Nitrogen-doped graphene supported highly dispersed palladium-lead nanoparticles for synergetic enhancement of ethanol electrooxidation in alkaline medium

Peng Wu [a,b,c], Yiyin Huang [b,c], Liqun Zhou [a], Yaobing Wang [b,c,*], Yakun Bu [b,c], Jiannian Yao [d]

[a] Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, P. R. China
[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, YangQiao West Road 155#, Fuzhou, 350002, P. R. China
[c] Key Laboratory of design and assembly of functional nanostructures, Chinese Academy of Sciences, YangQiao West Road 155#, Fuzhou, 350002, P. R. China
[d] Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

ABSTRACT

In this work, a series of palladium and palladium-lead nanoparticles supported on active carbon, graphene and nitrogen-doped graphene are synthesized via a one-step reduction method. Atomic absorption spectroscopy, X-ray powder diffraction, transmission electron microscope and X-ray photoelectron spectroscopy are used to characterize the catalysts. The results indicate that metal nanoparticles are more uniformly dispersed on the surface of N-doped graphene than those on graphene, without any aggregation. Various electrochemical techniques are carried out to evaluate the electrocatalytic ethanol oxidation activity and durability. The peak current for ethanol electrooxidation of Pd/N-doped graphene increases to $70.2\,mA\,cm^{-2}$, obviously higher than that of Pd/Graphene ($38.0\,mA\,cm^{-2}$) and even surpasses that of Pd/C ($51.9\,mA\,cm^{-2}$). N-doped graphene support not only possesses faster dehydrogenation but provides an electron effect to Pd. Introduction of Pb into the catalyst causes the formation of abundant oxygenated species on the catalyst surface at low potential. Based on the synergistic effect of N and Pb towards Pd particles, the PdPb/N-doped graphene catalyst (Pd: Pb = 8:1.0) exhibits remarkably enhanced activity up to $152.3\,mA\,cm^{-2}$ for ethanol oxidation, which is 4.0 and 2.9 times higher than that of Pd/Graphene and Pd/C, respectively. The catalytic durability and stability are also greatly improved.

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1. Introduction

As a kind of attractive energy conversion device for electronics vehicles, direct ethanol fuel cells (DEFCs) have attracted much attention owing to their low emission, high efficiency and no toxicity [1–3]. Currently, the ethanol oxidation reaction (EOR) in alkaline medium of these catalysts involves release of twelve electrons and cleavage of the C–C bond. However, the C–C bond cleavage is difficult to be implemented at low temperature [4,5]. To address this issue, lots of researches have been devoted to electrochemical oxidation of ethanol in alkaline medium because of the faster oxidation kinetics in alkaline medium relative to acid

medium [6,7]. Besides, lots of possible derivatives such as CH_3COH and CHCO are produced on catalyst surface during ethanol electrooxidation [8] and prevent further adsorption and electrooxidation of ethanol molecules in solution, leading to a decrease in the catalyst efficiency. These drawbacks have become a bottleneck in the commercialization of DEFCs. Consequently, anode catalysts with high catalytic activity and high durability are extremely desired [9,10].

Pd catalyst is considered as an excellent alternative for the application of alkaline ethanol fuel cells as the following two reasons: one is that Pd gives the higher electrocatalytic activity and the less poisoning effect compared with Pt for ethanol oxidation in alkaline medium [11–14]; the other is that Pd is much more abundant than Pt on the earth, which makes Pd less expensive than Pt [11]. The anodes used Pd–based electrocatalysts needed further improvement in catalytic activity and stability to fulfill

* Corresponding author. Tel./fax: +86 591 2285 3916.
E-mail address: wangyb@fjirsm.ac.cn (Y. Wang).

commercialization of DEFCs. Much effort has been devoted to improve the performance of Pd catalysts by introducing other one or more elements. For example, Au, Ag, Ni, Cu, Sn and Pb were selected as promoting elements to enhance the activity of Pd catalyst for ethanol electrooxidation [15–20]. Among these elements, Pb seems to have stronger promoting effects. A number of studies have devoted to enhanced electrooxidation of small organic molecules by Pb addition [21–25]. The promoting effects of Pb in the Pd–based catalysts can be attributed to the geometric effect, the electronic effect and the bifunctional mechanism [21].

Aside from active carbon, carbon nanocoils [26], carbon nanohorns [27], graphite nanofiber (GNF) [28], carbon nanotubes (CNT) [29–31] and graphene (G) [32,33] were also used to support Pd–based nanoparticles. Due to the high electric conductivity and special structural properties, graphene have been considered as the most promising support material in fuel cell electrodes [33]. Chemical doping is an important way to modulate the surface structure and physicochemical property of graphene [34–36]. The incorporation of electron-rich nitrogen atoms into graphene can not only improve the dispersion state of the nanoparticles on the graphene surface [37,38], but also modify the surface structure of carbon materials and strengthen interaction between metal nanoparticles and supports [39–42]. However, the synergetic effect of N-doping and second active component towards noble metal on small organic molecule electrooxidation have been rarely reported until now, which will be revealed in this study.

Based on the above considerations, herein, N-doped graphene was selected as a support and PdPb nanoparticles were used as the active component for synthesis of the novel PdPb/NG nanocatalyst. The PdPb/NG nanocatalyst was prepared via simply reducing metal ions on N-doped graphene surface. The electrocatalytic performance of PdPb/NG towards ethanol oxidation was systemically investigated, compared with Pd/C, PdPb/C (8:1.0), Pd/G, Pd/NG, PdPb/G (8:1.0). The origin of high performance of the catalysts was also revealed.

2. Experimental

2.1. Synthesis of catalysts

All analytically pure reagents were used as received without any further purification, and all solutions were prepared with double-distilled water. The support preparation was as follows:

Graphite oxide (GO) was prepared according to the previous literature by Hummers [43,44] from graphite powder (Aldrich, powder, < 20 micron, synthetic) [44]. N-doped graphene was further prepared from as-prepared graphite oxide and the typical experiment procedure was as follows: N-doped graphene was synthesized by adding appropriate amount of graphite oxide (GO), double-distilled water and ammonium hydroxide under ultrasonic stirring for 60 min. Then, the well-dispersed suspension solution was transferred into a Teflon bottle of 80 mL held in a stainless steel autoclave, which was filled up to the capacity of 75%, sealed and maintained at 200 °C for 6 h. After the autoclave had been cooled down to room temperature naturally, the precipitate was collected and washed repeatedly with double-distilled water, and then dried in the freezer dryer at −55 °C for 24 h under vacuum. After suitable grinding, the mixture was annealed under argon atmosphere at 600 °C for 4 h. The final material was obtained after cooling to room temperature in the furnace. The same method without ammonium hydroxide was used to prepare graphene (G). Active carbon from Vulcan XC-72R was first pretreated with concentrated HNO_3 for 2 h in a flask with a reflux set placed in an oil bath at 120 °C.

The PdPb/NG catalyst was synthesized as follows: appropriate amount of N-doped graphene, 8 ml of 18.9 mM $PdCl_2$ and 75.6 mM

HCl aqueous solution were mixed with 50 ml of ethylene glycol (EG) in a flask under ultrasonic stirring. Then, a specific volume of 18.9 mM $Pb(CH_3COO)_2$ solution was then added dropwise to the suspension with constant stirring for 1 h. Then, 80 mg of $NaBH_4$ was dissolved in 50 ml of water and this solution was added dropwise into the suspension above to reduce Pd^{2+} and Pb^{2+} ions. This redox reaction was conducted for 2 h. Then the suspension was filtered, washed with double-distilled water and dried in a vacuum oven overnight to obtain the PdPb/NG composite. The as-prepared catalysts were defined as PdPb/NG (8:x), where the ratio of 8:x stands for the reactant ratio in the synthesis and x was equal to 0.2, 0.4, 1.0 and 3.0, respectively. The similar synthetic method was used to prepare the Pd/C, PdPb/C (8:1.0), Pd/G, Pd/NG and PdPb/G (8:1.0) catalyst for comparison. The total Pd metal loading of all these catalysts was maintained at 20 wt.%.

2.2. Physical and electrochemical characterization

The Pd and the atomic ratio of Pd/Pb of catalysts were determined by atomic absorption spectroscopy (AAS, Spectra AA-220). The dispersion of the catalyst was characterized using a JEOL JEM-1010 transmission electron microscope (TEM) at 200 kV. The X-ray powder diffraction (XRD) was conducted using a Philip X'Pert Pro MPP X-ray powder diffractometer with Cu Kα radiation (λ = 1.54 Å) at the scan rate of 5° min^{-1} with a step of 0.02°. The chemical valences of elements in the catalyst were analyzed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250) with an Al Kα X-ray source of 1487 eV. The chamber pressure was kept below 3×10^{-10} mbar during test and specific correction was conducted by using a C 1s binding energy of 285 eV.

Electrochemical measurements were conducted by using a CHI660E electrochemical working station (CH Instrument Inc.). A mercuric oxide electrode (Hg/HgO/1 M KOH, 0.098 V vs. SHE [45]) and a Pt rod were used as the reference and counter electrodes, respectively. A piece of glassy carbon (0.1256 cm^2) covered by the catalyst was used as the working electrode. For the working electrode preparation, a specific amount of the catalyst was dispersed in a suspension of 45 μl of 20 wt.% nafion solution (DuPont, USA) and 1955 μl of isopropyl alcohol under ultrasonic stirring. A 4 μl aliquot of the slurry was spread on the glassy carbon surface which was first polished with Al_2O_3 paste, treated in an ultrasonic bath and then rinsed by double-distilled water and anhydrous ethanol in sequence. The electrode was dried at 60 °C for 30 min. The total Pd loading on the electrode was kept at 4 μg. All solutions were first de-aerated with high purity N_2 before measurements. The CO stripping experiments were performed as follows: after de-aerating with N_2, CO was admitted into the KOH solution in the electrolytic cell and adsorbed on the as-prepared catalysts for 15 min. The excess CO was eliminated with high purity N_2 prior to the stripping tests. All electrochemical measurements were conducted in a thermostatic water bath at 30 °C.

3. Results and discussion

The presence of Pd and Pb in the catalysts was verified by AAS analysis. The practical Pd loadings in Pd/G and Pd/NG were 19.2 wt.% and 19.1 wt.%, respectively. The Pd loadings in PdPb/NG catalysts with different Pd/Pb atomic ratios (8:0.2; 8:0.4; 8:1.0; 8:3.0) were 19.3 wt.%, 19.5 wt.%, 19.3 wt.% and 19.5 wt.% and the practical atomic ratios of Pd:Pb in PdPb/NG were 8:0.09, 8:0.31, 8:0.80 and 8:2.54, respectively, which was obviously lower than its initial added amount in the synthesis process because Pb was not completely reduced and deposited by $NaBH_4$ [46].

The XRD patterns of Pd/G, Pd/NG and PdPb/NG with different Pd/Pb atomic ratios catalysts are shown in Fig. 1. The first broad