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Reduced Graphene Oxide Supported Bimetallic Cobalt–Palladium Nanoparticles with High Catalytic Activity towards Formic Acid Electro-oxidation

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In this work, we report the growth of uniformly dispersed bimetallic cobalt–palladium nanoparticles (NPs) on reduced graphene oxide (RGO) nanosheets to prepare CoPd–RGO composites *via* a two-step procedure, where firstly formed Co NPs are used as seeds for the subsequent growth of Pd. The generation of Co NPs on RGO is performed by an *in-situ* reduction reaction with the reducer ethylene glycol under oil bath at 180 °C. According to composition, size and microstructure analyses, NPs in the resulting CoPd–RGO have an average particle size of 5 nm, and Pd is added to one side of Co NPs, thus forming Co–Pd bimetallic interfaces. The involved formation mechanism is suggested. The composite is used as an electro-catalyst for the formic acid oxidation in alkaline electrolyte, and the catalytic performance is investigated by cyclic voltammetry and chronopotentiometry etc. The results show that the composite has the highest electro-catalytic activity, the best electrochemical stability and the highest resistance to CO poisoning than those of the monometallic composite and commercial Pd black at the same loading. This is due not only to the small size of NPs with Co–Pd bimetallic interfaces providing more active atoms accessible for reactants, but also to the electric synergistic effect between metals and graphene.

KEY WORDS: Composite materials; Nanoparticles; Electric properties; Materials synthesis; Microstructure

1. Introduction

Fuel cells have attracted considerable attention as a viable alternative to hydrogen fuel cells for portable power applications[1–7]. With a high energy density, direct formic acid fuel cells (DFAFCs) are expected to be the first cells for commercial applications[8–12]. Palladium (Pd)-catalyzed formic acid oxidation reaction (FAOR) is one of the most important reactions in DFAFCs. However, Pd as an electro-catalyst makes fuel cells very expensive. CO poisoning and aggregation/growth of Pd nanoparticles (NPs) during the anode reaction rapidly degrade the performance of DFAFCs[13]. A conductive support material has been demonstrated to play a role in altering the electronic characteristic and geometry of catalyst particles dispersed on the system[14,15]. Thus, there is a strong motivation to increase the utilization of Pd catalysts *via* their dispersion as small particles on a support material.

As a novel one-atom-thick graphitic carbon system, graphene is a two-dimensional macromolecule and has been actively pursued as a fascinating material with extraordinary properties. Owing to its extremely high specific surface area (2600 m^2 g^{-1}), good electrical conductivity and chemical stability, graphene has also attracted great attention as an electro-catalyst support. Chen et al.[16] have developed a facile method for synthesizing Pd NPs with a very narrow size distribution supported on graphene by the redox reaction between $PdCl_4^{2-}$ and graphene oxide, and the Pd NPs–graphene is very "clean" because of the surfactant-free synthesis, allowing it to show a high electro-catalytic ability in the FAOR. Cheaper and more effective electro-catalysts are desired for the development of fuel cell technologies. A composite composed of a noble metal and a transition metal has been found to have higher electro-catalytic activity than the single noble metal electro-catalyst[17,18], which is explained by the modification of the noble metal electronic structure as well as the synergistic effect between two metals. Wang et al.[19] have synthesized Au–Pd core–shell nanocrystals with a tetrahexahedral structure by using Au nanocubes as structure-directing

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cores. In comparison, electro-catalysts with a noble metal added to one side of a transition base metal, thus forming bimetallic interfaces which provide more active atoms accessible for reactants, have more advantages for the full use of the noble metal.

Herein, we report that the uniformly dispersed bimetallic cobalt (Co)−Pd NPs on reduced graphene oxide nanosheets (CoPd−RGO composites) are prepared *via* a two-step procedure where firstly formed Co NPs are used as seeds for the subsequent growth of Pd. The generation of Co NPs on RGO is performed by an *in-situ* reduction reaction with the reducer under oil bath at 180 °C. The composite's morphology, microstructure, size and composition are characterized by transmission electron microscopy (TEM), selected area electron diffraction (SAED), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The involved formation mechanism is suggested. The composite is used as an electro-catalyst for the formic acid oxidation in alkaline electrolyte. The electro-catalytic performance and possible origin of the high activity and stability for the FAOR have also been investigated by cyclic voltammetry and chronopotentiometry etc.

2. Experimental

2.1. Materials

Natural graphite powder (spectrum pure), H_2SO_4 (98 wt%, A.R.), $KMnO_4$ (A.R.), H_2O_2 (30 wt%, A.R.), HCl (36−38 wt%, A.R.), NaOH (A.R.), $BaCl_2$ (C.P.), HCOOH (A.R.) and anhydrous ethanol were all purchased from Sinopharm (Group) Shanghai Chemical Reagent Co. $CoCl_2\cdot 6H_2O$ was obtained from Sinopharm Chemical Reagent Co. Ltd. K_2PdCl_6 was purchased from Nanjing Ning-Shi Chemical Reagent Co. Ltd, and ethylene glycol (EG) was obtained from Shanghai Jiu-Yi Chemical Reagent Co. Ltd. Commercial Pd black catalyst was purchased from Sigma−Aldrich Co. LLC. All reagents were used as received without further purification. Deionized water with a resistivity of exceeding 18.0 MΩ cm from a JL-RO 100 Millipore-Q Plus water purifier was used throughout the experiments.

2.2. Synthesis of graphite oxide

Graphite oxide was synthesized from natural graphite powder using the modified Hummers' method[20]. Typically, 10 g of graphite powders were added into 230 mL of 98 wt% H_2SO_4, followed by an intense stir for 5 min at room temperature, then 30 g of $KMnO_4$ was introduced into the mixture. Under continuously vigorous stirring, the mixture was kept under low (10−15 °C), middle (35 ± 3 °C) and high (98 °C) temperatures for 2 h, 30 min, and 30 min reactive stages, respectively. Subsequently, 230 mL of diluted H_2O_2 (5 wt%) was added into the above mixture. Finally, the suspension was vacuum filtrated using 460 mL of deionized water and 300 mL of diluted HCl (5 wt%). $BaCl_2$ aqueous solution was used to test whether the filtration solution contained SO_4^{2-}, and NaOH (5 mol/L) was added to produce flocculation. The resulting products were centrifuged, followed by drying at 50 °C in an oven.

2.3. Synthesis of Co−RGO composite

For synthesizing the Co−RGO composite, 48.5 mg of graphite oxide was dispersed in 80 mL of EG by sonication for 20 min. In this reaction, EG acts as a reducing, stabilizing and dispersing agent. Then the solution was combined with 125.1 mg of $CoCl_2\cdot 6H_2O$ under vigorous stirring and subjected to oil bath heating at 180 °C for 1 h. The entire solution's pH was adjusted to 10 by adding NaOH (1.0 mol/L). After the end of the heating, the solution was cooled to room temperature, and the product was washed and centrifuged by deionized water for several times to remove the excess EG, then dried at 40 °C in a vacuum oven. Finally, the cobalt impregnated reduced graphene oxide (Co−RGO) was obtained.

2.4. Synthesis of CoPd−RGO composite

Typically, 7 mL of 11.26 mmol/L K_2PdCl_6 and 267 mg Co−RGO were dispersed in a beaker with 50 mL deionized water. The resulting solution was uniformly dispersed by sonication for 10 min, then vigorously stirred for 24 h at room temperature. The black product was washed and centrifuged with deionized water for several times, and finally dried in a vacuum oven at 40 °C.

2.5. Characterizations

TEM, HRTEM images and SAED patterns were obtained on a JEOL JEM-2100 TEM operating at 200 kV. The SEM image and EDS elemental mappings were obtained on a JEOL JEM-6510 tungsten filament SEM including Oxford INCA X-act X-ray energy dispersive spectroscopy. XPS was measured on a Thermofish K-alpha X-ray photoelectron spectrometer. Binding energies were determined with reference to carbon's $C1s = 284.6$ eV. The products' composition and crystallographic properties were analyzed by XRD on a Rigaku Ultima III diffractometer (using $CuK\alpha = 0.15418$ nm radiation) at a scanning rate of 5° per min in the range of 5°−90°.

2.6. Electrode preparation

For electrode preparation, 5.4 mg Co−RGO, 5.7 mg commercial Pd black, and 5.1 mg CoPd−RGO were dispersed in 250 μL anhydrous ethanol and 250 μL Nafion (Sigma−Aldrich, USA) under ultrasonic agitation to form the electro-catalyst ink, respectively. The electro-catalyst ink (15 μL) was then deposited on the surface of a glassy carbon electrode (GCE, geometric area = 0.1256 cm^2) and dried at room temperature.

2.7. Electrochemical measurements

Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A conventional three-electrode cell was used, including a GCE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum foil as the counter electrode. The potentials were measured with SCE as the reference.

3. Results and Discussion

3.1. TEM observation

Fig. 1 shows TEM images of as-prepared CoPd−RGO composites. Fig. 1(a) reveals that the composite has a uniform dispersion of NPs on the RGO surface, and a continuous