Chinese Journal of Catalysis 35 (2014) 884–890

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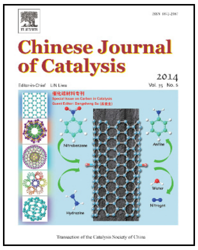

Article (Special Issue on Carbon in Catalysis)

Solution phase synthesis of halogenated graphene and the electrocatalytic activity for oxygen reduction reaction

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ARTICLE INFO

Article history:
Received 3 April 2014
Accepted 18 April 2014
Published 20 June 2014

Keywords:
Halogen-doping
Sulfur-doping
Graphene
Oxygen reduction reaction
Electrocatalyst

ABSTRACT

Metal-free carbon electrocatalyts for the oxygen reduction reaction (ORR) are attractive for their high activity and economic advantages. However, the origin of the activity has never been clearly elucidated in a systematic manner. Halogen group elements are good candidates for elucidating the effect, although it has been a difficult task due to safety issues. In this report, we demonstrate the synthesis of Cl-, Br- and I-doped reduced graphene oxide through two solution phase syntheses. We have evaluated the effectiveness of doping and performed electrochemical measurements of the ORR activity on these halogenated graphene materials. Our results suggest that the high electronegativity of the dopant is not the key factor for high ORR activity; both Br- and I-doped graphene promoted ORR more efficiently than Cl-doped graphene. Furthermore, an unexpected sulfur-doping in acidic conditions suggests that a high level of sulfide can degrade the ORR activity of the graphene material.

1. Introduction

Since the invention of the hydrogen fuel cells in 1838, the electrocatalysis of the oxygen reduction reaction (ORR) has emerged as an attractive research topic, for it potentially allows enormous energy to be delivered for small mass [1]. The ORR reaction is critical for various types of fuel cells and metal-air batteries. Nowadays, much of the research focus is on developing a low cost and robust ORR electrocatalyst with Pt-grade activity while being environmentally benign [2,3]. Metal-free N-doped carbon materials, in particular, have been discovered to offer the above advantages while delivering almost equivalent performance to Pt after thermal treatment [4]. However, the origin of electrocatalytic activity on N-doped carbons remains unclear due to a lack of understanding about the role that the dopant plays in the active site. This has prevented further development of metal-free ORR electrocatalyst and a solution should be actively pursued.

Recent research has established a hypothesis that the breaking of electroneutrality in the graphitic carbon lattice is responsible for forming active centers for ORR [5]. In order to validate this concept, an experiment would require a simple system which allows the dopant electronegativity to be tuned from the level of nitrogen down to a level close to carbon. To achieve this, halogen group elements are perhaps the ideal candidates since the electronegativity difference versus carbon ($\Delta\chi$) for Cl, Br, and I are 0.61, 0.41, and 0.11, respectively, by the Pauling scale. Unfortunately, current methods of halogen doping into carbon typically require harsh reaction conditions (e.g., high temperature treatment or laser ablation) and the direct use of highly toxic gases [6–9]. It would certainly be desirable to make a solution phase halogenation method for carbon ma-

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DOI: 10.1016/S1872-2067(14)60108-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 6, June 2014

terials under ambient conditions available.

In this report, we demonstrate two solution phase preparations of Cl-, Br-, and I-doped reduced graphene oxide (RGO) in different solvent systems and compare the effectiveness of the two doping procedures. Importantly, the electrocatalytic activity for ORR is carefully evaluated for each halogenated graphene material.

2. Experimental

2.1. Materials

RGO was prepared by a thermal exfoliation method on graphite oxide, which was synthesized according to a reported modified Hummer's method [10]. All other chemicals KCl (≥99%), KBr (≥99%), and KI (≥99%), NaClO (12.5% in water), concentrated H_2SO_4 (≥98%) and CCl_4 were purchased from Ajax Finechem Pty Ltd and Sigma-Aldrich, and used as received.

2.2. Preparation of halogenated RGO (X-RGO)

2.2.1. Preparation X-RGO in concentrated H_2SO_4

Halogen-containing solutions were firstly prepared by adding 0.1 mol/L equivalent amount of NaClO, KBr and KI into 10 mL of 10 mol/L H_2SO_4 in a 20 mL glass bottle. Note that NaClO was used instead of KCl because the chloride anion is too stable to be oxidized by the concentrated acid. In a typical preparation of X-RGO, 2.0 mg of RGO was introduced into the halogen-containing acid solution and dispersed in an ultrasonic bath for 30 min. With the bottle capped, the solution was stirred at ambient conditions overnight. The modified RGO was then filtered and washed with water and ethanol, and finally dried at 40 °C for collection.

2.2.2. Preparation of X-RGO in halogen-dissolved CCl_4

The procedure for RGO modification in halogen-dissolved CCl_4 was similar to that in H_2SO_4 except a halogen gas (X_2) extraction step was involved. Basically, 15 mL of CCl_4 and 2.0 mL of concentrated H_2SO_4 was placed in a capped glass bottle and 0.1 mol/L equivalent of a halide salt was added into the two-phase mixture and shaken vigorously to dissolve the X_2 gas into the organic phase. Since HCl does not dissolve in the organic phase, an equivalent amount of NaClO was used instead to generate Cl_2 gas. The X_2-dissolved CCl_4 was then extracted and transferred to another bottle for RGO modification. The modification procedure was as described previously.

2.3. Characterization

The materials were characterized mainly by X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FT-IR) spectroscopy. XPS was performed with a Kratos XPS spectrometer using a monochromated Al Kα source. The survey scan and high-resolution scan were measured at a pass energy of 160 and 20 eV/s, respectively. All spectra were corrected against the C *1s* (C–C) peak at 284.8 eV as a reference and the full-width at half-maximum (FWHM) values were held constant for all peaks. Transmission electron microscopy (TEM) was carried out on a JEOL 1010 microscope and the micrographs were taken at an accelerating voltage of 100 kV. Ultraviolet-Visible (UV-Vis) spectroscopy was used to confirm the identity of a particular halogen dissolved in CCl_4 solvent. This was performed on an Agilent Technologies Cary 60 UV-Vis spectrophotometer.

2.4. Electrochemical measurements

The electrochemical measurements of ORR activity were carried out using a CHI920D bipotentiostat instrument coupled with a RRDE-3A electrode rotor (ALS Co., Ltd.). In a typical cell, a rotating Pt ring/glassy carbon (GC) disk electrode, a Pt wire counter electrode and a HgO/Hg reference electrode stabilized in 0.1 mol/L KOH were employed in a three-electrode system. All electrochemical reactions were performed in an O_2-saturated 0.1 mol/L KOH electrolyte; the O_2 saturation was done by purging with the gas for at least 30 min before the measurements. Linear sweep voltammetry on a rotating ring-disk electrode (LSV-RRDE) was performed using the above setup at a sweep rate of 10 mV/s, the electrode was rotated constantly at 1500 r/min and the ring potential was held at + 0.5 V versus the reference electrode. All the potentials were quoted with respect to the reference electrode. The collecting efficiency of the RRDE was determined by using a bare glassy carbon disk in an Ar-saturated standard ferricyanide electrolyte (5 mmol/L potassium ferricyanide in 0.1 mol/L KNO_3 solution) under a rotation rate of 1500 r/min. The collecting efficiency was found to be ~0.32 by calculating the ratio of the ring current (at oxidizing potential) and the disk current (at reducing potential) for the one-electron transfer reaction.

3. Results and discussion

In the preparation of X-RGO, concentrated H_2SO_4 was employed to generate X_2 gases at laboratory scale from the various halide sources. Each reaction follows one of the chemical equations shown below:

$$2\ NaClO + 2\ H_2SO_4 \rightarrow 2\ NaSO_4 + Cl_{2(g)} + 2\ H_2O \tag{1}$$

$$H_2SO_4 + 2\ H^+ + 2\ Br^- \rightarrow Br_{2(g)} + SO_{2(g)} + 2\ H_2O \tag{2}$$

$$H_2SO_4 + 8\ H^+ + 8\ I^- \rightarrow 4\ I_{2(g)} + H_2S_{(g)} + 4\ H_2O \tag{3}$$

In this way, the highly oxidative X_2 gases can react with RGO in the solution phase and introduce the desired C–X species. Since halogens in their gaseous form are typically unstable in an aqueous medium, we have examined the effectiveness of this chemical modification in both H_2SO_4 and CCl_4. Figure 1(a) is the schematic diagram of the X-RGO preparation procedures in the two media. The typical sheet-like morphology of the raw RGO material was confirmed by TEM and is shown in Fig. 1(b). The presence of X_2 gases in CCl_4 after the solvent extraction was also identified by their characteristic absorption bands in the UV-Vis spectra as shown in Fig. 1(c); the excitation wavelengths for Cl_2, Br_2, and I_2 are respectively 346, 414, and 512 nm, which are in agreement with the reported values [11,12].

Composition analysis of the surface of the modified X-RGO requires a highly sensitive analytical technique and XPS was