



# Hybrid of porous cobalt oxide nanospheres and nitrogen-doped graphene for applications in lithium-ion batteries and oxygen reduction reaction



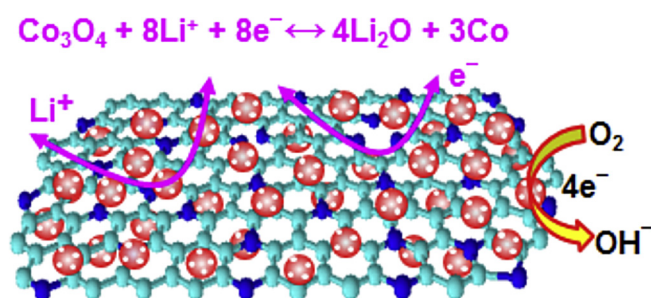
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## HIGHLIGHTS

- A complex precursor is developed from graphite oxide,  $\text{Co}^{2+}$  and melamine resin (MR).
- Hybrid of porous  $\text{Co}_3\text{O}_4$  nanospheres and N-doped graphene ( $\text{Co}_3\text{O}_4/\text{NG}$ ) is achieved.
- MR is beneficial to promote uniform N-doping and distribution of  $\text{Co}_3\text{O}_4$ .
- The  $\text{Co}_3\text{O}_4/\text{NG}$  hybrid exhibits superb Li-ion storage performances.
- The  $\text{Co}_3\text{O}_4/\text{NG}$  hybrid shows excellent catalytic activity toward oxygen reduction.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A new single-source precursor has been developed from the hydrothermal reaction of graphite oxide (GO), melamine resin (MR) monomers, and  $\text{CoCl}_2$  to prepare a sandwich-like hybrid of ultrathin nitrogen-doped graphene (NG) sheets and porous  $\text{Co}_3\text{O}_4$  nanospheres ( $\text{Co}_3\text{O}_4/\text{NG}$ ). This unique structure endows the  $\text{Co}_3\text{O}_4/\text{NG}$  hybrid with large surface area and enhanced electrochemical performances as both anode material for Li-ion batteries and electrocatalyst for oxygen reduction reaction (ORR). As an anode material, it exhibits high reversible capacity, excellent cycling stability and rate performance (1236 and 489  $\text{mAh g}^{-1}$  over 200 cycles at 0.1C and 2C, respectively; 371  $\text{mAh g}^{-1}$  at 5C). As an ORR electrocatalyst, it shows superior catalytic activity and high selectivity for the four-electron reduction pathway compared to the bare  $\text{Co}_3\text{O}_4$  and NG alone. Moreover, the  $\text{Co}_3\text{O}_4/\text{NG}$  hybrid is insensitive to methanol, and is much more stable than Pt/C catalyst over long term operation.

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## 1. Introduction

Reliable clean energy supply is vital for the sustainable development of modern society. As the most promising energy storage devices and important power sources for portable electronics and hybrid electric vehicles, Li-ion batteries (LIBs) have attracted

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tremendous attention during the past decades [1,2]. Although significant advances have been made, it is still a great challenge to develop advanced electrode materials with high energy density and excellent stability, especially when used at large current [3,4]. In addition, Fuel cells (FCs) are typical electrochemical conversion systems which can generate electricity with little or no emission [5,6]. Nevertheless, high cost of the Pt-based catalyst for oxygen reduction reaction (ORR) at the cathode impedes commercialization of FCs. Consequently, noble-metal-free ORR catalysts with high activity and sufficient durability are highly desired [7–9].

$\text{Co}_3\text{O}_4$  has been intensively investigated as one of the promising anode materials for LIBs due to its high theoretical capacity of  $890 \text{ mAh g}^{-1}$ , which is more than twice that of graphite ( $372 \text{ mAh g}^{-1}$ ) [10]. Unfortunately, it usually suffers from rapid capacity loss and poor cycling stability due to its large volume change and severe particle aggregation associated with  $\text{Li}^+$  insertion and desorption [11,12]. In addition, its rate capability is bad because of its intrinsic low electronic conductivity as a typical p-type semiconductor [13]. To circumvent these issues various  $\text{Co}_3\text{O}_4$  nanostructures and their carbonaceous nanocomposites have been prepared for LIBs applications [14–16]. The combined carbonaceous materials can not only buffer the volume change of  $\text{Co}_3\text{O}_4$  during electrochemical cycling, but also enhance conductivity of the nanocomposites [17]. As a new allotrope of carbon family, graphene features extraordinary conductivity, large surface area and good flexibility, and thus nanocomposites based on  $\text{Co}_3\text{O}_4$  and graphene are actively pursued for energy-related applications [18–21]. For example, the  $\text{Co}_3\text{O}_4$ /graphene nanocomposites prepared by solvothermal method with subsequent heat treatment exhibited a large reversible Li-storage capacity, good cycling performance and rate capability, highlighting the advantage of anchoring electrochemically active nanoparticles on graphene sheets to maximally utilize both components for Li-storage [22,23]. Recently, composite anode materials based on N-doped graphene (NG) and  $\text{Co}_3\text{O}_4$  have also been synthesized by using graphene oxide (GO) sheets as the carbonaceous additives, urea or  $\text{NH}_3$  as both the dopant for doping graphene with nitrogen and the precipitant for growth of  $\text{Co}(\text{OH})_2$  or  $\text{Co}_3\text{O}_4$  [24,25]. It was reported that the doped nitrogen atoms in NG could provide favorable nucleation and anchoring sites for  $\text{Co}_3\text{O}_4$  nanoparticles [26]. However, the doped nitrogen atoms in the nanocomposites prepared by the above mentioned methods using urea or  $\text{NH}_3$  as the dopant were inclined to distribute on the edges of NG, and thus more  $\text{Co}_3\text{O}_4$  nanocrystals were mainly distributed on the edge than the inner area of the NG sheets [27], resulting in unsatisfactory Li-ion storage performances.

In this work, we demonstrate that a sandwich-like hybrid of porous  $\text{Co}_3\text{O}_4$  nanospheres and N-doped graphene ( $\text{Co}_3\text{O}_4$ /NG) can be prepared via hydrothermal reaction of melamine resin (MR) monomers [(1,3,5-triazine-2,4,6-triyltrinitrilo) hexamethanol], GO and  $\text{Co}^{2+}$  with subsequent thermal treatment. Herein, MR is employed not only as a linking agent between  $\text{Co}^{2+}$  and GO, but also as a novel nitrogen source to dope nitrogen atoms on both the edges and inner areas of graphene framework upon pyrolysis, resulting in uniform distribution of both nitrogen atoms and porous  $\text{Co}_3\text{O}_4$  nanospheres on the whole surface of NG nanosheets. Compared with most of the reported  $\text{Co}_3\text{O}_4$ -based composites, the as-prepared  $\text{Co}_3\text{O}_4$ /NG hybrid exhibits better Li-ion storage performances because it possesses more active sites, faster electronic and ionic conductivity, and better buffer effect on volume variation of the active material. Furthermore, the  $\text{Co}_3\text{O}_4$ /NG hybrid shows superb ORR catalytic activity with excellent stability, holding great promise for applications in fuel cells and metal-air batteries as a non-noble-metal electrocatalyst.

## 2. Experimental

### 2.1. Materials preparation

$\text{Co}_3\text{O}_4$ /NG hybrid was prepared through hydrothermal reaction of GO, MR, and  $\text{CoCl}_2$  followed by a two-step heat treatment. First, GO powders were synthesized by the modified Hummer's method as described elsewhere [28]. Secondly, melamine (1 g) and formaldehyde aqueous solution (37 wt%, 1.8 mL) were added into deionized water (10 mL) under stirring, and the mixture was heated at  $70^\circ\text{C}$  for 10 min to obtain a transparent MR solution [29]. Thirdly, 3 mL MR and 1 mmol  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were successively introduced to 30 mL GO aqueous dispersion (2 mg/mL). After stirring for 1 h, the mixture was hydrothermally treated at  $180^\circ\text{C}$  for 12 h. The precipitates separated by centrifugation were washed with deionized water and ethanol, and were dried overnight at  $60^\circ\text{C}$  in vacuum. Finally, the obtained precipitates were pyrolyzed at  $450^\circ\text{C}$  under  $\text{N}_2$  atmosphere for 2 h, and were further heated at  $250^\circ\text{C}$  in air for 1 h to obtain the  $\text{Co}_3\text{O}_4$ /NG hybrid.

For comparison, NG nanosheets were synthesized in the absence of  $\text{CoCl}_2 \cdot \text{H}_2\text{O}$  through the same procedure as that for preparation of the  $\text{Co}_3\text{O}_4$ /NG hybrid. Bare  $\text{Co}_3\text{O}_4$  particles were also prepared by the similar procedure without addition of GO, and the hydrothermal product was directly calcined at  $450^\circ\text{C}$  in air for 1 h.

### 2.2. Materials characterization

The phase composition of the products was identified by X-ray powder diffractometer (XRD, Rigaku Ultima IV,  $\text{CuK}\alpha$  radiation). The surface chemical composition of the materials was determined by X-Ray photoelectron spectroscopy (XPS, Thermo ESC ALAB 250 XI multifunctional imaging electron spectrometer with a monochromatic  $\text{AlK}\alpha$  X-ray Source). The morphology and microstructure of the samples were characterized by scanning electron microscope (SEM, JEOL JSM-6510LV) and transmission electron microscope (TEM, FEI Tecnai G20). The content of NG in the  $\text{Co}_3\text{O}_4$ /NG hybrid was quantified by thermogravimetric analysis (TGA, NETZSCH STA 449 F3) performed in an atmosphere of air from room temperature to  $700^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ . The surface area and pore structure of the samples were measured on an automated gas sorption analyzer (Autosorb-iQ, Quantachrome Instruments U.S.) with  $\text{N}_2$  as adsorbate. The specific surface areas and pore size distributions were calculated from the nitrogen adsorption/desorption data by using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method, respectively.

### 2.3. Electrochemical measurements

Lithium storage performance of the materials was evaluated at room temperature using CR2032 type coin cells with lithium metal as the counter and reference electrodes. The working electrodes consisted of active materials ( $\text{Co}_3\text{O}_4$ /NG, NG, or  $\text{Co}_3\text{O}_4$ ), acetylene black and polyvinylidene fluoride with a weight ratio of 8:1:1.1 M  $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate and dimethyl carbonate (EC/DMC, 1:1 V/V) was used as the electrolyte. Polypropylene microporous membrane (Celgard-2300) was employed as the separator. The cells were assembled in an argon-filled glove box with  $\text{H}_2\text{O}$  and  $\text{O}_2$  contents below 0.1 ppm. Cyclic voltammograms (CVs) were measured by using an electrochemical workstation (CHI 760E, CH Instruments Inc., Shanghai) at a scan rate of  $0.1 \text{ mV s}^{-1}$  in the voltage range of 3.0–0.005 V vs.  $\text{Li}^+/\text{Li}$ . The galvanostatic charge and discharge (GCD) measurements were carried out on Neware BTS test system (Shenzhen, China) at different current rates from 0.1 to 5C (1C =  $890 \text{ mA g}^{-1}$ ) between voltage limits of 3.0–0.005 V versus  $\text{Li}^+/\text{Li}$ . Electrochemical impedance

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