



The enhanced electrocatalytic activity of graphene co-doped with chlorine and fluorine atoms



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ABSTRACT

Graphene co-doped with fluorine and chlorine heteroatoms was prepared through a one-step synthesis and was investigated as the oxygen reduction electrocatalysts. Voltammetric measurements show that fluorine and chlorine co-doped graphene has remarkable catalytic activity toward the electrochemical reduction of oxygen in alkaline solution. Besides having a high tolerance to methanol crossover effect, the co-doped graphene also showed a better stability than that of commercial Pt/C electrocatalysts and of the chlorine-doped graphene that was prepared by the same approach. The charge transfer resistance of the co-doped graphene was substantially lower than that of the chlorine-doped graphene, suggesting that there may exist a synergistic interaction between fluorine and chlorine dopants. The rapid synthetic method reported here provides an effective approach for future investigation of halogen (co-) doped graphene.

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1. Introduction

Oxygen reduction reaction (ORR) plays an extremely important role in fuel cells and next generation metal–air batteries [1,2]. Currently, the most reliable ORR electrocatalysts are still Pt and its alloys [3,4]. However, the high cost and poor tolerance to methanol crossover and CO poisoning effects have hindered the broad usage of Pt-based catalysts [5]. It is therefore desired to develop more robust catalysts to replace Pt-based ORR electrocatalysts, especially those low cost non-precious metal [6,7] or metal-free catalysts [8–10]. Promising results have been achieved with transition metal sulfides/oxides/carbides [11–13] and N4-macrocycles compounds [14], as well as heteroatom-doped carbon materials that include carbon nanotubes (CNTs), graphene, and graphitic arrays [15–25]. Among these carbon-based materials, graphene doped or co-doped with heteroatoms such as nitrogen (N), boron (B), halogen (Cl, Br, I), phosphorous (P), and sulfur (S), has recently attracted increasing attention due to their unique electrochemical property and great stability for ORR [20–24].

The high ORR activity of heteroatom-doped graphene has been attributed to the electronegativity difference between carbon

($\chi = 2.55$) and the dopants (i.e., B = 2.04, N = 3.04, P = 2.19) [8,17], which causes the redistribution of electrons on the graphene surface, facilitating the adsorption of oxygen molecules either at the doping sites or the neighboring carbon atoms. When the electronegativity difference is almost negligible (i.e., S = 2.58, Se = 2.55), “electron spin” redistribution may become responsible [26]. In view of the strong electronegativity of halogen (F = 4.0, Cl = 3.16, Br = 2.96, I = 2.66), halogen-doped graphene (HDG) are anticipated to be very active in ORR and the electroactivity would increase from I- to F-doped graphene [20,27,28]. However, experimental confirmation of such a prediction remains elusive as the synthesis of HDG has so far been difficult, if not impossible, due to the toxicity of halogen molecules (e.g. F₂, Cl₂, Br₂), particularly the fluorine gas is too reactive and toxic to be handled in standard laboratories [20,21]. As a result, there are few methods reported for the synthesis of graphene doped with different halogen atoms.

A few HDGs (e.g. I-doped graphene) have recently been prepared from reduced graphene oxides (rGO) and their derivatives [20,21,27], however the involvement of Hummer's process leads to the final graphene products having an inferior electrical conductivity to the pristine graphene. So far, there is no report about the synthesis of graphene co-doped with different halogen atoms. Whether there is any synergetic interactions among different halogen dopants, similar to carbon nanotubes and graphene co-doped with B and N [16,24], remains to be answered.

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In the following a method for the rapid synthesis of chlorine-doped and chlorine and fluorine co-doped graphene was developed. Electrochemical measurements indicate that the as-prepared products have great electrocatalytic activity toward ORR in alkaline solution, where the onset potential is nearly the same as that of commercial Pt/C catalysts.

2. Experimental

2.1. Materials and synthesis

CCl_3F and CCl_4 were purchased from Aladdin Reagent Company (Shanghai, China). Magnesium metal was purchased from Xiya Reagent (Chengdu, China). Unless otherwise stated, all reagents were of analytical grade and were used as received. Deionized water was prepared with a Milli-Q system (18.2 M Ω cm, Millipore, USA). For the preparation of fluorine and chlorine co-doped graphene (ClFG), in a typical experiment 6.0 ml of CCl_3F was refluxed at 60 °C in a 100.0 ml flask for 10.0 minutes. 1.0 g of Mg ribbon was ignited in air and was then quickly thrown into the flask containing CCl_3F vapor. The burning Mg instantly generated a large amount of black products in the flask and stopped burning after a few seconds. Ethanol was then added to the reactor to remove organic intermediate species. The black solid, collected from ethanol solution, was transferred to another flask containing 50.0 ml of 1.0 M HNO_3 to remove MgF_2 , MgO , excessive Mg, etc. The cleaned solids were collected by centrifugation and were rinsed with deionized water and ethanol several times. The solid products were finally dried at 80 °C for 12 h in vacuum. The fabrication of chlorine doped graphene (ClG) was carried in the same way as fluorine and chlorine co-doped graphene, except that CCl_4 was used and the heating temperature was increased accordingly to reach the reflux state of CCl_4 .

2.2. Characterization

The ClFG and ClG products were characterized with X-ray diffraction (Bruker D8) using Cu K α radiation ($\lambda = 0.15406$ nm), scanning electron microscopy (Nova NanoSEM 200) operated at an acceleration voltage of 10 kV, atomic force microscopy (Veeco Nanoscope IIIa) with a tapping mode at a scan rate of 1 Hz, Raman spectroscopy (JY-T643200, France) under ambient conditions by using a 514 nm laser excitation, and energy dispersive X-ray analysis (Nova NanoSEM 200). X-ray photoelectron spectroscopy (XPS) was performed on a spectrometer from Kratos Axis UltraDld, using mono Al K α radiation at a power of 120 W (8 mA, 15 kV). For the gas chromatography and mass spectrometry measurements, samples were collected by adding ethanol to the flask to dissolve them.

2.3. Electrochemical measurements

Electrochemical measurements were conducted on a CHI660C electrochemical workstation using a three-electrode system, in which the reference and counter electrodes were saturated Ag/AgCl electrode and platinum foil, respectively. To prepare the working electrodes, the doped graphene products were dispersed in ethanol (1.0 mg/ml) and 2.0 μL of the slurry solution was dropped on a glassy carbon electrode (with a diameter of 3.0 mm). After ethanol evaporates, another 2.0 μL of the slurry was added. In total, 20.0 μL of the graphene ethanol mixture was added to a glassy carbon electrode. The above process was followed by casting with 2.0 μL Nafion solution (5% in isopropanol) as the binder. Electroactivity of the doped graphene was evaluated by CV and LSV on a rotating disk electrode (RDE) in oxygen saturated KOH solution ($[\text{KOH}] = 0.1$ M). Prior to each measurement, the alkaline solution was purged with high purity nitrogen or oxygen for 30.0 min. The solution was maintained at 25.0 ± 0.5 °C with a water bath. For comparison, commercial 40.0 wt% Pt-C catalyst (Vulcan XC-72R) was also investigated in this study. Typical CVs were measured between -0.8 and 0.0 V at a scan rate of 50.0 mV s $^{-1}$. Electrochemical impedance spectroscopy of $\text{K}_3\text{Fe}(\text{CN})_6$ (5.0 mM) was measured on an Autolab PGSATAT302 electrochemical station (Holland), supplied with a FRA2.0 module. The impedance measurements were performed at room temperature, using the as-prepared ClG, Pt/C or bare glassy carbon electrode as the working electrode.

3. Results and discussion

3.1. Synthesis and characterization of ClG

As illustrated in the right panel of Fig. 1, liquid CCl_4 in a three-neck flask was heated with an oil bath at a preselected temperature to reach a reflux state and was maintained there for 10 min. A piece of burning magnesium ribbon (0.4 mm \times 4.2 mm), ignited in air, was thrown into the flask through one of the side necks. The energy released by burning magnesium initiated radical polymerization, which behaved like an explosion and completed instantly. GC/MS analysis of a sample from the reactor indicates the formation of C_2Cl_6 , C_3Cl_6 , C_4Cl_6 , C_6Cl_6 , etc. Although the oil bath temperature investigated in this study was all above boiling temperature of CCl_4 (76.7 °C), our measurements nevertheless indicate that the yield of graphene increased with oil bath temperature and the highest yield of 73% was achieved at 140 °C. Notably, when the heating temperature was below 100 °C, the most dominant (almost exclusive) product in the gas phase is C_6Cl_6 (See Table 1) and the amount of black solids product was also low.

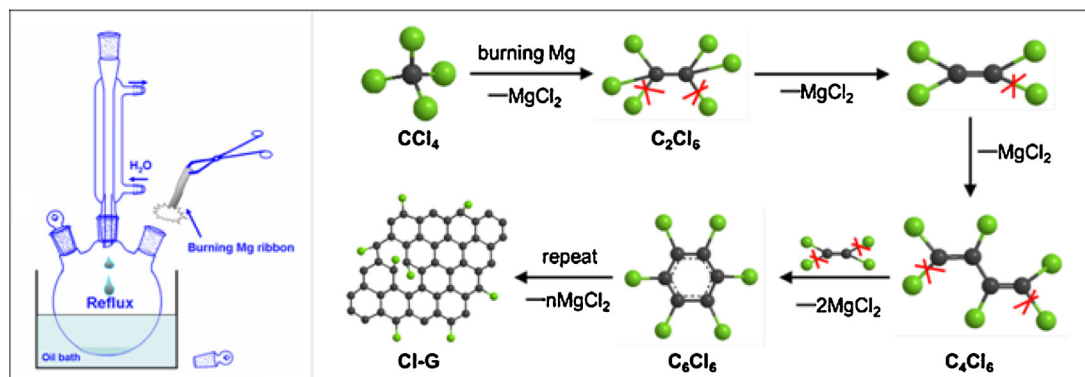


Fig. 1. Schematic illustrations of the reaction equipment (left) and the formation mechanism of chlorine-doped graphene (right).

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