Contents lists available at ScienceDirect

# Journal of Colloid and Interface Science

Regular Article

Hierarchically porous fluorine-doped graphene nanosheets as efficient metal-free electrocatalyst for oxygen reduction in gas diffusion electrode

Karim Kakaei *, Amin Balavandi

Department of Physical Chemistry and Nano Chemistry, Faculty of Science, University of Maragheh, P.O. Box 55181-83111, Maragheh, Iran

GRAPHICAL ABSTRACT
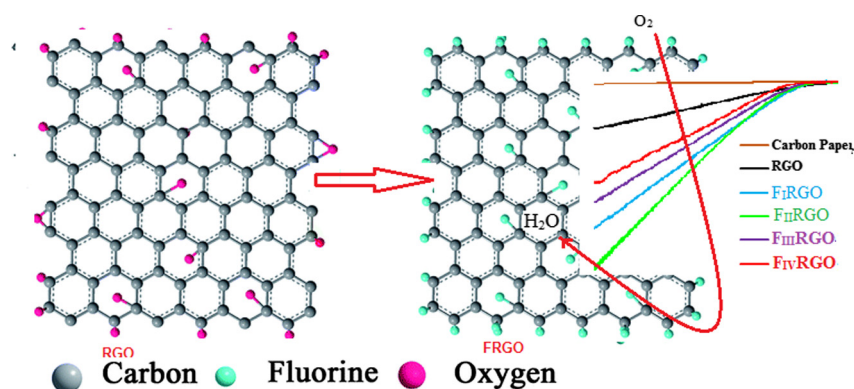
ARTICLE INFO

ABSTRACT

Here a simple yet cost-effective strategy is developed to fabricate fluorine-doped graphene nanosheets, we successfully, prepared fluorine doped graphene via thermal treatment of graphene oxide and NaF (sodium fluoride) in H_2SO_4 solution phase. Importantly, the electrocatalytic activity for oxygen reduction reaction (ORR) is carefully evaluated for fluorographene (FG). None-metal graphene electro catalysts for the ORR are attractive for their high activity and economic advantages. A significant research effort is also directed to the so-called "metal-free" ORR on heteroatom-doped graphene surfaces. The electrochemical activity of F-RGO in the ORR is investigated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) using rotating disk electrode (RDE) measurements on glassy carbon and on gas diffusion electrode (GDE) based carbon paper in oxygen saturated alkaline aqueous solutions.

1. Introduction

Graphene, an atomic monolayer two-dimensional honeycomb lattice with hexagonal symmetry sp²-hybridized carbon of graphite [1] which it has huge capability for the application in the field of nano-composites and nano-electronic instruments due to its excellent electrical, chemical, thermal, mechanical and structure properties [2–4]. To date, heteroatoms such as N, B, S,O, P, F, Se, I, Cl, Br and their mixtures have been doped on graphene, leading to the formation of "Graphene-alloy", a new type of 2D nano-materials which ensemble graphene but with part of the carbon atoms substituted by one or more types of foreign atoms and then presenting enhanced catalytic activity for oxygen reduction reaction (ORR) [5–7], biological application [8], Photocatalytic hydrogen generation [9], supercapacitor [10] and etc. Between these

heteroatom-bonded materials, N-doped graphene is a promising candidate for replacing Pt-based electrocatalysts because of its high ORR catalytic activity, long-term stability and low cost [11]. Due to the kinetic sluggishness of the ORR with the four-electron transfer pathway in the electrodes, introducing new electrocatalysts for ORR [12]. Reduced graphene oxide (rGO) shows both advanced physical and chemical adsorption capability due to high electrical conductivity of its well-developed sp^2 networks and abundant surface-active oxygen functional groups enabling it as a replacement to the commercial Pt/C catalysts in the fuel cell instruments. However, non-zero band gap of graphene leads to weaken its catalytic activity and limits its applications when it is used as metal free electrocatalyst [13].

In the field of energy, fuel cells are the strong candidate for hopeful clean energy generation devices in which electrocatalysts are crucial for the ORR [14,15]. As a result of the energy crisis in the world, solar cells, fuel cells and metal-air batteries are most attractive as clean and sustainable energy conversion devices due to they can help address the ever increasing global energy demand [16]. Therefore, it is essential to search for non-precious metal or metal free electrocatalysts with long-term operation stability and high catalytic activity to reduce the cost of electrocatalysts in fuel cells [17]. Up to now, Pt based carbon nanomaterials is considered to be the most effective ORR electrocatalysts. However, catalysts based-metal still suffer from several issue, such as: limited reserves, not good durability, high expensive and CO poisoning, which has barrier the large scale commercialization of fuel cells [18].

Fluorinated reduced graphene oxide (FRGO) is an attractive 2D material. FRGO indicant a mechanical strength comparable to that of unalloyed graphene and its conductivity can be modulated from metalloid to insulating by tuning its stoichiometry. A theoretical calculation show that by partially fluorinating graphene the material energy band gap can be changed from 0.8 to 2.9 eV [19]. Several experimental results have demonstrated the band gap and electronic transport properties of fluorinated graphene [20]. Doping of the graphene surface with fluorine atoms induces a band gap or localized states in the band structure, depending on the amount of chemisorbed atoms. A band gap over 3 eV is opened by double-side fluorination of graphene, while one-side fluorination results in the formation of the localized states and consequently variable range hopping conduction [21].

Fluorine doping has been investigated in functionalization carbon black electrochemical properties [6,16] but nobody had reported any application of it in ORR except for recent our new reference that GO has been co- doped by halogen groups and produced halogenated doping RGO in the absence and presence of fluorine in H_2SO_4 solution [22].

In this work we optimize the amount fluorine in RGO to obtain graphene-based high performance metal-free ORR electrocatalysts with fluorine to obtain the better ratio of fluorine doped RGO and also better price/performance ratio than any other ORR electrocatalysts.

2. Experimental

2.1. Synthesis of reduced graphene oxide (RGO)

For the electrochemical exfoliation reaction, a DC power supply was used to allow output voltages of up to ±5V. For our purpose, a Pt wire was used as counter- electrode and a piece of graphite rod was inserted as anode working electrode. The ionic liquid (IL) Urea choline chloride/water solution was used to carry out the exfoliation process as previously reported by our groups [22,23]. An effective area of 1cm² of the graphite rod was in direct contact with the IL. The electrochemical process was performed at +5V. During the reaction, graphite flakes peeled off from the working electrode until the area in contact with the IL was consumed (∼55 min). The electrochemical exfoliation products were washed with water and surfactant until the pH was neutral and the products were separated by filter and ultra-centrifugation at 10,000 rmp at 25 °C [23].

2.2. Synthesis of fluorinated reduced graphene oxide (FRGO)

Different Fluorine- containing solutions were prepared by slowly adding one of the reactant 0.1, 0.2, 0.3 or 0.4 M equivalent amount of NaF into 15 mL of 10 M H_2SO_4 in a 30 mL glass bottle. In a typical preparation of F-RGO, 2.0 mg of RGO was introduced into the fluorine-containing acid solution and dispersed in an ultrasonic bath for 30 min. with the bottle capped, the solution was stirred at ambient temperature overnight. The modified RGO was then filtered and washed with water and ethanol [22,24]. The resulting composite structures were then dried at 40 °C for 2 h and denoted as F_IRGO, F_{II}RGO, F_{III}RGO and F_{IV}RGO (I, II, III and IV are related to the 0.05, 0.1, 0.2 or 0.3 M of NaF).

2.3. Fabrication of gas diffusion electrodes (GDEs)

GDEs consisted of a backing layer, a gas diffusion layer and a catalyst layer. The three-layer for GDE was fabricated by casting of 60 wt.% active carbon vulcan XC-72 slurry and 40 wt.% PTFE on a TGP-090H carbon paper (Electrochem) as reported in the earlier article [25]. The catalyst layer was prepared according to the above procedure in Section 2.2 and pasted on the diffusion layer. The catalyst layer prepared from a blend of one of the graphene materials RGO, F_IRGO, F_{II}RGO, F_{III}RGO and F_{IV}RGO with Catalyst loading of 0.8 mg cm^{-2} and 10% of Nafion solution (5%).

3. Results and discussion

The structural characterization and the electrochemical properties of the electro-catalysts were carried out using microscopic and spectroscopic techniques. Fig. 1 shows a representative SEM image of RGO nanosheets and F_x-doped RGO coating on carbon paper substrate. SEM images of the RGO sample reveals a rather flat morphology for RGO and an exfoliated morphology (Fig. 1a). From the SEM image shown in Fig. 1b–e, it can be seen that F_XRGO is constructed by randomly stacked graphene nanosheets and shows an interconnected 3D. Porous structure with the pore diameter in the range of half micrometer and highly wrinkled and corrugated surface. The TEM image of F_XRGO in Fig. 1f–h exhibits two dimensional ultrathin and flexible crumpled graphene nanosheets aggregate and overlap with each other, which is totally different from the original flat and smooth RGO nanosheets (Fig. 1a) and is more crumpled and wrinkled than RGO.

The EDX spectrum (Fig. 2) shows the presence and of each element (C, O) and (C, O, F,) in RGO and FxRGO samples and confirming the uniform incorporation of fluorine atoms in graphene sheets.

The structures of FxRGO were investigated by FT-IR spectroscopy, as shown in Fig. 3. The carbonyl stretching mode of C=C at 1625 cm^{-1}, the carbonyl stretching mode of —C=O at 1670 cm^{-1}, and the O—H stretching mode at 3435 cm^{-1} are observed in the spectrum of RGO.

In the spectra of FxRGO prepared in the presence of in the absence of NaF and H_2SO_4 solution, two specific absorption peaks at 1206 cm^{-1} and 1185 cm^{-1} are observed, which are assigned to the covalent C—F bonds and C—H bonds, respectively.

Detailed structural information of FxRGO and RGO was further studied by XRD spectroscopy measurement. The XRD pattern of