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Vertically oriented reduced graphene oxide supported dealloyed palladium–copper nanoparticles for methanol electrooxidation

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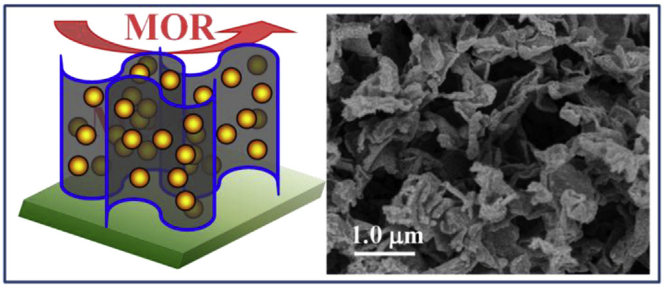
HIGHLIGHTS

- Vertical reduced graphene oxide supporting dealloyed PdCu particles is reported.
- The vertical orientation is achieved by a one-step cyclic voltammetric technique.
- The catalyst exhibits excellent performance for methanol electrooxidation.
- The electrodeposition technique is rapid, simple and green.

GRAPHICAL ABSTRACT



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ABSTRACT

Vertically oriented graphene-based nanocatalysts represent an emerging class of electrocatalysts due to their large surface area and excellent electrical transport ability. Herein, we report a vertically oriented reduced graphene oxide supported dealloyed palladium–copper nanoparticle catalyst (PdCu/VrGO) synthesized by a facile cyclic voltammetric electrodeposition of graphene oxide in the presence of Na_2PdCl_4 and copper ethylenediamine tetraacetate. The structure and composition are characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Raman spectroscopy, and X-ray photoelectron spectroscopy. Meanwhile, the electrochemical properties are measured by cyclic voltammetry and chronoamperometry. The PdCu/VrGO catalyst exhibits excellent electrocatalytic activity towards methanol oxidation, with the mass activity of 762.8 A g^{-1}, which is 7.1 times that of a commercial Pd/C catalyst. In addition, PdCu/VrGO shows good chemical stability and superior tolerance to CO poisoning. These results demonstrate that vertical reduced graphene oxide provides a promising platform for the development of electrochemical nanocatalysts.

1. Introduction

The increasing worldwide energy demand and environmental concerns draw great attention in seeking effective and clean energy technologies to replace the burning of fossil fuels. Fuel cells are one promising example of such technologies due to their low emissions and high energy efficiencies [1,2]. Platinum (Pt) is traditionally used as the electrocatalyst in fuel cells, but its high cost and scarcity hinder the widespread commercialization of fuel cells [3,4]. Intense research efforts have been focused on developing Pt-free catalysts,

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and among them, palladium (Pd) has aroused increasing interest due to its higher abundance, lower cost than Pt and the outstanding electrocatalytic oxidation of a large variety of alcohols in alkaline environment [5,6]. Nevertheless, the activity and the durability of pure Pd catalysts are far from satisfactory and need to be further enhanced [7,8]. Various methods have been explored to improve the electrocatalytic performance of Pd catalysts, including reduction of particle size and control of particle shape [9–11]. Alloying Pd with other less expensive transition metals (e. g., Cu, Co, Ni, etc.) [12,13] is another popular way that can significantly increase the catalytic activity and the CO tolerance while decrease Pd consumption because of the synergistic effects between different components or the modified electronic structure. Moreover, the catalytic activity can be further enhanced by surface dealloying of the non-noble metal atoms from Pd alloys due to the formation of Pd-rich shell [14].

On the other hand, in order to maximize the available surface area of nanosized electrocatalysts for both mass transport and electron transfer, it is very necessary to immobilize nanocatalysts on a support with a high surface area and excellent electronic conductivity to obtain high catalyst dispersion. Graphene has been paid a great deal of attention as a catalyst support [15,16] owing to its ultrahigh surface area (theoretical value of 2630 $m^2\ g^{-1}$), outstanding electrical conductivity (intrinsic electron mobility of $2 \times 10^5\ cm^2\ V^{-1}\ s^{-1}$), and excellent mechanical strength and chemical stability. However, due to the irreversible restacking of individual graphene sheets, catalyst nanoparticles are usually sandwiched between the graphene layers, causing a decrease of catalytic sites [17–19]. Recently, vertically oriented graphene (VG), where the graphene sheets stand upright on a substrate and therefore the graphene film has a highly exposed surface and open structure, shows a better potential than conventional stacked graphene in energy storage and conversion fields [20–22], including used as superior catalyst support materials for fuel cells [23,24]. However, the VG was usually obtained by chemical vapor deposition which is complicated, expensive, and moreover difficult in compatibility with the fabrication process of practical electrochemical devices. Thus, the facile preparation of VG as catalyst supports on a large scale from low-cost graphene oxide is very attractive but challenging.

Herein, we devote our attention to the preparation of vertically oriented reduced graphene oxide (VrGO) to support palladium–copper (PdCu) alloy electrocatalyst through electrodeposition. Electrodeposition is one of the simple, rapid and green techniques for the fabrication of “clean” binder-free electrode materials [25,26]. We first applied the electrodeposition method for reduced graphene oxide (rGO) preparation [27,28] and recently achieved the structure control of rGO sheets from horizontally layered stacking to nearly vertical orientation on electrode surface [29,30]. In this work, the VrGO supported PdCu alloy (PdCu/VrGO) was obtained by a direct cyclic voltammetric (CV) electrolysis of a mixture solution of graphene oxide (GO) and the precursors of Pd and Cu. Electrochemical dealloying of the less noble Cu from the PdCu alloy was additionally performed. The resultant PdCu/VrGO catalyst exhibits high electrocatalytic activity and good chemical stability for methanol oxidation reaction (MOR). To our knowledge, this is the first prototype about dealloyed electrocatalyst nanoparticles supported by vertically oriented reduced graphene oxide. Both the compositional (i.e., alloying) and the geometrical factors (i.e., porous dealloyed nanoparticles and open structure of the catalyst coating) are contributed to the excellent electrocatalytic performance.

2. Experimental

2.1. Materials and chemicals

Natural flake graphite with an average particle size of about 50 μm was purchased from Shanghai Carbon Co., Ltd. (Shanghai, China). $PdCl_2$ powder was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Nafion 117 solution and a commercial Pd/C catalyst (10 wt % Pd, Sigma–Aldrich 205699) were purchased from Shanghai Hesen Co., Ltd. (Shanghai, China). All other chemicals were of analytical grade and used as received. Deionized water was used throughout for solution preparation.

2.2. Preparation of graphene oxide (GO)

Graphite oxide was prepared by the improved method with a minor modification [31]. In a typical procedure, a mixture of concentrated H_2SO_4/H_3PO_4 (60: 4 mL) was added to a mixture of graphite flakes (1.0 g) and $KMnO_4$ (6.0 g). The reaction was heated to 50 °C and stirred for 12 h. Then the reaction was cooled to room temperature and poured onto ice water (~250 mL). After 1.0 mL of 30% H_2O_2 was added drop by drop, the mixture was centrifuged and the obtained solid product was washed with 2.0 M HCl aqueous solution to remove the metal impurities, followed by repeatedly washing with deionized water until its solution pH increased to neutral (~6.5). Finally, the product was purified by dialysis for one week using a dialysis membrane with a molecular weight cut off of 8,000 to 14,000 g mol^{-1} to remove the remaining metal ions. The resulting yellow-brown solid was dried for 24 h at 45 °C in oven. The prepared graphite oxide powder was then exfoliated in 0.067 M pH = 8.0 phosphate buffer solution by ultrasonication for 3 h to form a 0.3 g L^{-1} GO colloidal dispersion.

2.3. Preparation of PdCu/VrGO hybrid

Na_2PdCl_4 (0.1 M) aqueous solution was first prepared by dissolving $PdCl_2$ (1.0 g) and NaCl (0.65 g) into 50.0 mL of deionized water with magnetic stirring for 10 h at room temperature. A certain amount of copper ethylenediamine tetraacetate (Cu-EDTA) (0.5 mM, the optimized concentration) was added into the dispersion containing 0.3 g L^{-1} GO and 4.0 mM Na_2PdCl_4 and then the mixture solution was used as the precursor for electrochemical preparation of PdCu/VrGO. The electrodeposition was carried out under magnetic stirring using cyclic voltammetry on a CHI 660C electrochemical workstation (CH Instruments, Shanghai) with a three-electrode system: a glassy carbon (GC) electrode (3 mm in diameter, 0.07 cm^2 in geometric area) as the working electrode, a Pt foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The scan was performed between −1.4 and 0.6 V at a rate of 50 mV s^{-1} for ten cycles. After electrodeposition, electrochemical dealloying of the less noble Cu from the PdCu alloy was carried out. Specifically, the electrode was transferred into 1.0 M H_2SO_4 solution and conducted between −0.2 and 1.2 V until the CV curves were reproducible. Finally, the working electrode was thoroughly washed with deionized water and dried at room temperature. As a comparison, Pd/VrGO was prepared similarly without adding the precursor of Cu. Hybrid of PdCu nanoparticles and flat-lying rGO (PdCu/flat-lying rGO) was also prepared using the same procedure from 0.3 g L^{-1} GO, 1.0 mM Na_2PdCl_4 and 0.5 mM Cu-EDTA followed by dealloying in 1.0 M H_2SO_4 solution. Hybrid of Cu and rGO (Cu/rGO) was prepared from 0.3 g L^{-1} GO and 0.5 mM Cu-EDTA without adding the precursor of Pd.