

Editor's Choice

A hybrid-assembly approach towards nitrogen-doped graphene aerogel supported cobalt nanoparticles as high performance oxygen reduction electrocatalysts



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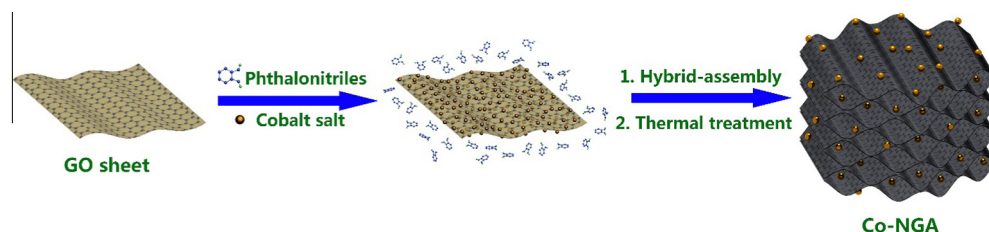
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GRAPHICAL ABSTRACT

A novel hybrid electrocatalyst consisting of nitrogen-doped graphene aerogel supported cobalt nanoparticles (Co-NGA) is archived by a facile hybrid-assembly of graphene oxide, o-phthalonitrile and cobalt acetate and the following thermal treatment, which exhibits a high catalytic efficiency for oxygen reduction reaction in basic media.



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ABSTRACT

As a novel electrocatalyst for oxygen reduction reaction (ORR), nitrogen-doped graphene aerogel supported cobalt nanoparticles (Co-NGA) is archived by a hybrid-assembly of graphene oxide (GO), o-phthalonitrile and cobalt acetate and the following thermal treatment. The hybrid-assembly process successfully combines the ionic assembly of GO sheets and Co ions with the coordination between o-phthalonitrile and Co ions, which can be converted to nitrogen doped carbon and Co nanoparticles in the pyrolysis process under nitrogen flow. Remarkable features of Co-NGA including the macroporous graphene scaffolds, high surface area, and N/Co-doping effect can lead to a high catalytic efficiency for ORR. As the results, the composites pyrolyzed at 600 °C (Co-NGA₆₀₀) shows excellent electrocatalytic activities and kinetics for ORR in basic media, which are comparable with those of Pt/C catalyst, together with superior durability.

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1. Introduction

The development of non-precious metal catalysts with high oxygen reduction reaction (ORR) activity and durability is a major

focus of various renewable energy applications such as fuel cells and metal-air batteries [1–11]. High performance ORR catalysts are required to lower the over potential and sustain the corrosive operating condition, which mainly relies on the platinum (Pt) based materials so far. Nevertheless, the scarcity, prohibitive cost, poor durability and intolerance to cross-over methanol of Pt unavoidably soar the cost of fuel cells and diminish their

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popularity. Since the first report on the ORR catalytic behavior of cobalt phthalocyanine (CoPc) [12], the composites of transition metal (Co, Fe, and Ni etc.) and nitrogen (N) doped carbon (TM-NC) have been intensively studied as one of the possible substituents for Pt catalysts [13–19]. Generally, the direct pyrolysis of the mixtures containing nitrogen, carbon, and transition metal precursors is the very often used method to produce TM-NC catalysts. However, the low controllability of such approaches set obstacles in understanding the relationship between the structure and the performances of TM-NC catalysts.

In this work, we report an unconventional strategy towards N-doped graphene aerogel supported Co nanoparticles (Co-NGA) by a hybrid-assembly of graphene oxide (GO), o-phthalonitrile and cobalt acetate and the following thermal treatment. The hybrid-assembly process successfully combines the ionic assembly of GO sheets and Co ions as well as the coordination between o-phthalonitrile and Co ions [20,21]. During the thermal treatment under nitrogen flow, the obtained composites can be converted to an interconnected macroporous framework of N-doped graphene sheets with uniform deposition of Co nanoparticles. As the catalysts for ORR, the Co-NGA composite pyrolyzed at 600 °C exhibits comparable electrochemical performance and much better durability in comparison with commercial Pt/C catalyst in alkaline electrolyte.

2. Results and discussion

The synthesis procedures for Co-NGAs are illustrated in Fig. 1. Typically, o-phthalonitrile, GO and cobalt acetate are firstly mixed in ethylene glycol (EG) and the resulting dispersion is then solvothermally treated at 180 °C for 12 h. During this process, the Co^{2+} ions from cobalt acetates can bind with the hydroxyl or carboxyl groups of GO via ionic interactions. At the same time, o-phthalonitrile will coordinate with the Co^{2+} ions [22] on the surface or the edge of GO sheets. Different from GA from pure GO sheets, the hydrogen bonding and π - π interactions of graphene sheets are not the only driving force for the formation of the composite. The ionic interactions between Co^{2+} and GO as well as the aromatic interactions between the Co^{2+} /o-phthalonitrile complexes and GO can also help the construction of the composites with three-dimensional (3D) architectures [23]. Finally, the thermal treatment of the composite at 400, 600 or 800 °C under nitrogen atmosphere yields nitrogen-enriched macroporous graphene framework with incorporation of cobalt nanoparticles. After the thermal treatment, the Co-NGA composites were obtained black monolithic hybrid aerogels composed of N-doped graphene networks and Co nanoparticles (Fig. 2a inset), suggesting the good structural stability of the electrocatalyst. According to the temperatures of the thermal treatment, the composites are named as Co-NGA₄₀₀, Co-NGA₆₀₀ and Co-NGA₈₀₀, respectively.

As exemplified by Co-NGA₆₀₀, the cross-sectional scanning electron microscopy (SEM) images indicate the composite has highly interconnected macroporous graphene scaffolds with the pore sizes ranging from 4 to 8 μm (Fig. 2a and b). The transmission

electron microscopy (TEM) image of Co-NGA₆₀₀ indicates that Co nanoparticles with a diameter of ~ 20 nm are uniformly deposited on the graphene surface (Fig. 2c), which should be derived from Co containing species during the thermal treatment [24], suggesting efficient assembly among the o-phthalonitrile, Co^{2+} ions and the graphene sheets. Such a geometric confinement of metal oxide NPs within graphene layers has been reported to enhance their interface contact and to suppress the dissolution and agglomeration of nanoparticles, thereby promoting the electrochemical activity and stability of the hybrids [25,26]. The high-resolution TEM (HRTEM) image of a typical Co nanoparticle further reveals that the carbon layers around the highly crystallized Co nanoparticle have high graphitic degree with a lattice spacing of 0.34 nm (Fig. 2d), which is attributable to the catalytic effect of Co [27,28].

The powder X-ray diffraction (XRD) patterns of the three Co-NGAs were further recorded to illustrate their microstructure. As shown in Fig. S1, the peak at 26° ($d = 0.36$ nm) in all the samples can be indexed to the (002) diffraction plane of graphite, which should be derived from the graphitic carbon obtained from the complexes of Co^{2+} and o-phthalonitrile as well as the overlapped graphene sheets in the composites. A weak diffraction at 36° can be found in the XRD spectra of Co-NGA₄₀₀ and Co-NGA₆₀₀, implying the existence of a small amount of Co_3O_4 , which might be derived from the reaction between Co^{2+} and oxygen containing species in the composites. In contrast, three characteristic peaks at approximately 44.2° , 51.5° and 76° can be observed in the XRD patterns of Co-NGA₆₀₀ and Co-NGA₈₀₀, which correspond to β -Co (001), (002) and (003), respectively (JCPDS 150806), indicative of the formation of crystalline cobalt particles after pyrolysis [29]. Remarkably, almost no diffraction from Co nanoparticles can be observed in the XRD spectra of Co-NGA₄₀₀, while Co-NGA₈₀₀ have more intensive peaks than Co-NGA₆₀₀, demonstrating that crystalline degree of Co species depends on the thermal treatment temperature. The sizes of the Co nanoparticles are calculated to be 23 and 26 nm with Scherrer equation for Co-NGA₆₀₀ and Co-NGA₈₀₀, respectively, which are in good agreement with the sizes of the Co nanoparticles from the HRTEM images (Figs. 2c, d and S2).

The porosity of Co-NGA₆₀₀ was further characterized by N_2 adsorption measurements and its N_2 adsorption/desorption isotherm shows a typical type IV curve with a combination of H2 and H4 hysteresis loop at relative pressures (P/P_0) of 0.45–1.0 (Fig. S2), implying the existence of mesopores in platelet-like structures [30], which should be owing to the packing of Co nanoparticles and the wrinkles of graphene [31]. Brunauer–Emmett–Teller (BET) analysis further reveals that the specific surface area of Co-NGA₆₀₀ is $268 \text{ m}^2 \text{ g}^{-1}$, which will undoubtedly facilitate its application as the ORR catalyst.

The X-ray photoelectron spectra (XPS) of the Co-NGA composites are further recorded, which reveal the presence of C1s, N1s, O1s and Co2p in these samples (Fig. 3a). The presence of oxygen can be ascribed to the resident oxygen containing groups from GO sheets. On the other hand, the C1s spectra of the samples are deconvoluted into four individual peaks (Fig. 3b), which are sp^2 -hybridized graphite-like carbon (C=C, 284.7 eV), sp^3 -hybridized diamond-like carbon (C–C, 285.2 eV), C–O (286.2 eV)

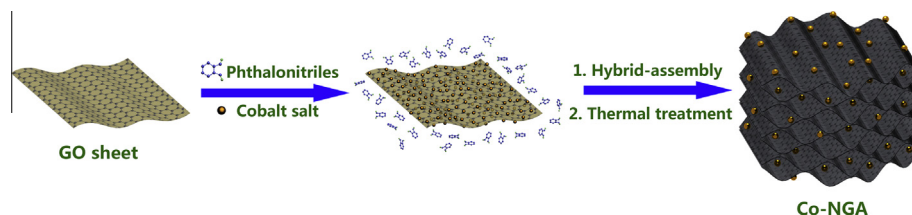


Fig. 1. Schematic illustration of the formation process for Co-NGA electrocatalysts.

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