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Reduced graphene oxide-$NiCo_2O_4$ nanoflowers as efficient electrocatalysts for the oxygen reduction reaction

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ABSTRACT

Two-dimensional materials have already become the focus of many researches due to their innovation potential in various fields related to their special structure. Particularly, more and more two-dimensional electrocatalysts are being developed for the oxygen reduction reaction (ORR). In this work, novel two-dimensional $NiCo_2O_4$ nanoflowers/reduced graphene oxide (NCONFs/rGO) nanocomposite ORR catalysts have been successfully synthetized via a two-steps method. The micromorphology and microstructure of the obtained samples were analyzed via XRD, SEM, TEM and Raman spectroscopy. The different characterizations showed a typical petal-like structure of $NiCo_2O_4$ and a good coupling between NCONFs and rGO. Electrochemical measurements demonstrated both superior NCONFs/rGO ORR activity (0.92 V of onset potential, vs. RHE) and an excellent catalytic stability (6.4% decrease in current during a 10,000 s test). Such outstanding performances have never been reported before for ORR catalysts and originate from the two-dimensional microstructure of materials combined with the supporting rGO layer.

1. Introduction

As the 21st century began, new energy devices such as Li-ion batteries (LIBs) and regenerative fuel cells (RFCs) have been employed in portable mobile devices, power stations and fuel-cell vehicles [1–12]. Being a critical step during the energy conversion process in RFCs, oxygen reduction reactions (ORR) have been widely studied. However, their kinetics is still slow and requiring exclusive utilization of noble metal-base catalysts in order to be activated. Many recent studies analyzed the activities in ORR reactions of mixed valence oxides characterized by a spinel structure, MCo_2O_4 (M = Mn, Fe, Ni, Zn). Particularly, $NiCo_2O_4$ showed ORR activity in alkaline solutions due to the Ni-Co double-metal-active-sites [13–17], which attracted increasing academic attention. For instance, Liu et al. reported that urchin-like $NiCo_2O_4$ spheres prepared via a hydrothermal method without any templates or surfactants exhibited superior stability in ORR [18]. Xiao et al. have developed three-dimensional macroporous $NiCo_2O_4$ sheets which showed higher ORR activity with respect to normal $NiCo_2O_4$ catalysts [19]. However, unsatisfactory catalytic activities arising from a high number of defects and small BET surface area still limit their practical applications.

In the past years, two-dimensional ultrathin materials have already become the focus of many studies because of their special two-dimensional carrier passageway, which effectively accelerates electron transfer processes [20–26]. Therefore, one way to enhance the ORR performance of catalysts is to process the materials into two-dimensions, with the effect of not only preventing the close packing of the materials, but also of providing an electron transfer shortcut. Moreover, conductivity is another key factor that seriously influences the ORR performance of catalysts. As a novel carbon material, graphene has attracted considerable interest due to its strong structural stability and superior conductivity [27–31]. Particularly, reduced graphene oxide (rGO) is an excellent choice as a support to catalytic reactions. A large number of surface functional groups of rGO provide many adsorption points, which allow functionalization of rGO surface with different materials and further prevent agglomeration [32].

In this work, we introduce a novel hierarchical $NiCo_2O_4$ nanoflowers/reduced graphene oxide composite (NCONFs/rGO) as an efficient ORR catalyst. Typically, NCONFs/rGO were successfully synthetized in two steps: (i) a solution-phase preprocessing; (ii) a

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subsequent reduction of both Ni-Co double hydroxide (LDH) and graphene oxide (GO). Micromorphology characteristics of the as-prepared samples were identified via X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and Raman spectroscopy. Results showed that the hierarchical petal-like $NiCo_2O_4$ nanosheets were uniformly coupled with rGO thin layers. After a series of electrochemical tests, we were excited to find that NCONFs/rGO had both superior catalytic activity (0.92 V onset potential and 0.86 V half-wave potential, versus reversible hydrogen electrode (RHE)) good structural stability and good property durability (retained 93.6% initial current after 10,000 s). Moreover, NCONFs/rGO demonstrated excellent methanol tolerance, pointing out their insusceptibility to fuel crossover in practical applications.

2. Experimental

2.1. Preparation

All reagents were of commercially available analytical grade and used without further purification. First, 1 mmol $CoCl_2 \cdot 6H_2O$ (Sinopharm Chemical Reagent Co., Ltd.), 0.5 mmol $NiCl_2 \cdot 6H_2O$ (Sinopharm Chemical Reagent Co., Ltd.) and 1.6822 g hexamethylenetetramine (Alfa Aesar) were dissolved in 200 mL of a 9:1 water-ethanol mixture. Second, the mixture was heated to and maintained at 90 °C for 30 min under magnetic string via an oil-bath, and then a turbid liquid containing dark green precipitations was obtained. For compounding, GO were dissolved in alcohol with 30 min sonication to form 20 wt.% GO/alcohol mixture, which was added into the obtained suspension. After 30 min stirring and 30 min sonication, the mixture was filtered off and washed with deionized water (DI water) and ethanol for several times. Next, the mixture was dried in a vacuum desiccator at 50 °C to form precursors. The as-prepared precursor was treated at 260 °C in the air for 120 min with a heating rate of 2 °C min^{-1}. The final product, NCONFs/rGO, was obtained after natural cooling. For comparison, NCONFs were synthetized under identical conditions without rGO.

2.2. Micromorphology

The powder X-ray diffraction patterns were obtained from an X-ray diffractometer (XRD, Rigaku D/max 2500 XRD with Cu-Kα radiation, $\lambda = 1.54178$ Å). The morphological and size analyses were visually measured via a field emission scanning electron microscope (FE-SEM, S-4800) and a transmission electron microscope (TEM, JEOLJEM-2100F). Raman spectra (LabRAN Aeamis, exciton wavelength 523 nm) was used to analyses the graphene layer from the Raman shift of 1300–1700 cm^{-1}. The surface chemical and element valence states of obtained samples were analyzed via X-ray photoelectron spectroscopy (XPS, ESCSLAB 250Xi).

2.3. Electrochemical experiments

Catalyst ink have been prepared by suspending 4 mg NCONFs/rGO samples in 1000 μL of a 4:6 water-isopropanol mixture. As surface binder, 20 μL of 5 wt.% Nafion solution was injected into the ink to support the ORR process. As a comparison, 4 mg of NCONFs was mixed up with 1 mg commercial Cabot carbon nanoparticles (Vulcan XC-72R) conductive agent to prepare the ink under the same conditions. After twice 15 min of ice-bath sonication, 20 mL and 31 mL of the ink were dropped onto a 0.19635 cm^2 glassy carbon rotating disk electrode (RDE) and a 0.24718 cm^2 glassy carbon rotating ring disk electrode (RRDE), respectively. All electrochemical experiments were performed using a computer-controlled electrochemical workstation (CHI 760D, CH Instrument) and carried out at room temperature in a conventional three-electrode system with a Pt foil as counter electrode and an Hg/HgO electrode as reference electrode. All potential values were calibrated with respect to RHE by the equation $E_{RHE} = E_{Hg/HgO} + 0.92$ V.

The open circuit potential (OCP) was measured before all experiments began. Both NCONFs and NCONFs/rGO on working electrode were firstly cycled in a potential range from 1.12 V to 0.22 V with a scan rate of 500 mV/s in N_2-saturated 0.1 M KOH. Typically, 20 segments were required for electrode activation. High purity nitrogen next passed through the electrolyte for 40 min then cyclic voltammetry (CV) was employed to collect N_2-saturated CV data at the same potential range with a scan rate of 50 mV/s. Before the next test, the electrolyte was purged by high purity oxygen for 40 min to reach O_2-saturated state then the O_2-saturated CV test was carried out under the same condition.

After that, linear sweep voltammetry (LSV) ran on RDE and RRDE with the scan rate of 5 mV/s and the electrode rotation rates were set to 2000, 1600, 1200, 800 and 400 rpm in sequence. Particularly, the ORR polarization curves in the case of 16.5 mL 3 M methanol were also collected via LSV at the electrode rotation rate of 1600 rpm.

Chronoamperometry was finally used to determinate the durability and methanol tolerance of catalysts for 10,000 s and 2000 s at −2.0 V, respectively. Particularly, 16.5 mL of 3 M methanol was injected into electrolyte at 500 s in the test of methanol tolerance.

3. Results and discussion

The obtained NCONFs and NCONFs/rGO were firstly characterized by XRD. The spectra are reported in Fig. 1 as a blue curve (NCONFs) and black curve (NCONFs/rGO), respectively. The main diffraction peaks at the diffraction angles of 18.9°, 31.1°, 36.6°, 44.6°, 55.4°, 58.9°, 64.9° and 78.0°, corresponding to (111), (220), (311), (400), (422), (511), (440) and (533) crystal plane. All peaks are in accord with the data from PDF standard card (No. 20-0781). The results did not display additional peaks so that the phase purity of $NiCo_2O_4$ nanocrystals was conclusive. Particularly, green curve in Fig. 1 demonstrates rGO diffraction pattern of rGO, which is inconspicuous in black curve due to its small dose.

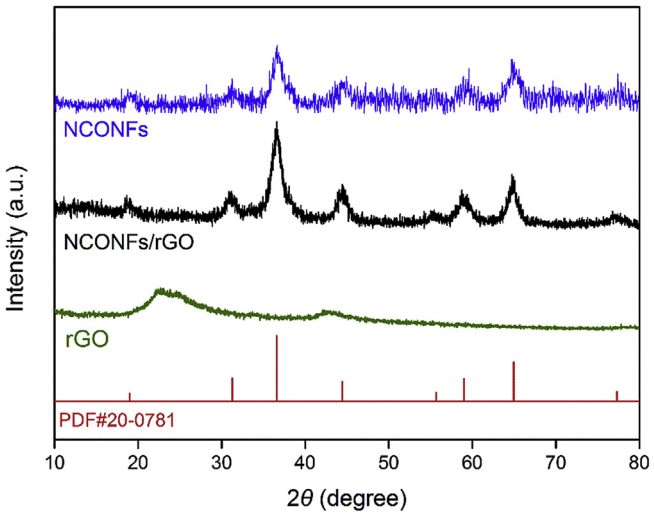

Fig. 1. XRD spectra of NCONFs (blue), NCONFs/rGO (black) and rGO (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)