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Nitrogen-doped graphene aerogels-supported cobaltosic oxide nanocrystals as high-performance bi-functional electrocatalysts for oxygen reduction and evolution reactions

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A hybrid material consisting of cobaltosic oxide (Co_3O_4) nanocrystals grown on nitrogen-doped graphene aerogels (N-GAs), denoted as Co_3O_4/N-GAs, is fabricated via a simple one-pot hydrothermal process and utilized as a high-performance bi-functional electrocatalyst for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The Co_3O_4/N-GAs hybrid for the ORR displays an outstanding electrocatalytic performance toward the ORR comparable with commercial Pt/C catalyst in an alkaline medium. Furthermore, our proposed hybrid is also highly active for the OER, making it a promising bi-functional catalyst for both ORR and OER. The obviously enhanced catalytic activity is ascribed to the synergistic effect between Co_3O_4 and N-GAs.

1. Introduction

Due to the gradual depletion of conventional energy sources, increasing demand has stimulated intensive research on alternative energy conversion and storage systems that are highly efficient, low-cost, and environmentally friendly. Electrocatalysts for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are critical for various energy technologies, including fuel cells, metal-air batteries and water splitting [1–5], while primary metal-air batteries and fuel cells depend on the ORR at the cathodes to function, water splitting for oxygen production may be accomplished by utilizing the OER. A major step forward from these conventional technologies is to develop bi-functional catalyst materials that can perform both ORR and OER with very low overpotentials. Such materials would enable advanced energy conversion and storage devices, including rechargeable metal-air batteries and regenerative fuel cells [5–7]. So far, the sluggish and strong irreversible nature of the oxygen electrochemical kinetics in conjunction with distinct potentials and conditions necessary for the ORR and OER has made it difficult to find single bi-functional material. As is well-known, platinum (Pt) performs very well for the ORR (and performs poorly for the OER); ruthenium oxide (RuO_2) and iridium oxide (IrO_2) perform very well for the OER (and perform poorly for the ORR) [8–10]. Although the hybrids of Pt (or Pt alloys) and these metal oxides (RuO_2 and IrO_2) can serve as highly active bi-functional catalysts for both ORR and OER [11–13], these precious metals are among the rarest elements on earth and, hence, are not practical for large-scale applications [14–16]. To overcome these obstacles, extensively increasing efforts have been made to develop bi-functional catalyst materials with excellent catalytic activity, good stability, and high rate capability, such as nitrogen-doped carbon materials [17], cobalt oxides supported on carbon materials [18,19], manganese oxides [20–22], spinels [23–26], transition metal chalcogenides [27], perovskites [28–30], cobalt phosphate/metaphosphate [31–33], and cobalt carbonate hydroxide [34].

Graphene, a two-dimensional (2D) monolayer of carbon atoms arranged in a hexagonal lattice, can serve as an intriguing support to disperse electroactive materials due to its high conductivity, large specific surface area, and extraordinary mechanical properties, thus improving electrical conductivity and structural integrity of modified electrodes [35]. To date, various graphene-based hybrids have been developed, which display improved electrocatalytic performance toward the ORR and OER [18,19,35]. Most of the previous work are focused on the preparation of graphene-based hybrids, however, 2D graphene sheets easily reaggregate or restack during drying due to physical interactions (e.g. van der Waals forces and π-π stacking), which significantly reduced the accessible surface area and limited electron transport [36]. Besides, graphene-based hybrids usually possess a limited number of reactive sites, which result in a low catalytic activity [37]. Therefore, there is still a big challenge to further optimize their electrocatalytic performance.

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To overcome above-mentioned issues of graphene, it is believed that three strategies are feasible. The first one is to assemble 2D graphene sheets into macroscopic three-dimensional (3D) architectures, which can effectively prevent restacking of graphene sheets, providing resultant graphene-based composites with the large specific surface area, porous structure, excellent mechanical strength, and fast electron transport kinetics due to the combination of 3D interconnected frameworks and intriguing properties of graphene [38–43]. Apart from the geometrical control, chemical doping, especially nitrogen-doping of graphene, is another effective way to improve the ORR and OER catalytic activity [44–46]. It is believed that the incorporation of nitrogen into graphene can effectively alter the spin density and charge distribution of neighboring carbons, thus leading to more active sites for ORR and OER [47]. Furthermore, a variety of transition metal oxides (e.g. Fe_3O_4 and Co_3O_4) incorporated with nitrogen-doped graphene (NG) [18], nitrogen-doped graphene aerogels (N-GAs) [48], graphene aerogels (GAs) [49], or graphene sheets [19] can dramatically improve the ORR and OER catalytic activity compared with the metal oxide/graphene counterpart and NG. Considering that both nitrogen-doping of graphene, 3D macroscopic frameworks and a variety of transition metal oxides can greatly improve the catalytic activity, it is highly demanded to develop graphene-based composites that combine three characteristics together. To the best of our knowledge, there are few reports in this aspect [18,48,50].

Herein, we report a novel hybrid composed of Co_3O_4 nanocrystals and 3D nitrogen-doped graphene aerogels (N-GAs), abbreviated as Co_3O_4/N-GAs, which is used as a bi-functional catalyst for the oxygen reduction and oxygen evolution reaction. Our fabricated Co_3O_4/N-GAs catalyst possesses higher activity and better stability for the ORR than a commercial Pt/C catalyst in an alkaline medium. In addition, the Co_3O_4/N-GAs hybrid is also highly active for the OER, making it an efficient bi-functional catalyst for both ORR and OER. This material was prepared via a facile, simple and green method with low-cost precursors, which can be easily adaptable for mass production. Therefore, our proposed catalyst may hold great promise as an ideal bi-functional catalyst for the advanced energy conversion and storage applications including rechargeable metal-air batteries and regenerative fuel cells.

2. Experimental

2.1. Materials and reagents

Graphite powder was purchased from Sinopharm Chemical Reagent Co., Ltd. Pt/C (20 wt% Pt on Vulcan XC-72) was obtained from Alfa Aesar. Cobalt acetate tetrahydrate was bought from Sinopharm Chemical Reagent Co., Ltd. Urea and D-glucose were purchased from Beijing Chemical Company (China). All other chemicals were of analytical grade and used without any further purification, including ethanol, $NaNO_3$, $KMnO_4$, H_2O_2, and KOH. Aqueous solutions were prepared with ultra pure water (18.2 MΩ cm) from a Milli-Q Plus system (Millipore).

2.2. Synthesis of Co_3O_4/N-GAs

Graphite oxide (GO) was gained from natural graphite flakes using a modified Hummers method [51]. The fabrication process for the Co_3O_4/N-GAs hybrid is demonstrated in Fig. 1. Briefly, GO was dispersed in deionized water by sonication, reaching a concentration up to 1.0 mg mL^{-1}. Afterwards, 20 mg cobalt acetate tetrahydrate, 1 g urea and 20 mg D-glucose were slowly added into 20 mL of the above dispersion. After constantly mechanical stirring for 10 min, a stable dark brown aqueous suspension was achieved (Scheme 1a). Subsequently, these quaternary components were sealed in a 50 mL Telfon-lined autoclave and hydrothermally treated at 180 °C for 12 h to form 3D graphene-based hydrogels (Scheme 1b). After that, the vessel was allowed to return to room temperature. The as-prepared hydrogels were directly dehydrated via a freeze-drying process to maintain the 3D architecture. The final fabricated product from this process is a black 3D hybrid of Co_3O_4/N-GAs (Scheme 1c). For comparison, GAs or N-GAs was also prepared through the same steps as those used to make Co_3O_4/N-GAs without adding any urea or cobalt salt in the ultrasonic vibration step.

2.3. Synthesis of Co_3O_4/GAs

The Co_3O_4 nanoparticles were prepared by a hydrothermal method reported by Joo et al. [24]. 0.55 g of cobalt acetate tetrahydrate ($Co(OAc)_2 \cdot 4H_2O$), 10 mL deionized water, and 17 mL absolute ethanol were added into a 50 mL beaker. The above mixture was stirred until the cobalt salt was completely dissolved. Afterwards, 2.4 mL of an aqueous ammonia solution (25%) was added to the solution and stirred for 10 min at room temperature. The suspension was transferred to a Teflon-lined autoclave, aged at 150 °C for 3 h, and then cooled to room temperature. The precipitates were centrifuged at 6000 rpm for 15 min and the supernatant solution was decanted. Co_3O_4/GAs was prepared through the same steps as those used to make Co_3O_4/N-GAs with the addition of 4 mg Co_3O_4 nanoparticles and without adding urea in the ultrasonic vibration step.

2.4. Characterization

The morphology and structure of as-prepared samples was analyzed by scanning electron microscopy (SEM, JSM-6701F, operating at 5 kV) and transmission electron microscopy (TEM, JEOL-2010 transmission electron microscope operating at 200 kV). The crystalline phases of the resulting materials were analyzed by powder X-ray diffraction (XRD, RIGAK, D/MAX2550 VB/PC, Japan). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCLAB 250 spectrometer using Al Kα as the exciting source (1486.6 eV photons) to identify the surface chemical composition and bonding state. Raman spectra were taken on a TriVista™555CRS Raman spectrometer at 785 nm.

2.5. Preparation of modified electrode

Prior to modification, the working electrode was polished successively with 1.0, 0.3 and 0.05 mm aluminum oxide slurry, then ultrasonically rinsed with distilled water, absolute ethanol and distilled water in turn for a little while. Afterwards, the cleaned glassy carbon (GC) electrode was blow-dried with N_2 at ambient temperature. In order to modify the GC electrode, a homogeneous ink was prepared by mixing 1.0 mg of catalyst and 1.0 mL of ethanol with the aid of ultrasonic vibration. A certain amount of catalyst ink was pipetted onto the GC electrode. After evaporation of ethanol, 2 μL of a diluted Nafion solution (5 wt% in ethanol) was put on the top of the modified film, and then dried in air to hold the attachment of the film to the electrode surface. The catalyst loading per area on the GC electrode was kept to be 212 μg cm^{-2}. For comparison, the same amount of GAs, N-GAs, Co_3O_4/GAs or Pt/C was also loaded onto the GC electrode.

2.6. Electrochemical measurements

Cyclic voltammetry (CV) measurements were performed with a CHI 660E electrochemical workstation (CH Instruments, Shanghai CHENHUA company) in a conventional three-electrode cell using the coated GC electrode (5 mm in diameter) as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. Rotating disk electrode (RDE, 5 mm in diameter), rotating ring disk electrode (RRDE, 5.61 mm in diameter) and current-time (*i*-*t*) chronoamperometric response measurements were carried out with a Pine Instrument Company AF-MSRCE modulator speed rotator on a CHI 660E electrochemical workstation with a standard three-electrode system. RDE and RRDE for the