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Amide-functionalized graphene with 1,4-diaminobutane as efficient metal-free and porous electrocatalyst for oxygen reduction

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ABSTRACT

A porous graphene catalyst was prepared with 1,4-diaminobutane (DAB) through amide functionalization and was used as a metal-free electrocatalyst for oxygen reduction reaction (ORR) in alkaline fuel cells. DAB was used as a junction among functionalized graphene layers to impart electrocatalytic activity for the ORR resultant from the interlayer charge transfer. The successful amidation and subsequent reduction in the process of catalyst preparation were confirmed using X-ray photoelectron spectroscopy. A hierarchical porous structure was also confirmed through the surface morphological analysis. The Brunauer–Emmett–Teller specific surface area and thermal stability increased by 2.6- and 1.5-fold, respectively, after successful amide functionalization. The as-prepared catalyst was proved an efficient metal-free electrocatalyst with better electrocatalytic activity, stability, and tolerance to the crossover effect than commercially available Pt/C for ORR by a direct four-electron involved pathway. These results indicate that the amide-functionalized graphene metal-free catalyst reported in this study is a promising alternative to traditional noble metal-based ORR catalysts.

1. Introduction

Considerable effort has been focused on the search for sustainable and renewable sources of green and clean energy because of the increasing demands and environmental impact of traditional energy resources such as fossil fuels [1,2]. Fuel cells (FCs) attracted significant attention as the next-generation energy sources because of their superior energy conversion efficiency and potential to provide clean energy [3,4]. FCs directly generate electricity by electrochemically reducing oxygen and by oxidizing fuel into water as the only by-product. The direct oxygen reduction reaction (ORR) [4,5] catalysis involving four electrons is an interesting research area; it has already attracted the attention of researchers worldwide because of its important role in the application of energy storage and conversion devices such as FCs and metal–air batteries in alkaline media [1–7]. However, the sluggish kinetic rate of ORR at the cathode is the main challenge for the large-scale commercialization of FCs [8]. Novel metals such as platinum (Pt) and its alloy materials have been regarded as the most efficient electrocatalysts for ORR in the cathodes [9–12]. Nevertheless, Pt-based materials are susceptible to the crossover effect caused by the diffusion of fuel molecules from the anode through the membrane to the cathode in FCs [8], CO poisoning [13,14], and poor durability [15]. The cost reduction of FCs is greatly hampered by the high cost and limited supply of Pt [16]. However, significant effort has been focused on the development of alternatives, including nonprecious metal or metal-free carbon nanomaterial-based ORR catalysts, to overcome the aforementioned challenges [5,8,17–22]. Thus, efforts should be exerted to identify alternative catalysts that are readily available and cost effective as well as have comparable or even better catalytic effects than Pt for cathodic ORR in FCs.

Graphene oxide (GO) [23] is the oxidized and exfoliated sheet of sp^2-hybridized graphene that carries various oxygenated groups such as epoxide, hydroxyl, carbonyl, and carboxyl. Among all the oxygenated groups, the carboxyl group is the most suitable site for reacting with the amine group to form an amide bond by a condensation reaction [24–27]. However, graphene itself possesses zero band gap, thereby posing as a considerable barrier for digital electronic device applications such as semiconductors, sensors, and electrocatalysts [24]. Several approaches, including implanting heteroatoms (e.g., N atom) onto a graphene plane, have been applied to overcome the disadvantage [24,28,29]. The N atom is considered the best candidate among various heteroatoms (i.e., B, S, P, and O) for carbon substitution because it has five valence

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electrons that tend to form a strong interaction with carbon atoms.

In the graphene lattice, N doping/functionalization creates a net positive charge on the adjacent carbon atoms to facilitate ORR by changing the O_2 chemisorption mode and by attracting electrons promptly from the anode; this phenomenon has been proved through quantum mechanics calculations and subsequent experimental observations [5,8,14]. Li Tao et al. [30] observed that the N atoms that induce charge polarization of carbon atoms may significantly contribute to the improved ORR performance [14,31,32]. They also reported that the sp^3 carbon atom-rich graphene can provide efficient catalysis to ORR because of better charge polarization [30]. In addition, recent research activities have confirmed the preceding findings and have further proved that the important role of doping/functionalization-induced charge transfer has a significant influence on the development of various heteroatom-doped/functionalized graphene-based new metal-free ORR catalytic materials for FCs [5,8,19,33–34].

This study developed a hierarchical porous and amide-functionalized reduced GO (rGO) as a substantially efficient metal-free electrocatalyst for ORR with sp^3-hybridized 1,4-diaminobutane (DAB) (rGO–DAB). This approach is employed, for first time to prepare a new class of amide-linked graphene-based ORR catalysts. The physical characterization verified the following merits of the as-obtained rGO–DAB. First, the rGO–DAB is a hierarchical porous material and has a high surface area. Second, rGO–DAB is thermally stable probably because of amide functionalization and layer-by-layer arrangement. Third, the sp^3-hybridized DAB is used as a junction among functionalized rGO layers to impart electrocatalytic activity for the ORR [30] resultant from the interlayer charge transfer [35]. Importantly, the net positive charge caused by the N atoms in the catalyst can provide an ideal model to focus on the contribution of the adjacent carbon atoms during the ORR electrocatalysis. Fourth, as expected, the rGO–DAB showed a superior electrocatalytic activity, stability, and tolerance to the crossover effect than the commercially available Pt/C for ORR as a metal-free electrocatalyst.

2. Experimental

2.1. Synthesis of amide-functionalized rGO–DAB

GO was prepared from graphite powder (Alderich, 325 mesh, 99.999%) by the modified Hummer's method [13,36,37]. Fig. 1 shows that for the GO–COOH preparation with a modified procedure [27], briefly, 50 mg GO and 25 mL of water were loaded into a 100-mL round bottom flask. A yellow-brown homogeneous solution was prepared by ultrasonic agitation until it became clear with no visible large particulate. Thereafter, 2.5 g of chloroacetic acid ($ClCH_2COOH$, Aldrich, Korea) and 3.2 g of NaOH were added into the aforementioned solution; this solution was maintained under stirring for 3 h at room temperature (RT, ~25 °C). Thereafter, 2.7 mL of HCl was added to the solution to neutralize NaOH, and filtered and washed with water for four times. A homogeneous suspension was produced by 30 min sonication in 10 ml of phosphate buffered saline (PBS, at pH 5.5) by adding 40 mg 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC, Aldrich, Korea) to activate rGO–DAB. Subsequently 40 mg of GO–COOH and 150 mg of N-hydroxysuccinimide (NHS, Aldrich, Korea) were added. A total of 80 mg DAB was added into the aforementioned suspension and maintained under 3 h sonication. For the final step, 80 mg of $NaBH_4$ was added and refluxed at 55 °C overnight. The as-obtained rGO–DAB was filtered, washed several times with distilled water, and dried under vacuum at 40 °C for 12 h. For comparison, rGO was prepared without the addition of DAB.

2.2. Physical characterization

Transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDX) were obtained using the TECNAI model FI-20 (FEI, The Netherlands). The scanning electron microscope (SEM) images were obtained on a JSM-7500F field emission scanning electron microanalyzer (JEOL). Raman spectra were obtained with a LabRam HR800 UV Raman microscope (Horiba Jobin-Yvon, France), with an excitation of 514 nm Ar^+ laser. The Brunauer–Emmett–Teller (BET) surface area and the pore size distribution were obtained through the Barrett–Joyner–Halenda (BJH) method using the adsorption and desorption of the nitrogen isotherm (BelsorpII mini, BEL Japan Inc.). X-ray photoelectron spectroscopic (XPS) images were obtained using a MultiLab 2000 with a 14.9 keV Al K X-ray source. Curve fitting was conducted using an XPSPEAK41 system software. The thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere with a TGA-50 Thermogravimetric Analyzer (Shimadzu, Japan) at a heating rate of 20 °C/min.

2.3. Electrochemical characterization

The 1 mg mL^{-1} suspension of rGO–DAB was prepared in water by ultrasonication. A 10-μL portion of rGO–DAB ink was dropped onto the prepolished glassy carbon electrode (GCE). The GO–COOH– and rGO-coated GCEs were prepared by following the same protocol. The commercially available Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72) suspension was prepared by dispersing 1 mg mL^{-1} of Pt/C in ethanol in the presence of 5 μL of 5% Nafion solution (in alcohol), and 28.3 μg cm^{-2} of Pt was loaded onto a GCE. All electrochemical measurements, including cyclic voltammetry (CV) and chronoamperometry (CA), were obtained using a three-electrode potentiostat (CHI 700C electrochemical workstation

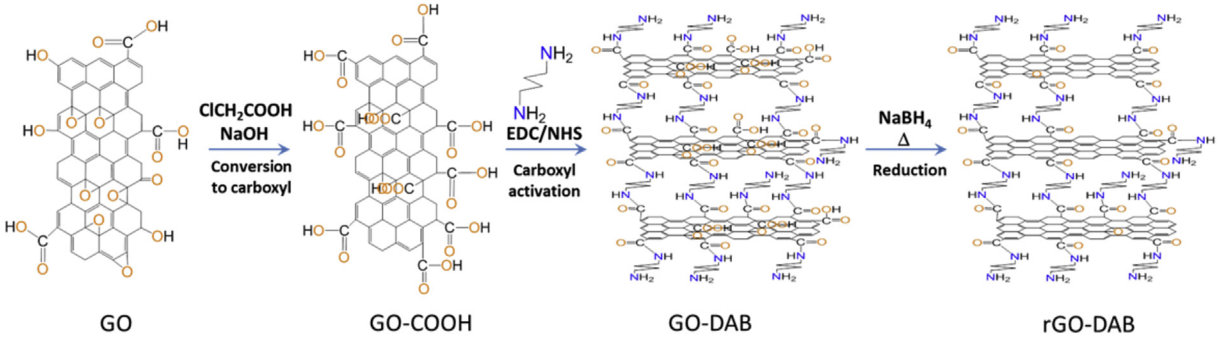

Fig. 1. The schematic diagram of rGO–DAB synthesis. (A colour version of this figure can be viewed online.)