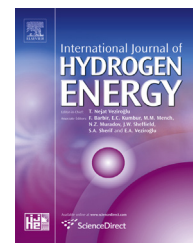


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Facile synthesis of graphene/N-doped carbon nanowire composites as an effective electrocatalyst for the oxygen reduction reaction

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ABSTRACT

A novel metal-free electrocatalyst for the oxygen reduction reaction (ORR) is one of the most important issues in fuel cells. Here, we report a facile method to synthesize reduced graphene oxide (rGO) decorated with nitrogen-doped carbon nanowires (rGO-CN) as an electrocatalyst for ORR. After the polymerization of polypyrrole nanowires on the rGO surface (rGO-PPy), the carbonization of rGO-PPy at 800 °C affords a unique nanostructured product by the integration of rGO sheets and the N-doped carbon nanowires with high nitrogen content. The morphology of rGO-CN is confirmed by TEM analysis and the chemical composition and interaction of the prepared samples are analyzed by XPS and FT-IR analysis. The electrocatalytic activity of rGO-CN toward ORR is also evaluated by the cyclic voltammetry. It is found that the rGO-CN electrode shows superior electrocatalytic performance toward ORR, compared to rGO and rGO-PPy, which demonstrates the promising potential of rGO-CN as a carbon-based, metal-free electrocatalyst for enhancing the electrocatalytic property towards ORR.

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Introduction

Fuel cells are considered a potential power source for future vehicles and stationary applications due to their high efficiency, high power density, and clean energy. The performance of fuel cells is largely limited by the sluggish oxygen reduction reaction (ORR), which substantially depends on the activity of the cathode catalyst. Platinum (Pt) and its alloys have long been recognized as the best electrocatalyst for ORR in fuel cells [1]. However, high cost due to the scarcity of Pt and

its insufficient durability limited the mass production and commercialization of electrocatalysts. Thus, considerable effort has been devoted to developing highly stable and cost effective non-precious metal or metal-free electrocatalysts with improved catalytic efficiency for ORR [2,3]. Recently, carbon nanomaterials and their composite materials have been intensively studied for replacing or reducing Pt based materials in fuel cell applications [4,5]. Among them, heteroatom-doped carbon materials for ORR have also been extensively investigated to reduce the cost and enhance the durability of fuel cells [4].

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Graphene, a one-atom-thick layer of graphite, packed into a two-dimensional network of sp^2 -hybridized carbon, is distinct from other types of carbon materials due to its outstanding thermal, mechanical and electrical properties [6,7]. Since graphene recently served as a worthy support material for anchoring metal/metal oxide nanoparticles and functional nanomaterials [8,9], graphene-based functional composites have been explored as ORR electrocatalysts because of the feasible synergetic effects with enhanced catalytic activity [10,11]. To date, doped graphene with various heteroatoms, such as sulfur (S), nitrogen (N), boron (B), and phosphorous (P), has attracted intense attention due to its reportedly high catalytic activity, high long-term durability and tolerance to poisoning as a metal-free ORR electrocatalyst [12–16]. For example, N-doped graphene, generally consisting of pyridinic N, pyrrole N and graphitic N atoms, has been widely studied as an electrocatalyst for fuel cells, due to its considerable electrochemical activity of ORR with an excellent durability [15,17]. However, its electrochemical activity is strongly affected by N atom content, the limited N content of 2–5% in N-doped graphene still revealed lower catalytic activity compared to Pt-based catalysts [18]. To utilize the outstanding properties of graphene and improve the catalytic efficiency towards ORR, the efficient nanostructure design of graphene-based composites with high content of C–N functional groups is of great interest [19–22].

Herein, we report the facile synthesis of graphene decorated with N-doped carbon nanowires as an efficient ORR electrocatalyst. The proposed method here involves the formation of polypyrrole (PPy) nanowires decorated on reduced graphene oxide (rGO-PPy) by *in situ* polymerization of pyrrole monomer in the presence of rGO. Subsequently, the synthesized rGO-PPy is annealed at 800 °C in an argon atmosphere to afford the N-doped carbon nanowires decorated on rGO (rGO-CN) by the carbonization of PPy nanowires. The unique nanostructure of graphene sheets decorated with conductive N-doped carbon wires provides high nitrogen content and high surface area for large amount oxygen access, which improves the electron transfer efficiency and the electrocatalytic activity.

Experimental

Synthesis of rGO-CN

First, graphene oxide (GO) was prepared by chemical exfoliation of the expanded graphite powder (grade 1721, Asbury Carbon) through a modified Hummers method by the microwave-assisted thermal expansion of graphite powder using the procedure described elsewhere [23]. The obtained GO powder was dispersed in deionized (DI) water for the GO aqueous solution with a concentration of 3.0 mg/ml. The GO solution was then treated with hydrazine hydrate (5 mL) at 40 °C for 24 h to obtain rGO. After reduction, rGO was filtered and washed several times with DI water and dried in a vacuum oven. The prepared rGO were redispersed in DMF for rGO solution with a concentration 0.5 mg/ml.

To synthesize PPy nanowires on rGO (rGO-PPy), *in situ* polymerization was performed in the presence of rGO using

pyrrole monomer (0.01 M), ferric *p*-toluene sulfonate (0.02 M) as an oxidizing agent and 1% polyvinyl pyrrolidone (PVP) as a surfactant at room temperature for 5 h. Then, the resultant composites were washed with ethanol and DI water several times and dried at 60 °C in a vacuum oven. The dried rGO-PPy sample was annealed at 800 °C under argon atmosphere for 1 h, resulting in rGO-CN by the carbonization of PPy nanowires.

Characterizations

The morphology of the samples was characterized using a field-emission scanning electron microscope (FE-SEM, JEOL, JSM-6500F) and a high resolution transmission electron microscope (HR-TEM, Hitachi, H-8100). X-ray diffraction (XRD) analysis was performed on a Rigaku X-ray diffractometer with Cu K α radiation. The chemical compositions of the prepared samples were analyzed using an X-ray photoelectron spectrometer (XPS, Thermo scientific) with monochromatic Al K α radiation with $h\nu = 1486.6$ eV. Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet IR 200 FT-IR spectrometer (Thermo Scientific). Raman spectra (DXR Raman spectrophotometer, Thermo Scientific) were obtained using 532 nm laser excitation.

Electrochemical measurements

Electrochemical measurements of the prepared samples were performed on a multi-channel potentiostat-galvanostat analyzer (VSP, Bio-logic) with a three-electrode system at room temperature, in which Pt wire was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. As the working electrode, the electroactive materials in ethanol (1 mg/ml) and Nafion in isopropyl alcohol solution (0.5 wt%) as binder were mixed by sonication. Then, 5 μ l of this mixture was coated on a glassy-carbon rotating disk electrode (RDE) and dried in air for the electrochemical characterizations. The electrochemical measurements using the modified glassy-carbon electrode were carried out in the O₂-purged 0.1 M KOH electrolyte solution at room temperature. The number of electrons transferred per oxygen molecule in the ORR process was determined by the Koutecky–Levich (K–L) equation given below:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}}$$

where j_k is the kinetic current density and ω is the angular velocity of the electrode. B could be determined from the slope of the K–L plots based on the following Levich equation:

$$B = 0.2 n F (D_{O_2})^{\frac{2}{3}} \nu^{-\frac{1}{6}} C_{O_2}$$

where n is the number of electrons transferred per oxygen molecule, F is the Faraday constant (96485 C mol^{−1}), D_{O_2} is the diffusion coefficient of O₂ in 0.1 M KOH (1.9 $\times 10^{-5}$ cm² s^{−1}), ν is the kinetic viscosity (1.0 $\times 10^{-2}$ cm² s^{−1}) and C_{O_2} is the bulk concentration of O₂ in 0.1 M KOH (1.2 $\times 10^{-6}$ mol cm^{−3}) [24,25].

Results and discussion

A schematic illustration of the fabrication process of the rGO-CN is shown in Fig. 1. In a typical procedure, after rGO was

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