



# Cobalt oxide anchored on nitrogen and sulfur dual-doped graphene foam as an effective oxygen electrode catalyst in alkaline media

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## ARTICLE INFO

### Article history:

Received 14 January 2016

Received in revised form 16 April 2016

Accepted 26 April 2016

### Keywords:

Graphene foam

Oxygen reduction reaction

Oxygen evolution reaction

Synergistic effects

## ABSTRACT

Developing highly active bifunctional catalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in the oxygen electrocatalysis based energy conversion or storage remains challenges. Herein, an efficient catalyst of cobalt oxide ( $\text{Co}_3\text{O}_4$ ) nanocrystals grown on nitrogen and sulfur co-doped graphene foam (NSGF) is prepared via a hydrothermal method. Scanning electron microscope (SEM) and transmission electron microscopy (TEM) measurements demonstrate  $\text{Co}_3\text{O}_4$  is of regular single crystal morphology in the  $\text{Co}_3\text{O}_4$ /NSGF composite with 1:1 mass ratio of cobalt to graphene foam. For ORR, the hybrid favors a direct  $4e^-$  pathway, similar to that of Pt/C, but outperforms Pt/C with a long-term durability. Besides, it achieves a small overpotential of  $\sim 0.48$  V vs. SCE at the current density of  $10 \text{ mA cm}^{-2}$  and there is only  $0.018$  V vs. SCE overpotential increasing after 200 cycles for OER testing. The good electrochemical activities of our fabricated bifunctional catalyst are attributed to electrochemical contributions of the loaded  $\text{Co}_3\text{O}_4$  nanocrystals, the integral structure of three-dimensional graphene foam, the heteroatoms doping effects and the synergistic effects between  $\text{Co}_3\text{O}_4$  and NSGF.

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## 1. Introduction

To cater the increasing energy demand and relax the current environment pollution, numerous research has been dedicated to oxygen reaction-based energy conversion and/or storage techniques [1–4]. However, the oxygen reactions suffer from kinetically sluggish problems due to the complex four-electron process, so that catalysts are employed to accelerate oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) processes. Currently, Pt-based alloys and  $\text{RuO}_2$  function as the best ORR and OER catalysts, respectively, while their respective OER and ORR performance is poor [5,6]. Besides, these noble metals are scarce, and they face high cost in large-scale applications. Consequently, one of the great challenges being faced is to develop clean, abundant and efficient alternative oxygen electrode catalysts.

To date, the first row transition metals have been studied generally as active electrode materials featured with high catalytic ability for both ORR and OER, such as cobalt and its derives, including mixed-metal oxides [7,8], hydro(oxy) oxides [4,9], phosphates [10], chalcogenides [11,12], and perovskites [3,13]. Among them,  $\text{Co}_3\text{O}_4$  is popular for affording small overpotential and high

stability in alkaline media. Recent theoretical studies have demonstrated that the exposed  $\text{Co}_3\text{O}_4$  (110), (111) and (311) surface planes are of highly catalytic activity for OER [14–16]. However, the easy aggregation and low conductivity of pure  $\text{Co}_3\text{O}_4$  decrease the active sites and hamper the transport of electrons during the oxygen reaction process. On the contrary, graphene support with its open ended structure, high electrical conductivity, large surface area and high chemical stability is desirable to derive 3d metal-based composite catalysts [17]. And the combination of  $\text{Co}_3\text{O}_4$  and heteroatoms doped graphene presented excellent ORR and OER performance [3,13]. For example, several remarkable  $\text{Co}_3\text{O}_4$ -based OER catalysts by adhering them on graphene sheets have been prepared [14,18,19]. When  $\text{Co}_3\text{O}_4$  anchored on N and/or S-doped graphene, the synergistic effects attributed a lot to the ORR and/or OER abilities [3,13,20–22]. In these cases, nitrogen doping in graphene creates a net positive charge on adjacent carbon atoms to accelerate the adsorption of  $\text{O}_2$ , and leads to more active sites, larger surface areas, and higher defect density [20,23], facilitating ORR [13,20,22]. Moreover, sulfur doped graphene performed enhanced ORR efficiency due to the nearly electronegativities between sulfur and carbon [10,20,24,25], and the nitrogen and sulfur co-doping generated synergistic effects. However, the structure of cobalt oxide existed differently, and reports on cobalt oxide exposing specific surface planes in catalyzing embedded in nitrogen and sulfur dual-doped 3D graphene as bifunctional catalysts were still not many.

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In this study, we successfully prepared a  $\text{Co}_3\text{O}_4/\text{NSGF}$  composite, comprising  $\text{Co}_3\text{O}_4$  single crystals and N, S dual-doped 3D graphene foam (NSGF), via a simple and facile hydrothermal approach using abundant raw resources. Herein,  $\text{NH}_3\cdot\text{H}_2\text{O}$  acted as both a nitrogen resource and alkali to adjust the pH of the solution ( $\text{pH} > 12$ ) controlling the crystal-particle size and  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  functioned as a reductive agent and sulfur resource. SEM and TEM methods characterized the formation of  $\text{Co}_3\text{O}_4$  single crystal on GF in  $\text{Co}_3\text{O}_4/\text{NSGF}$  when the mass ratio of Co to GF was 1:1. The hybrid displayed good bifunctional performance as an oxygen electrode catalyst in alkaline media, which was mainly ascribed to heteroatoms doping effects and the synergistic effects between cobalt oxide and graphene foam support.

## 2. Experimental

### 2.1. Materials

Graphite powder was purchased from Sinopharm Chemical Reagent Co., Ltd. Pt/C (20 wt%, Pt on Vulcan XC-72) was purchased from Alfa Aesar. 5% Nafion perfluorinated resin solution (in ethanol) and ruthenium (IV) oxide were obtained from Sigma. All of these reagents were analytical grade, and used without further purification, including KOH,  $\text{NH}_3\cdot\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ , KCl,  $\text{NaNO}_3$ ,  $\text{KMnO}_4$ ,  $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . Ultra pure water was obtained from a Milli-Q water system (18.2 M $\Omega$  cm).

### 2.2. The preparation of GF substrate

In a typical process, graphene oxide (GO) was prepared by oxidation of graphite flakes via a modified Hummers' method [26]. Then, it was dispersed into ultra pure water at a concentration of 30 mg mL<sup>-1</sup> and subject to freeze-drying process to form the graphene oxide foam, abbreviated as GOF. Next, GOF was first heated to 300 °C with a ramp rate of 1 °C min<sup>-1</sup>, and then heated up 1050 °C for 5 min at a rate of 10 °C min<sup>-1</sup> in flowing argon atmosphere. And the cooled product was graphene foam, named as GF.

### 2.3. The preparation of cobalt oxide/nitrogen, sulfur-doped graphene foam

To fabricate the final catalyst, a hydrothermal method was used. In brief, 23.1 mg of  $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$  was dissolved in ultra pure water and  $\text{NH}_3\cdot\text{H}_2\text{O}$  was added until the pH of the solution was over 12. The solution was stirred in hot-water conditions for half an hour and cooled to room temperature. Followed by mixing with 2.7 mg of GF in a 1:1 (w/w) ratio (Co atom to GF) and 8.3 mg of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , the mixture was sealed to Teflon-lined stainless autoclave at 180 °C for 12 h. The obtained product was subject to freeze-drying, getting the 1:1  $\text{Co}_3\text{O}_4/\text{NSGF}$  cake. By varying the amount of  $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$  to 11.6, 7.7, 46.2 and 69.3 mg, different ratios (Co atom to GF) composites were obtained, corresponding to 1:2 and 2:1  $\text{Co}_3\text{O}_4/\text{NSGF}$ , respectively. For comparative studies, more samples were constructed. The preparations of 1:1  $\text{Co}_3\text{O}_4/\text{SGF}$  (non-nitrogen),  $\text{Co}_3\text{O}_4/\text{N}$  (non-graphene foam and sulfur) and NSGF (non- $\text{Co}_3\text{O}_4$ ) were similar to that of 1:1  $\text{Co}_3\text{O}_4/\text{NSGF}$  only by adjusting the amount of the original materials.

### 2.4. Characterizations of the as-prepared samples

The morphology and structure of as-prepared samples were characterized 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). X-ray powder diffraction (XRD) measurements were taken at ambient temperature with  $2\theta$  degree range from 10° to 80° at

40 kV on RIGAKU X-ray diffractometer (D/MAX2550 VB/PC, Japan) equipped with Cu K $\alpha$  radiation (0.15418 Å). Raman spectra were performed on a Tri Vista™555CRS Raman spectrometer at 785 nm. The Brunauer-Emmett-Teller (BET) surface area and pore volume were evaluated by using nitrogen adsorption-desorption isotherms measured on an ASAP2020 volumetric adsorption analyzer at 77 K. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCLAB 250 spectrometer using Al K $\alpha$  as the exciting source (1486.6 eV photons) to identify the surface chemical composition and bonding state.

### 2.5. Preparation of modified electrodes

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. Afterwards, the cleaned glassy carbon (GC) electrode was blow-dried with  $\text{N}_2$  at ambient temperature. In order to modify the GC electrode, a homogeneous ink was prepared by mixing 4.0 mg of catalyst, 1.5  $\mu\text{L}$  of 5 wt% Nafion solution and 2.0 mL of ethanol with the aid of ultrasonic vibration. A certain amount of catalyst ink was pipetted onto the GC electrode, and then dried in the air to hold the attachment of the film to the electrode surface. The catalyst loading per area on the GC electrode was always kept to be 0.212 mg cm<sup>-2</sup>. For comparison, the same amount of 1:1  $\text{Co}_3\text{O}_4/\text{N}$ , NSGF, 1:1  $\text{Co}_3\text{O}_4/\text{SGF}$  or Pt/C was also loaded onto the GC electrode.

### 2.6. Electrochemical measurements of the samples

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 (3 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*) chronoamperometry 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. CV measurements for the ORR were operated at the scan rate of 10 mV s<sup>-1</sup> in an  $\text{O}_2/\text{N}_2$ -saturated 0.1 M KOH solution. RDE and RRDE measurements for the ORR were performed at the scan rate of 10 mV s<sup>-1</sup> in an  $\text{O}_2$ -saturated 0.1 M KOH solution, and the RDE electrode was polished by 0.3 and 0.05 mm aluminum oxide slurry and RRDE was only dealt with 0.05 mm aluminum oxide slurry. For RRDE measurements, the collection efficiency of platinum ring was 37.0%. CV and RDE measurements for the OER were carried out at the scan rate of 10 mV s<sup>-1</sup> in a  $\text{N}_2$ -saturated 0.1 M KOH solution. All electrochemical measurements were performed 3 times to avoid any incidental error and all potentials in this study were reported relative to the saturated calomel electrode (SCE).

## 3. Results and discussion

### 3.1. Characterizations of $\text{Co}_3\text{O}_4/\text{NSGF}$ composites

Fig. 1a depicts XRD patterns of the synthesized samples. Pure GF sample exhibited a broad diffraction peak (005) at  $2\theta = 25.8^\circ$ . In the case of 1:1  $\text{Co}_3\text{O}_4/\text{NSGF}$  hybrid, the (111), (220), (311), (222), (400), (422), (440) and (511) peaks matched well with those of cubic  $\text{Co}_3\text{O}_4$  (PDF-#78-1969). And  $\text{Co}_3\text{O}_4$  were also formed in 1:2 and 2:1  $\text{Co}_3\text{O}_4/\text{NSGF}$  composites. The strong peaks suggested the high crystallinity of  $\text{Co}_3\text{O}_4$  nanoparticles (NPs). The nitrogen adsorption-desorption isotherm (Fig. 1b) assessing the porous nature clearly

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