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A two step method to synthesize palladium–copper nanoparticles on reduced graphene oxide and their extremely high electrocatalytic activity for the electrooxidation of methanol and ethanol

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HIGHLIGHTS

- A two step method for the preparation of Pd–Cu/RGO hybrids containing different amounts of Cu.
- After the two step reaction, the catalysts form a bimetallic structure of a small Pd–Cu core and a thin Pd rich shell.
- The samples have better catalytic property for alcohol electrocatalytic oxidation than many other Pd-based catalysts.

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ABSTRACT

Palladium–copper nanoparticles (Pd–Cu NPs) supported on reduced graphene oxide (RGO) with different Pd/Cu ratios (Pd–Cu/RGO) were prepared by a two step method. The Pd–Cu/RGO hybrids were characterized by transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction and thermogravimetric analyses. Cyclic voltammetry and chronoamperometry were used to investigate the electrochemical activities and stabilities of the Pd–Cu/RGO catalysts for the electro-oxidation of methanol and ethanol in alkaline media. The Pd–Cu/RGO catalysts exhibited high catalytic activities and good stabilities. This is because the catalysts have a bimetallic structure consisting of a small Pd–Cu core surrounded by a thin Pd-rich shell which improves the catalytic activities of the Pd–Cu/RGO hybrids. Thus they should be useful in direct methanol and ethanol fuel cells.

1. Introduction

A fuel cell is an electrochemical engine that can convert the free energy change of a chemical reaction directly into electrical energy [1]. Since direct alcohol fuel cells (DAFCs) are highly efficient power generators and have good environmental performance, they are considered to be the best choice for clean and efficient power generators and so they have attracted a great deal of attention from researchers, companies and governments [2]. Alcohols, like methanol and ethanol, are the most promising candidates for DAFCs since they are easily handled, transported and stored, and they have high theoretical energy densities [3].

DAFCs have been extensively studied, but they still have many problems including a shortage of appropriate anodic catalysts and low catalytic activities. Studies have shown that Pt-based catalysts are promising catalysts since they have the highest catalytic activities among the anode electrocatalysts for methanol and ethanol oxidation [4]. However, Pt and Pt-based catalysts have some disadvantages like their high costs due to the limited supply of Pt. To solve this problem, palladium (Pd) has emerged as an attractive replacement for Pt-based catalysts in fuel cells. Compared to Pt, Pd has a lower price, a higher abundance and better electrocatalytic activity and it is especially effective in alkaline environments [5].

A great deal of effort has been made to improve the catalytic efficiency of Pd catalysts for methanol and ethanol oxidations. One approach is to control the size and morphology of the Pd nanostructures. A variety of chemical protocols have been developed for achieving partial control of nanostructures. For instance, nanoparticles, nanocubes, nanoflowers, nanowires, nanotubes, and

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nanoporous (or mesoporous) and dendrite structures have all been fabricated [6–13]. Among these, Pd nanoparticles are of particular interest in catalysis due to their high surface areas and good catalytic activities.

Alloying Pd with a second metal (M = Co, Ni, or Sn) is also a way to reduce the Pd dosage and to enhance catalytic performance [14–17]. However, catalysis at the electrode of a fuel cell is a surface phenomenon and the catalytic activity of Pd depends on the dispersion or exposed percentage of Pd atoms in the catalyst [18]. Therefore, the design of hybrids which contains more Pd at the outer surface of the material is being pursued in order to make the most efficient use of the Pd metal. This is a promising way to enhance the catalytic performance. This new class of catalysts can significantly enhance the kinetics of methanol and ethanol oxidation reactions, and at the same time these catalysts possess improved Pd stability under typical fuel cell operating conditions [19].

Another way to enhance the activity of noble metals nanocatalysts and to lower the usage of it is to load the nanocatalyst onto the surface of a suitable support material [20]. Carbon materials are inexpensive and have large surface areas and good electrical conductivities. So they are ideal support materials for nanoparticle catalysts. Carbon black and carbon nanotubes have been used as support materials for dispersing and stabilizing Pd-based catalysts [21–26]. Graphene, a sp^2-hybridized two dimensional mono-layer carbon sheet, has became a popular support material for nanoparticles because of its superior thermal and electric conductivities, high chemical stability, broad electrochemical window and unique graphitized basal plane structure [27–29]. Many monometallic and bimetallic nanoparticles, such as Pd [30], Au [31], Pt–Cu [32], Pd–Ag [33] and Au–Pd [34] have been dispersed on graphene, and these materials have shown impressive catalytic behaviors for various reactions.

In this paper, Pd–Cu bimetallic hybrids supported on reduced graphene oxide (RGO) were investigated for the oxidation of methanol and ethanol. Herein a two-step method for the preparation of Pd–Cu/RGO hybrids which contain different amounts of Cu is presented. Sodium citrate was used as an ecofriendly reducing agent to reduce H_2PdCl_4, $CuSO_4$ and GO in one pot with the subsequent galvanic displacement reaction between first step sample and $PdCl_4^{2-}$ in aqueous solution [35]. Due to the modification of the structure and composition, we anticipate the catalytic activities can be quite different from those of the pure metals Pd NPs. The catalytic activity of these Pd–Cu/RGO hybrids for the electro-oxidation of methanol and ethanol was studied.

2. Experimental details

2.1. Materials

Natural graphite powder was purchased from Qingdao Graphite Factory. Potassium permanganate, sodium nitrate, concentrated sulfuric acid, hydrogen peroxide (30%), hydrochloric acid, ethylene glycol (EG), sodium citrate, potassium palladium (II) chloride (K_2PdCl_4) and copper sulfate were all from Sigma. All other reagents were purchased from Tianjin Chemical Reagent Company. All reagents were analytical grade and were used as received without any further purification.

2.2. Synthesis of Pd–Cu/RGO hybrids

A modified Hummers' method was employed to produce graphite oxide from natural graphite powder [36]. Pd–Cu/RGO was prepared by a two-step method. In a typical process, 8 mL K_2PdCl_4 aqueous solution (0.5 mg mL^{-1}), 12 mL $CuSO_4$ aqueous solution (1 mg mL^{-1}) and sodium citrate (120 mg) were dissolved in ethylene glycol (EG) in a flask and stirred for 0.5 h to obtain a homogenous solution. The solution was then added to 6 mL prepared graphene oxide suspension (4.2 mg mL^{-1}) with stirring and its pH was adjusted to 10 by the dropwise addition of a 5 wt % KOH/EG solution. The mixed solution was heated to 160 °C and maintained at this temperature for 6 h. The resultant precipitate was collected by filtration and then washed three times with deionized water and finally dried in air for 12 h. This resulted in the first step sample designated as Pd–Cu/RGO-1.

The Pd–Cu/RGO-1 was then added to a flask containing only an aqueous solution of K_2PdCl_4 (11 mL, 0.5 mg mL^{-1}). The mixture was stirred for 4 h at 80 °C and the resultant solid was collected by filtration, washed with deionized water, and dried in air for 12 h. This sample is designated as Pd–Cu/RGO. The weight percent of Pd in the Pd–Cu/RGO was about 10 wt % and the atomic ratio of Pd to Cu was 1:1 (Pd–Cu(1:1)/RGO). In order to find which ratio led to the best catalytic activity, Pd–Cu (1:0.8)/RGO, and Pd–Cu (1:1.2)/RGO with the same 10 wt % of Pd were also prepared using the same procedure.

2.3. Characterization

2.3.1. X-ray diffraction analysis

The X-ray diffraction (XRD) spectra of the samples were measured using an X-ray diffractometer (BDX3300) with a reference target: Cu Ka radiation ($\lambda = 1.54$ Å), voltage: 30 kV and current: 30 mA. The samples were measured from 30° to 90° (2θ) at steps of $4° min^{-1}$.

2.3.2. X-ray photoelectron spectroscopy (XPS) analysis

Elemental analysis was conducted on an X-ray photoelectron spectrometer with a Mg Ka anode (PHI1600 ESCA System, PERKIN ELMER, US).

2.3.3. Thermogravimetric analysis

Prior to thermogravimetric analysis (TGA), the samples were dried in a vacuum at 50 °C for 2 days. TGA was performed with a Rigaku-TD-TDA analyzer with a heating rate of 10 °C/min.

2.3.4. Transmission electron microscopy (TEM) observation

TEM and line profile measurements were performed using a Philips Tecnai G^2F20 microscope at 200 kV.

2.4. Electrochemical measurements

The electrochemical measurements, including cyclic voltammetry and chronoamperometry, were performed with a CHI 660D electrochemical work station (CH Instruments, Inc, Shanghai) at ambient temperature. The counter and reference electrodes were a platinum mesh and a Hg/HgO (1.0 M KOH) electrode, respectively. The working electrode was prepared by dropping 5 μL of catalyst ink onto a glassy carbon electrode (GCE) with a diameter of 3 mm. The ink was prepared by ultrasonically mixing 4 mg of Pd–Cu/RGO with 1.9 mL of ethanol and 0.1 mL of Nafion solution. The electrolyte was 1 M KOH/1 M CH_3OH or 1 M KOH/1 M CH_3CH_2OH, and oxygen was removed from all solutions by purging the electrolyte with an inert gas for 20 min.

3. Results and discussion

The morphology of both the first step sample (Pd–Cu/RGO-1) and second step sample (Pd–Cu/RGO) were observed by TEM. The TEM images of Pd–Cu (1:1)/RGO-1 (Fig. 1a) and Pd–Cu (1:1)/RGO (Fig. 1b) show that the Pd–Cu nanoparticles were well dispersed on the rGO layers and they have a narrow size distribution. The