Journal of Power Sources 278 (2015) 43–49

Contents lists available at ScienceDirect

Journal of Power Sources

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

Deoxyribonucleic acid-directed growth of well dispersed nickel–palladium–platinum nanoclusters on graphene as an efficient catalyst for ethanol electrooxidation

Jingwen Ma, Jun Wang, Guanghui Zhang, Xiaobin Fan, Guoliang Zhang, Fengbao Zhang, Yang Li*

State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, China

H I G H L I G H T S

- Graphene-supported trimetallic NiPdPt alloy nanoclusters have been successfully synthesized by a simple method.
- NiPdPt nanoclusters are well dispersed on DNA-modified reduced graphene oxide.
- The synthesized NiPdPt/DNA-rGO exhibits superior catalytic activity and stability towards ethanol electrooxidation reaction.
- The best ratio of NiPdPt/DNA-rGO for ethanol electrooxidation in alkaline solution belongs to 1:1:1.

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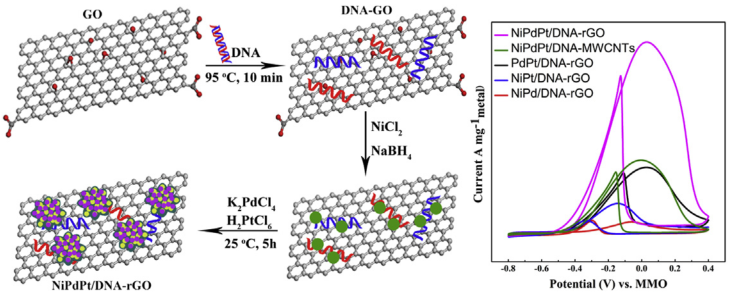

A R T I C L E I N F O

Article history:
Received 25 September 2014
Received in revised form
22 November 2014
Accepted 12 December 2014
Available online 13 December 2014

Keywords:
Nickel
Palladium
Platinum
Trimetallic nanoclusters
Graphene
Ethanol electrooxidation reaction

A B S T R A C T

Trimetallic NiPdPt alloy nanoclusters with diameter of about 10 nm are successfully dispersed on the deoxyribonucleic acid-modified reduced graphene oxide (DNA-rGO) by using $NaBH_4$ as reductant. The prepared NiPdPt nanoclusters grown on DNA-rGO (NiPdPt/DNA-rGO) composite are used as electrocatalysts for ethanol electrooxidation in alkaline solution. Cyclic voltammetry and chronoamperometry are used to investigate the electrochemical activities and stabilities of the catalysts. The $Ni_1Pd_1Pt_1$/DNA-rGO (molar ratio of Ni, Pd, Pt is 1:1:1) has extraordinary electrocataltic activity, with their mass current density reaching 3.4 A $mg^{-1}{}_{metal}$ and better stability. As compared with the bimetallic counterparts and NiPdPt grown on multi-wall carbon nanotubes, $Ni_1Pd_1Pt_1$/DNA-rGO retains the highest mass current density after a 2000 s current-time test at 0 V.

1. Introduction

The direct ethanol fuel cells (DEFCs) have drawn increasing attention because of numerous advantages [1]. Compared with the counterparts such as methanol and formic acid, ethanol has higher

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* Corresponding author.
E-mail address: liyang1895@tju.edu.cn (Y. Li).

http://dx.doi.org/10.1016/j.jpowsour.2014.12.040
0378-7753/

theoretical mass energy density and lower toxicity, and can be easily obtained from fermentation of agricultural products or other biomass [2–5]. However, the complete ethanol oxidation reaction is hard to achieve due to the difficulty of breaking C—C bonding in ethanol to form CO_2 and H_2O [6,7]. Therefore, it is crucial to synthesize an efficient anode catalyst with a high activity to break the C—C bond. Pt and Pt-based catalyst are generally considered the promising catalysts for the oxidation of small organic molecules. But the high cost of Pt catalysts has impeded its applications in the DEFCs [8]. Besides, Pt-based catalysts are easily poisoned by the intermediate products. Therefore, numerous efforts have been devoted to the development of an anodic catalyst with high activity, low cost and stable performance.

In order to synthesize a new kind of catalyst with both high activity and low cost, fabrication of multi-metallic nanoparticles including non-noble metal is demanded [9]. Pt-based bimetallic or multi-metallic catalysts can reduce the usage of the noble metal Pt and resist intermediate products poisoning due to the increased number of d-band vacancies of Pt [10,11]. To date, a large amount of Pt based bimetallic materials have been synthesized and showed enhanced catalytic activity, such as Pt—Au [12,13], Pt—Ag [14], Pt—Pd [10,15–18]. Among these materials, the Pt—Pd is more stable at high potentials [16] and exhibits significantly enhanced catalytic performance. As a non-noble metal, Ni is abundant in nature. Moreover, the presence of Ni in Pd/Pt has been found to be favorable for the improvement of catalytic activity due to the synergistic effect between Ni and Pd/Pt, which can enhance the activity and stability of the catalyst [19,20].

In addition, in order to further improve the activity of catalysts and reduce the use of precious metals, it is helpful to load catalysts onto a low cost supporting material with high surface area and good electrical conductivity. Graphene, a two-dimensional carbon material with a single or several atomic layers, is considered to be an excellent support due to its outstanding physical and chemical properties [21–23]. The sp^2 conjugation in the carbon lattice of graphene makes electrons transfer rapidly even at ambient temperature, which endow graphene-based materials excellent performance as electronic devices [24]. There have been many examples of metallic nanoparticles grown on graphene for fuel cells. For instance, Zhang et al. [15] anchored Pt—Pd alloy nanoparticles on graphene surface, and found that the obtained graphene-based composite exhibited much higher electrocatalytic activity toward methanol oxidation reaction than the PtPd nanoparticles and Vulcan-supported Pt—Pd nanoparticles. Using ethanol as the reductant, Chen and co-workers [17] synthesized the graphene-PtPd alloy nanoparticles with high electrocatalytic performance for ethanol oxidation.

In this study, NiPdPt nanoclusters can be homogeneously dispersed on DNA-modified reduced graphene oxide (DNA-rGO) by a facile route (Scheme 1). The resulting DNA-rGO supporting NiPdPt nanoclusters (NiPdPt/DNA-rGO) with small size distribution are shown to act as efficient catalysts for ethanol electrooxidation.

2. Experimental

2.1. Synthesis of NiPdPt/DNA-rGO catalyst

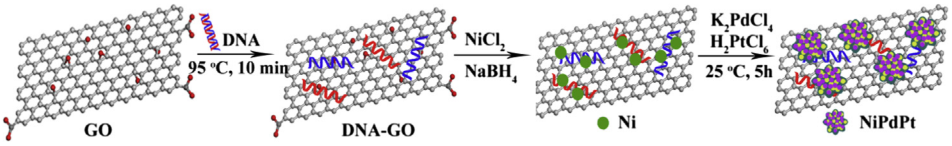
Graphite oxide was prepared by Hummers method and exfoliated into graphene oxide (GO) by sonication in water. A simple three-step method is employed for preparing NiPdPt/DNA-rGO catalysts. In the first step, 30 mg DNA was added into 45 mL of homogenous GO aqueous dispersion (1 mg mL^{-1}) and sonicated for 2 h, and then the mixture was heated to 95 °C for 10 min. In the second step, 5 mL 20 mM $NiCl_2$ was added to the mixture, meanwhile 15 mL 300 mM $NaBH_4$ was added dropwise subsequently. After refluxed with magnetic stirring for 30 min, 5 mL 20 mM K_2PdCl_4 and 5 mL 20 mM H_2PtCl_6 were added into the solution slowly. Then the mixture solution was cooled down to 25 °C and stirred for 5 h. The product was separated by centrifugation, washed with water for several times. The PdPt/DNA-rGO, NiPd/DNA-rGO, NiPt/DNA-rGO and the multi-wall carbon nanotubes-supported NiPdPt were also prepared through the same method. In addition, the NiPdPt/DNA-rGO was obtained through the same synthetic process, only without adding DNA.

2.2. Characterizations

The NiPdPt/DNA-rGO catalyst was characterized by high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F20), X-ray photoelectron spectroscopy (XPS) (PerkinElmer, PHI 1600 spectrometer) and Raman spectroscopy (NT-MDT NTEGRA Spectra). The X-ray diffraction (XRD) was performed on a Bruker-Nonius D8 FOCUS diffractometer. The exact composition of the NiPdPt/DNA-rGO catalyst was determined by inductively coupled plasma optical emission spectrometer (ICP-OES) (Vista-MPX).

2.3. Electrochemical measurements of NiPdPt/DNA-rGO catalyst

A CHI 660E electrochemical workstation was used to study the electrochemical activities of the synthesized catalysts towards ethanol oxidation reaction. A conventional three-electrode system was used with a glassy carbon electrode (GCE) (3 mm in diameter) as a working electrode, a platinum wire as the counter electrode and Hg/HgO electrode (MMO) as the reference electrode. Before every experiment, the GCE was polished carefully with alumina slurry to create a mirror surface. The electrode was then sonicated with absolute ethanol and double-distilled water for approximately 5 min, respectively, and then dried under nitrogen. To test the electrochemical catalytic ability of the obtained composites through ethanol oxidation reaction, the catalyst ink was prepared by mixing 1 mL of prepared catalyst (3 mg mL^{-1}) with 2 mL of a 0.5 wt% Nafion solution, followed by ultrasonication for 15 min to obtain a uniform dispersion (1 mg mL^{-1}). Nafion is viscous, so it can be used as the adhesive for improving the adhesion between catalyst and the substrate. Furthermore, Nafion also acted as the protector to prevent the catalyst from detaching [15,25,26]. The electrocatalyst ink (10 μL) was then dropped on the surface of the GCE and dried at the ambient temperature overnight. All the



Scheme 1. Illustration of the preparation of NiPdPt/DNA-rGO.