

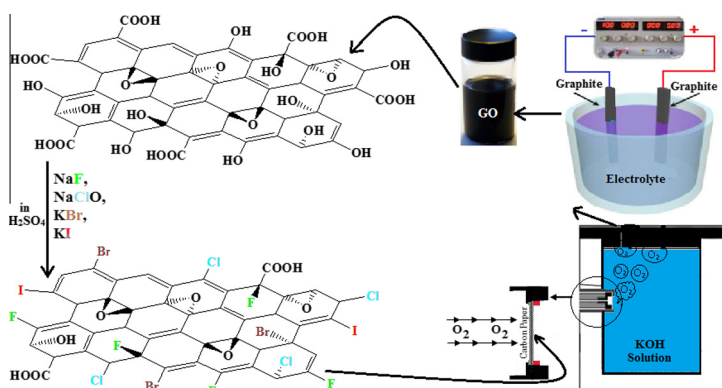
Synthesis of halogen-doped reduced graphene oxide nanosheets as highly efficient metal-free electrocatalyst for oxygen reduction reaction



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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 11 August 2015

Revised 10 October 2015

Accepted 13 October 2015

Available online 22 October 2015

Keywords:

Reduced graphene oxide synthesis
Halogen-doped graphene nanosheets
Gas diffusion electrode
Metal free
Oxygen reduction

ABSTRACT

We demonstrate F-, Cl-, Br- and I-doped reduced graphene oxide (XRGO) as metal-free graphene electrocatalysts for oxygen reduction reaction (ORR) in alkaline media. Reduced graphene oxide (GO) is prepared from graphite electrode using electrochemical exfoliation. In situ doping of halide in a graphene film has many problems. In this technique, different halides individually or all of them were mixed with the RGO and ionic liquids precursor at H_2SO_4 solution. Then we have evaluated the effectiveness of doping and performed electrochemical measurements of the ORR activity on XRGO. Fourier-transform infrared spectroscopy spectra show a variety of the halogen-containing functional groups. Energy-dispersive X-ray spectroscopy analysis confirmed the presence of doped halogens in RGO. Raman spectroscopy shows a high density of defects in the RGO layer. The electrochemical properties of the XRGO catalysts on carbon paper as a gas diffusion electrode (GDE) are investigated by several electrochemical methods in oxygen saturated alkaline solutions. The catalytic activity of the XRGO and Pt-C electrodes for ORR is 50 and 30 mA cm^{-2} at -1 V in GDEs. This enhanced efficiency is the result of the influence of the nature and percentage of the halogen, especially fluorine presence in the graphene layer.

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1. Introduction

Electro-catalysts for the oxygen reduction reaction (ORR) are key components of fuel cells (FCs). The FC, a device that converts

chemical energy into electrical energy from a fuel through chemical reaction with oxygen, has drawn a lot of attention in terms of both fundamentals and applications [1–3]. Pt and its alloys remain the most efficient ORR catalysts, but the high cost and scarcity of Pt hamper further development of FC technologies based on these materials [4]. Recently, researchers have focused on developing a low cost and efficient ORR electro-catalyst with Pt-grade activity

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[5]. Metal-free N-doped carbon nanomaterials such as N-doped graphene have been found to give the above advantages, while providing an efficiency equivalent to Pt particles. However, activity of Nitrogen-doped carbons due to insufficient information about the role of N-doping in the active site (defect) remains unclear [4–6].

Another powerful method to enhance the graphene active site is halogen-doping (X-doping) [7], which can modify graphitic carbon materials to be used in many technological fields such as photocatalytic [8], lithium storage [9], stem cells [10] and ORR [11,12]. Sun et al. found that the doping of fluorine (F) alone on carbon blacks can induce superior high ORR electro-catalytic performance that is competitive with Pt or other best non-Pt electro-catalysts [13]. Graphene is one of the allotropes of carbon and can be used for many technological applications, such as supercapacitors, batteries and FCs [14].

Substitution of halogen or nitrogen atoms on graphene sheets can change the electronic structures of the host, providing a promising way to tailor the transport and electronic properties of graphene for electrochemical applications. However, X-doping [15] or N-doping [16] of the carbon materials so far has inevitably required harsh reaction conditions such as high temperature or hazardous materials. Thus, it is very difficult to control the distribution and bonding configurations of the dopants in the π -conjugated framework, leading to a poor understanding about the doping effects [17].

Halogen atoms show both the resonance donating due to the existence of lone pair of electrons and the electron withdrawing due to electro-negativity type effect.

The electronic structure of graphene can change significantly by attachment of halogen atoms. Chlorinated graphene has a much smaller band gap of 0.9 eV and brominated graphene has almost zero band gap. The electrochemical properties of halogen (X = Cl, Br, I) doped graphene show the fastest heterogeneous electron transfer for Cl-doped graphene and the slowest for I-doped graphene [18]. However, the band gap of fluorinated graphene sheets (FGS) can be varied from 0 eV to 3 eV with changing degrees of fluorination and the full FGS operates with the highest band gap of approximately 3.1 eV such as an insulator. From the chemical viewpoint, graphene oxide (GO) can be considered to be a two-dimensional layer of carbons containing various oxygen functionalities, such as phenols, alcohol, carboxylic and epoxies groups. Theoretical calculation predicts that the zero band gap of graphene can be opened by halogenations, thus, they can successfully change the electronic structure of graphene. The variation of band gap energy by halogen substitution or chemical doping could be reflected in a superior photo-catalytic activity of modified graphene with respect to GO [8,19].

Graphene, a single layer of sp^2 -bonded carbon atoms neatly arranged in a honeycomb lattice, is the 2D material shown to exist in a suspended form, defying previously held concepts that suspended two-dimensional materials were thermodynamically unstable. Graphene has exhibited a series remarkable physical properties, many of them could be related to its unusual electronic structure near the Fermi level [20]. In this work, we employ an electrochemical method that uses an ionic liquid (IL) to prepare GO [21–23]. Because of strong electrostatic/chemical interaction between GO and IL the well-dispersion of GO by IL can improve [24]. When gating IL on graphene, an electric double layer (EDL) is formed between IL and graphene. Since the thickness of the EDL is very thin, ~ 1 nm, a very large gate capacitance is utilized, inducing an extremely high charge density in graphene even at a low gate voltage [25].

Herein, we describe a simple, scalable and controllable method for the halogenations of reduced graphene oxide (RGO) with simultaneously fluorine, chlorine, bromine and iodine by electrochemi-

cal exfoliation of GO and obtained XRGO in presence of IL and halogen salts (X = F, Cl, Br, I). In particular, we consider halogen atoms on a RGO lattice. These atoms themselves are covalently bonded and represent an example of realistic weakly reactive adsorbents. Importantly, the electro-catalytic activity for ORR is carefully evaluated for halogenated RGO material.

2. Experimental

2.1. RGO electro-synthesis

RGO is fabricated from graphite electrodes using ionic liquid-assisted electrochemical exfoliation. Static potentials of 5 V were used to the two graphite electrodes using a DC power supply [26]. The graphite rods were employed as anode and counter-electrode into the IL/water solution with a separation of 1 cm the IL urea and choline chloride was mixed with water at 1:2 ratio [22].

2.2. Preparation of halogenated RGO (XRGO)

Halogen-containing solutions were ready by adding 0.1 mol/L equivalent amount of KBr, KI, NaClO and NaF into 15 mL of H_2SO_4 10 mol/L in a glass bottle. In order to prepare of XRGO, 2.0 mg of RGO was added into the halogen-containing acid solution and dispersed by ultrasonic for 30 min. Then the solution was stirred at room conditions overnight. After filtration, the XRGO was washed with ethanol and water and finally dried at 40 °C to fabricate X_{II} RGO [27]. On the other hand, X_{II} RGO is a RGO nanosheets which doping by F, Cl, Br and I. Note that NaF has individually been introduced in the H_2SO_4 to produce FRGO and the other salts in the absence of NaF were mixed and X_I RGO was obtained. X_I RGO is formed of RGO doped by Cl, Br and I.

2.3. Gas diffusion electrode (GDE) preparation and rotating disk electrode (RDE) modification

A mixture containing a homogeneous suspension of prepared XRGO, isopropanol (Merck), water, 10 wt.% Nafion solution was homogenized by sonication for 20 min, then painted on carbon paper (TGPH-0120T Toray). The obtained composite structure was dried in air by vacuum pump and denoted as FRGO, X_I RGO and X_{II} RGO. The Pt–C catalyst was used as reference catalyst and painted on TGPH in the same solution and denoted as (Pt–C/CP) electrode. And also, 20 μ L of the as-synthesized catalysts solution (0.5 mg) in Nafion and isopropanol (ink) were drop-cast onto a freshly polished GC surface (6.28 mm²). Catalyst films were typically dried overnight at ambient temperature.

2.4. Electrochemical measurements

The ORR was investigated at the GDE with geometric area of 1 cm² in 0.5 M potassium hydroxide. Measurements were carried out at 25 °C with flowing oxygen in a conventional three-electrode compartment [2]. By flowing water through the jacket of the electrochemical cell with circulating water the temperature of the cell is controlled. The GDEs were placed in the Teflon holder containing a high pyrolytic graphite disk as a current collector and oxygen was supplied from the back of the electrode. The Ag/AgCl reference electrode was inserted close to the surface of working electrode.

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