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Pyridine-functionalized graphene oxide, an efficient metal free electrocatalyst for oxygen reduction reaction

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ABSTRACT

Here, a novel approach for the preparation of pyridine functionalized graphene nanosheets (Py-EGO) is developed. Using a simple thermal treatment, pyridine was linked to reduced graphene oxide using epoxy group or hydroxyl group that existing at a surface of the graphene. The electrochemical behavior of Py-EGO for the reduction of oxygen was studied. The results showed that the new nanocomposite has a powerful potential as an electrocatalyst for oxygen reduction reaction (ORR) especially compare to N-doped graphene oxide, in alkaline solution. In addition, the Py-EGO electrocatalyst exhibited tolerance to methanol crossover effect. The results of our studies indicate that Py-EGO has a better durability, much higher selectivity, much better electrochemical stability and high catalytic activity towards the ORR than that of commercial Pt/C electrocatalyst. The Pt-free electrocatalyst improves catalytic activity and reduce the cost of electrocatalyst for ORR. The proposed simple method for synthesize Py-EGO electrocatalyst promising its further application in fuel cells.

1. Introduction

Increasing demands for clean energy has stimulated extensive research on the development of technologies those can effectively convert chemical energy into electricity at low cost and with high efficiency. In oxygen reduction reaction (ORR) slow cathodic kinetic and the demands of the complex 4-electron ORR pathway pose major barriers to reduce the Pt loading to fabricate electrocatalyst. Besides, degradation of the electrocatalyst caused, e.g., by poisoning, particle detachment, agglomeration and/or carbon corrosion also needs to be tackled to obtain reliable systems. On the other hand, catalysts for ORR are at the heart of key electrochemical technologies for direct methanol fuel cells and polymer electrolyte membrane fuel cells [1–5].

Recently, consideration effort has been devoted to explore Pt-free and even metal-free catalysts to improve catalytic activity and reduce cost of electrocatalysts [6–8]. Doped carbon and particularly N-doped carbon has attracted increasing attention as a promising metal-free electrocatalyst for ORR due to its excellent electrocatalytic performance and low cost. Recent studies have showed that different carbon materials including mono-doped or co-doped by nonmetallic heteroatoms such as N, S, P and I, have electrocatalytic activity compare to Pt and exhibit superior selectivity and durability [9–12]. One of effective method to modify materials, such as change in electronic properties and improve surface chemistry, is chemical doping of them with foreign atoms [13–15]. For the N-doped carbon, some researchers have explained that the metallic-like catalytic property results from the increase in electron density at the Fermi level, allowing the electrons to reach the conduction band [8].

Graphene with its unique specific surface area, good thermal, mechanical and chemical properties [10] has shown its interesting applications in methanol and proton exchange membrane fuel cells. Graphene acts as an electron mediator, provides numerous reaction sites and induces the adsorption of pollutants via $\pi-\pi$ interactions [16]. Ionic liquids (ILs) functionalized graphene sheets have been synthesized in various solvents, with good dispersibility and long-term stability. Based on previous studies, use of ILs can increase intrinsic activity of ORR electrocatalysts about 2 to 3 times higher intrinsic activity *vs.* ORR electrocatalysts without IL [17,18].

Herein, we report a successful fabrication of pyridine functionalized reduced graphene oxide (ionic liquid functionalize exfoliated graphene oxide), Py-EGO, as a powerful electrocatalyst for oxygen reduction reaction. The synthesized catalyst exhibited high electrocatalytic activity toward ORR at lower overpotential with improved current density in comparison with N-doped graphene oxide. The Py-EGO showed a close onset potential, limiting current density and half-wave potential *vs.* Pt-rGO catalyst. In addition, the Py-EGO electrocatalyst also exhibited tolerance to methanol

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crossover effect. The simple method to synthesize Py-EGO electrocatalyst promising its further application in fuel cells.

2. Experimental

2.1. Reagents and apparatus

Graphite, KOH, H_2SO_4, KNO_3, $KMnO_4$, K_2PtCl_6, commercial Pt/C and H_2O_2 solution (33%) were purchased from Merck. KOH solution (0.1 mol L^{-1}) was prepared from KOH.

The synthetic materials were characterized by Transmission Electron Microscopy (using a Philips CM120), Field Emission Scanning Electron Microscopy and energy-dispersive X-ray spectroscopy (EDS) (were made on a Philips XL-30 at an accelerating voltage of 20 kV), Atomic Force Microscopy images (operating in contact mode) were prepared in Bruker Nanosinstrument AFM (Germany). X-ray diffraction spectra were prepared on a Bruker D8/Advance X-ray diffractometer (using Cu-Ka radiation). Moreover, X-ray photoelectron spectroscopy (XPS) measurements were performed using an ultra-high vacuum (UHV) set-up equipped with the concentric hemispherical analyzer. XR3E2 X-ray source was used as incident radiation. JASCO FT-IR (680 plus) spectrometer was used to record the Infrared spectra, using KBr pellets were used to characterize EGO.

A potentiostat/galvanostat (Model PGSTAT-30, Eco-Chemie, the Netherlands) controlled by the GPES software, with a three-electrode system, was used to characterize the electrochemical properties of the electrocatalysts. A glassy carbon-wire (as the counter electrode) and an Ag/AgCl electrode ($KCl_{sat'd}$) were used and a reference electrode. For perpetration of the working electrode, Py-EGO, rNGO, rGO, Pt-rGO and Pt/C electrocatalysts ink were prepared by dispersing the electrocatalysts powder (2.0 mg) into 1.0 mL of double distillate water (2.0 mg mL^{-1}) using an ultrasonic bath at least 30 min. Then, 20 μL of each of the

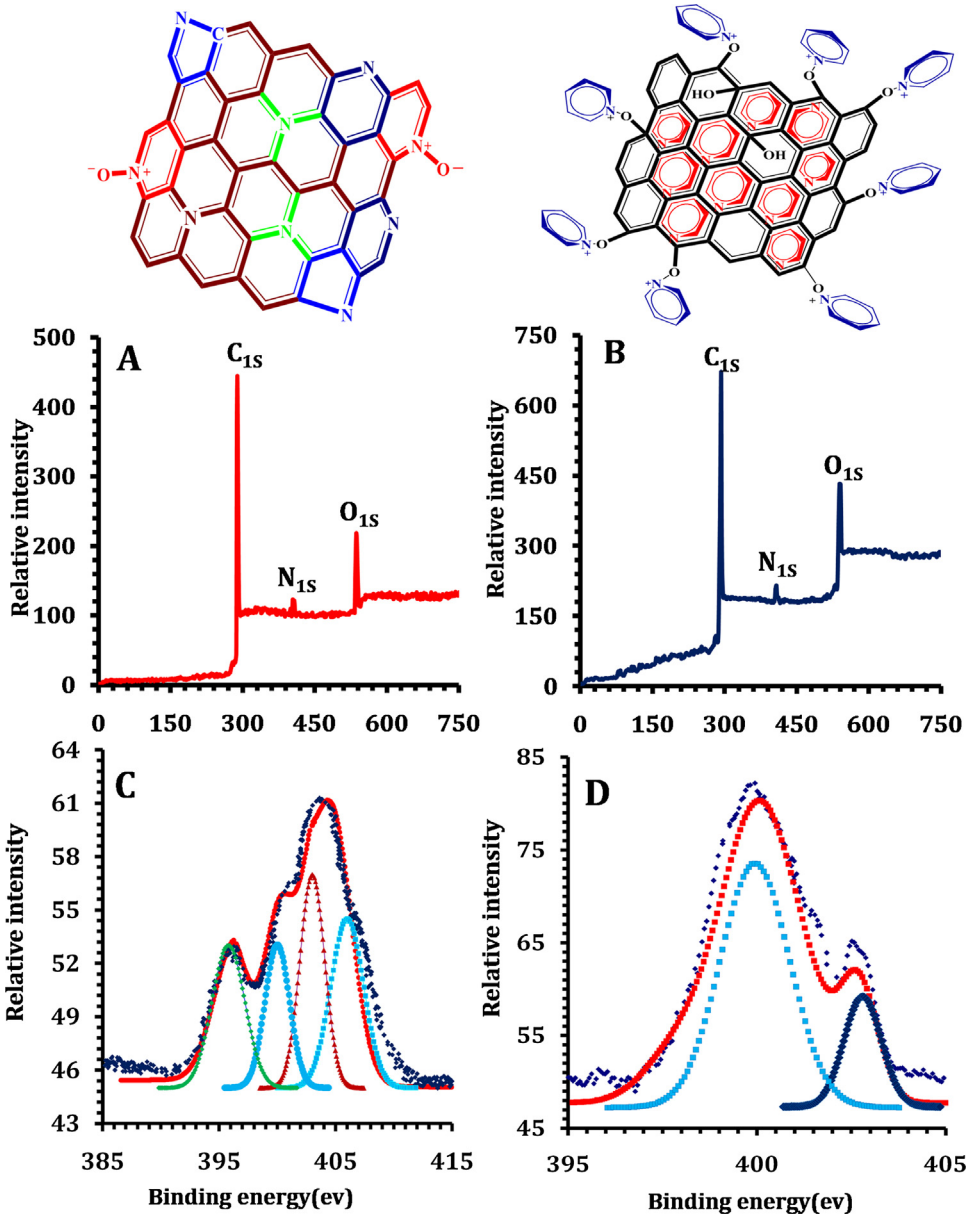

Fig. 1. Survey XPS data for A): rNGO, B): Py-EGO; High resolution XPS spectra of N 1s for C): rNGO, and D): Py-EGO.