indicates that the Pd:Pt:Ni atomic ratio in the PdPtNi/MWCNT is around 20:1:29, which is in good agreement with the stoichiometric ratio (20:1:27) in the precursor solutions.

Download English Version:

<https://daneshyari.com/en/article/5146162>

Download Persian Version:

<https://daneshyari.com/article/5146162>

[Daneshyari.com](https://daneshyari.com)