



Short communication

Remarkable electrochemical properties of electrochemically reduced graphene oxide towards oxygen reduction reaction are caused by residual metal-based impurities



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ABSTRACT

Oxygen reduction reaction (ORR) is one of the most important electrochemical reactions in the field of energy storage. Remarkable catalytic properties towards ORR at “metal-free” electrochemically reduced graphene oxide (ErGO) were previously reported. We demonstrate here that the remarkable enhancement towards ORR of a “metal-free” ErGO is caused by residual metallic impurities instead of ErGO itself.

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1. Introduction

Oxygen reduction reaction (ORR) is of key importance for fuel cells as well as vanadium-air battery and zinc-air batteries [1,2]. Currently, the most efficient and widely used catalyst for ORR is platinum which has high cost and limited resources [3]. Therefore, an intensive search for non-Pt catalysts with low cost and comparable catalytic properties is encouraged. A large number of literature reports have been published on the utilization of carbon nanomaterials, such as carbon nanotubes [4–9] carbon nanoribbons [10,11] and graphene materials [12–16] as catalytic surfaces for ORR. Meanwhile, metal-based catalytic particles embedded onto graphene or carbon nanotubes are also efficient catalysts for ORR [17–21]. It is well-known that, similar to carbon nanotubes, graphene materials, especially those prepared from graphite, contain significant amount of metallic impurities, and several reports also pointed out that the remarkable ORR catalytic properties were caused by residual metallic impurities within the carbon materials [22–26].

We wish to address the reported “metal-free” electrocatalysis at electrochemically reduced graphene oxide (ErGO) [21]. Even through a similar work on chemically reduced graphene oxide has been reported previously by us [22], the influence of impurities on the electrochemistry of the electrochemically reduced graphene oxide is still necessary to study. This is due to the fact that electrochemical reduction does not use reagents which also contain traces of impurities [27]. In addition, there

is large number of article claiming metal-free ORR on graphene (including electrochemically reduced graphene oxide) and these claims should be verified [21]. The graphene oxide (which was later reduced by electrochemical means) was synthesized from graphite using Hummers method [28]. It is important to note that, the Hummers method involves using permanganate as an oxidant to oxidize graphite into graphite oxide (GiO), followed by ultrasonication treatment to form graphene oxide (GO) and thereafter electrochemical reduction was performed to obtain ErGO. It is known for decades that graphite contains large varieties of metallic impurities with a contribution of up to 2 wt.% [29–34]. These impurities include Fe, Ni, Co, Mo, Mn, V, and Cr [30]. Previous reports have indicated that even a trace amount of impurities can dramatically influence the electrocatalytic properties or dominate the electrochemistry of the carbon materials [22–26,35–39]. The treatment of graphite with Hummers method (utilizing KMnO_4) leads to the incorporation of Mn-based impurities at high ppm levels in the resulting graphite oxide and further propagates to subsequent graphene derivatives [24,40]. Here we show that this is also the case for electrochemically reduced graphene oxide, which in actual fact, is not metal-free and where the metallic impurities could be responsible for the catalysis towards ORR.

2. Material and methods

2.1. Materials

Sulfuric acid (95–98%), sodium nitrate, hydrochloric acid (37%), phosphoric acid (85%), potassium chlorate (98%), *N,N*-dimethylformamide

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(DMF), potassium phosphate dibasic, sodium phosphate monobasic, potassium ferricyanide, potassium ferrocyanide, potassium hydroxide, Co_3O_4 , FeO, Fe_2O_3 , Fe_3O_4 , FeOOH and NiO particles were purchased from Sigma-Aldrich. Graphite (natural, powder, flake size of 45 μm) was obtained from Asbury Carbons (Asbury, New Jersey). MnO_2 powder was purchased from Alfa Aesar. Potassium permanganate and fuming nitric acid (>90%) were obtained from J. T. Baker.

2.2. Apparatus

The scanning electron microscopy (SEM) images were obtained by a JEOL 7600 F field emission scanning electron microscopy (JEOL, Japan). All voltammetric experiments were measured by using an electrochemical analyzer Autolab PGSTAT 101 (Ecochemie, Utrecht, The Netherlands) connected to a personal computer and controlled by NOVA software Version 1.8 (Metrohm Autolab B. V.). The electrochemical measurements were performed by using a three-electrode configuration at room temperature. A glassy carbon (GC) electrode was used as the working electrode, a platinum disk and a Ag/AgCl (saturated) electrode were used as the auxiliary and reference electrodes, respectively. Trace metal analysis was performed using an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS, Japan). Prior to analysis, samples were digested by using a Milestone Ethos one microwave digestion system (Italy) using ultrapure nitric and hydrochloric acids (J. T. Baker).

2.3. Procedure

2.3.1. Synthesis of graphite oxide by Staudenmaier oxidation method

17.5 mL of sulfuric acid (95–98%) and 9 mL of nitric acid (>90%) were added to a reaction flask containing a magnetic stir bar. The mixture was cooled at 0 °C for 15 min. 1 g of graphite was then added to the mixture under vigorous stirring to avoid agglomeration and obtain a homogeneous dispersion. 11 g of potassium chlorate was slowly added to the mixture (over 15 min) at 0 °C in order to avoid sudden increases in temperature and the formation of chlorine dioxide gas, which is explosive at high concentrations. After the complete dissolution of potassium chlorate, the reaction flask was loosely capped to allow evolution of gas and the mixture was stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was poured into 1 L of ultrapure water and filtered. GiO was then redispersed and washed by centrifugation (10000 rpm) repeatedly in 5% HCl solutions to remove sulfate ions. GiO was finally washed with ultrapure water until a neutral pH of supernatant was obtained. The GiO slurry was then dried in a vacuum oven at 30 °C for 5 days prior to usage.

2.3.2. Synthesis of graphite oxide by Hummers oxidation method

Graphite (0.5 g) was stirred with 23.0 mL of H_2SO_4 (95–98%) for 20 min at 0 °C prior to the addition of NaNO_3 (0.5 g) in portions. The mixture was left to stir for 1 h. KMnO_4 (3 g) was then added in portions at 0 °C. The mixture was subsequently heated to 35 °C for 1 h. Water (40 mL) was then added into the mixture and resulted in the temperature of the mixture to rise up to 90 °C. The temperature was maintained at 90 °C for 30 min. Additional water (100 mL) was added into the mixture. This was followed by a slow addition of 30% H_2O_2 (~10 mL). The warm yellow solution was centrifuged (10000 rpm) and washed with warm water (100 mL) followed by a copious amount of ultrapure water until a neutral pH of supernatant was obtained. The GiO slurry was then dried in a vacuum oven at 30 °C for 5 days prior to usage.

2.3.3. Electrochemical reduction of graphene oxide

The prepared graphite oxides were first dispersed in DMF to obtain a 5 mg/ml suspension with 30 min ultrasonication treatment to obtain exfoliated graphene oxide (Hu–GO and St–GO). The graphene oxide was reduced on the GC electrode by using LSV in the range between 0 V and –1.2 V in 50 mM phosphate buffer solution (pH 7.2). 2 scans were applied to ensure that the graphite oxide was reduced with no

more reduction peaks shown in this potential range. The prepared electrode was dipped into ultrapure water before use, to rinse off any adsorbed materials.

2.3.4. Electrochemical experiments

Metal oxide and hydroxide particles were dispersed in DMF to prepare 5 mg/mL suspensions for modification of the glassy carbon electrode. The GC electrode was cleaned with ultrapure water, and polished with a 0.05 μm alumina polishing cloth, and then cleaned with ultrapure water again. For linear sweep voltammetry (LSV) measurements, the prepared suspensions were sonicated for 5 min and subsequently a 1 μL of suspension was drop-casted onto the GC electrode and was allowed to dry at room temperature. All ORR measurements were performed in 0.1 M KOH solution at a scan rate of 10 mV/s.

3. Results and discussions

In this work, natural graphite was employed as starting material to produce graphite oxide by applying Hummers (Hu–GiO) [28] and Staudenmaier (St–GiO) [41] oxidation methods. Consequently, Hu–GiO and St–GiO were exfoliated *via* ultrasonication treatment and subsequently electrochemically reduced and hereafter labeled as Hu–ErGO and St–ErGO, respectively. The oxidation methods based on Hummers and Staudenmaier approaches were investigated since the Hummers method uses KMnO_4 as oxidant while the Staudenmaier utilizes KClO_3 as oxidant.

Prior to electrochemical reductive treatment, the Hu–GiO and St–GiO were extensively characterized by ICP-MS for trace metal analysis. St–GiO contains 6.00 ppm of Mn, 574.04 ppm of Fe, 0.38 ppm of Co and 4.11 ppm of Ni while Hu–GiO contains 1931.99 ppm of Mn, 298.01 ppm of Fe, 0.21 ppm of Co, and 1.31 ppm of Ni. The presence of approximately 300 times more Mn-based impurities in Hu–GiO than St–GiO further confirmed the fact that the employment of Hummers oxidation method will embed a large amount of Mn-based impurities into the prepared graphene materials which could remain difficult to remove.

The morphology of the graphene oxide and electrochemically reduced graphene oxide materials were obtained *via* SEM as shown in Fig. 1. Fig. 1A and C show the morphologies of St–GO and Hu–GO, which resemble stacked structure of graphene oxide layers. Fig. 1B and D show the corresponding ErGO materials.

The oxygen reduction reaction performances of St–ErGO and Hu–ErGO were examined in an air-saturated 0.1 M KOH solution as shown in Fig. 2A. These were compared against bare GC, edge plane pyrolytic graphite (EPPG), basal plane pyrolytic graphite (BPPG) as well as metal oxide and hydroxide particles that are likely to be present as impurities in the ErGO materials. Hu–ErGO exhibited the lowest onset potential (defined as potential at 10% of the wave current [42]) for ORR at –173 mV (vs. Ag/AgCl; this corresponds to 829 mV vs. RHE). On the hand, St–ErGO showed an onset potential at –263 mV, which was relatively close to the onset potentials of bare GC, EPPG and BPPG electrodes. It should be noted that St–ErGO contains a lower amount of Mn-based impurities as the Staudenmaier oxidation method applied for the preparation of its St–GiO precursor uses KClO_3 as oxidant. The EPPG electrode which is typically used as a non-catalytic control case and benchmark for the electrochemistry of sp^2 carbon materials due to its large proportion of edge sites per area compared to other forms of ordered carbon materials [43], exhibited an onset potential of –280 mV. Similarly, BPPG and bare GC electrodes which were also used as control cases showed similar onset potentials at –269 mV and –285 mV, respectively. All the three electrodes applied as control cases (EPPG, BPPG and bare GC electrodes) showed more negative onset potentials than Hu–ErGO. In order to investigate why Hu–ErGO showed a lower onset potential, we performed linear sweep voltammograms on various metal oxide and hydroxide particles which are likely to be present as impurities in Hu–ErGO and St–ErGO (Fig. 2B). The

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