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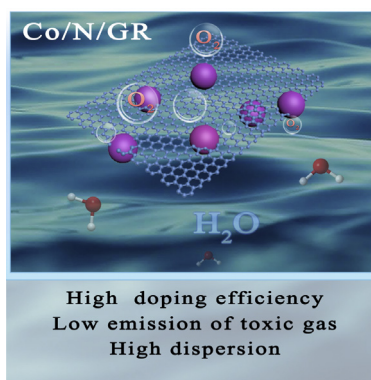
## Cobalt nanoparticles/nitrogen-doped graphene with high nitrogen doping efficiency as noble metal-free electrocatalysts for oxygen reduction reaction



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## GRAPHICAL ABSTRACT



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## ABSTRACT

Nitrogen-doped graphene (N/GR) has been considered as active metal-free electrocatalysts for oxygen reduction reaction (ORR). However, the nitrogen (N) doping efficiency is very low and only few N atoms are doped into the framework of GR. To boost the N doping efficiency, in this work, a confined pyrolysis method with high N doping efficiency is used for the preparation of cobalt nanoparticles/nitrogen-doped GR (Co/N/GR). Under the protection of SiO<sub>2</sub>, the inorganic ligand NH<sub>3</sub> in cobalt amine complex ([Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>) is trapped in the confined space and then can be effectively doped into the framework of GR without the introduction of any carbon residues. Meanwhile, due to the redox reaction between the cobalt ions and carbon atoms of GR, Co nanoparticles are supported into the framework of N/GR. Due to prevention of GR layer aggregation with SiO<sub>2</sub>, the Co/N/GR with high dispersion provides sufficient surface area and maximum opportunity for the exposure of Co nanoparticles and active sites of N dopant. By combination of enhanced N doping efficiency, Co nanoparticles and high dispersion of GR sheets, the Co/N/GR is remarkably active, cheap and selective noble-metal free catalysts for ORR.

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## 1. Introduction

Fuel cells are an environmental friendly power source that directly transforms chemical energy of fuel into electricity through chemical reaction with oxygen or another oxidizing agent. The

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cathodic oxygen reduction reaction (ORR) is the most important reaction in determining the performance of fuel cell. Upon to this point, platinum (Pt)-based materials are known to be the most active electrocatalysts for ORR, which generate high activity and low over potential [1–3]. Despite of considerable efficiency of the noble metal-based electrocatalysts, large scale commercialization is still limited due to their high cost, low abundance and poor durability. Therefore, substitution of Pt catalysts with noble metal-free catalysts has been drawn more attention. One non-precious metal alternative to Pt is nitrogen (N)-doped carbon nanomaterials, which exhibit high ORR activity and good stability in alkaline solution, as summarized in recent reviews [1,2,4–11]. To verify the experimentally observed activity, the indispensable role of N incorporation for the enhanced electrocatalytic activity in N-doped carbons is also proved by theoretical studies [12–16].

Among these carbon nanomaterials, graphene (GR), a graphitic single atomic plane, is an ideal building block for the design of various novel functional materials [17–19]. In ORR application, many advanced noble metal-free catalysts are constructed through doping of GR framework with N, which can effectively decrease the overpotential and enhance the catalytic activity [1,2,4–7,17,20–26]. Doping of N atoms facily modifies materials intrinsically, tailors electronic properties, manipulates surface chemistry and produces local changes to the elemental composition of host materials, which consequently perk up the electrocatalytic activity. To further boost the ORR activity, some researchers have studied and confirmed the introduction of transition metal into N-doped GR is a desired way to promote the ORR activity efficiently [1,2,4–7,17,20,21], perhaps inspired by the high activity of metal/N/C prepared by the pyrolysis of nitrogen-rich molecules and transition-metal salts [27]. Experimentally, the synergistic effect between the N/GR and transition metal yields much better catalytic activity on transition metal/N/GR catalysts as compared to either N/GR or transition metal only [2,4–7,19,22,23,25,26,28–31]. Theoretically, the computational calculations also confirm that activity of Fe/N/GR is comparable to that on Pt/C [32–34]. Noting the vital role of N doping in boosting the ORR activity, different fabrication procedures have been used for preparation of N/GR or metal/N/GR (M/N/GR), such as thermal pyrolysis of graphene oxide (GO) with nitrogen-containing organic compounds [26,28,35–37], simultaneous reduction and doping with  $\text{NH}_3$  [38,39], template-directed chemical vapour deposition (CVD) [40]. Compared with the undoped GR, these N/GR or M/N/GR showed improved performance as noble metal-free ORR electrocatalysts. Although considerable progress and achievement for ORR application has been obtained by N-doped GR, limited attention is focused on the N doping efficiency during the preparation of GR-based noble-metal free ORR catalysts. For example, N-doped GR prepared through CVD method often involves the use of an expensive machine, low utilization of gas, and flowing gas of toxic organic compounds as precursors (such as pyridine [40]). By using a different method, N/GR can be easily prepared by thermal pyrolysis of GO in the presence of nitrogen-containing organic compounds, such as pyrrole [35], polyaniline [38,41], metal-organic frameworks [42], phenanthroline [26,37], thiourea [43], iron phthalocyanine [36], urea [44], vitamin B12 [45], dopamine [46], or melamine [47]. However, it should be noted that most of these heteroatoms are released in the form of gas at extreme temperature, such as  $\text{NO}_x$ , ammonia ( $\text{NH}_3$ ), and hydrogen cyanide (HCN) [48,49]. Because of gas flowability, only partial N atoms are effectively doped into carbon framework and most of N atoms are emitted, consequently limiting doping efficiency. Besides the low doping efficiency, another question is that the toxicity of heteroatom-containing compounds and produced gases are harmful to the environment and human health [50]. Due to the volatility of organic vapour at high temperatures under a flowing atmosphere of inert protective gas, a high nitrogen

precursors/GO ratio is required to enhance the N content of GR-based catalysts (Table S1). Although most of nitrogen precursors are easily decomposed at high temperature, direct pyrolysis of these organic compounds in the absence of GO at inert atmosphere can also produce carbon materials. Then, carbon residues produced by the pyrolysis of these organic compounds may remain on the surface of GR during the pyrolysis of nitrogen precursors/GO mixture [42], which thus are expected to contribute to the electrochemical activity. In other words, the N/GR prepared by thermal pyrolysis method is carbon/GR composites rather than “clean” GR. So, it is desired to prepare “clean” N/GR without any carbon residue to show the real activity of GR. Although thermal annealing of GO in the presence of  $\text{NH}_3$  offers a simple method for simultaneous doping and reduction of GO without the introduction of any carbon residue [39,51]. However, toxic gas is discharged by the reduction of GO under a flow of  $\text{NH}_3$  (pyrolysis at high temperature about several hours). Hence, from the perspective of environmental protection and health, it's very crucial to find a relatively economical method with minimum gas emission and least harmful for environment and the preparation of high dispersed heteroatom-doped GR for application in ORR.

In this work, a confined pyrolysis method is used for the preparation of cobalt nanoparticles/nitrogen-doped highly dispersed GR (Co/N/GR), as shown in Scheme 1. Three purposes are simultaneously achieved by confined pyrolysis cobalt amine complex/GO ( $[\text{Co}(\text{NH}_3)_6]^{3+}/\text{GO}$ ) under the protection of  $\text{SiO}_2$ : high nitrogen doping efficiency, low emission of toxic gas, and high dispersion of “clean” GR layers without any carbon residues. The volatile  $\text{NH}_3$  species produced by the decomposition of the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  are trapped and sandwiched by the  $\text{SiO}_2$  film. Owing to the entangled of  $\text{NH}_3$  in the confined nanospace, the N can be effectively doped into the framework of GR and then a high doping efficiency was obtained. Compared to high ratio of organic compounds/GO in the open system, the low ratio of  $[\text{Co}(\text{NH}_3)_6]^{3+}/\text{GO}$  used for the preparation of Co/N/GR and scarce escape of  $\text{NH}_3$  in a confined nanospace leads to low emission of toxic gas. Because of inorganic ammonia ligands used as N precursor, N atoms can be doped into the framework of GR without introduction of any other carbon residues. In addition, the  $\text{SiO}_2$  films not only hinder the escape of volatile nitrogen species at high temperature but also prevent the irreversible aggregation of GR layers [39]. The high dispersion of Co/N/GR prepared by confined method provides sufficient surface area and more opportunity for fully exposure of Co nanoparticles and N dopant. Table S1 lists the reported preparation methods for the N/GR-based ORR electrocatalysts by using different nitrogen-containing precursors, different ratios and N contents. From the comparative data in Table S1, our preparative method is special because: (1) high nitrogen doping efficiency in the confined nanospace; (2) low emission of toxic gas because of low  $[\text{Co}(\text{NH}_3)_6]^{3+}/\text{GO}$  ratio and confined nanospace of  $\text{SiO}_2$  shell; (3) high dispersion of GR layer without aggregation under the protection of  $\text{SiO}_2$  shell; (4) “clean” GR surface without any carbon residues because of the complete decomposition of inorganic  $[\text{Co}(\text{NH}_3)_6]^{3+}$  at high temperature.

## 2. Experimental

### 2.1. Materials

Nafion (5 wt.%) was purchased from Sigma-Aldrich. Pt/C commercial electrocatalysts with Pt loading amount of 20 wt.% were purchased from Johnson Matthey corporation. Tetraethyl orthosilicate (TEOS),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , KOH, and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  were purchased from Aladdin Reagent Company.

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