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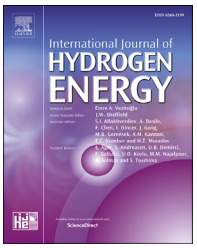

Thermal treated 3D graphene as a highly efficient metal-free electrocatalyst toward oxygen reduction reaction

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ABSTRACT

Thermal treated 3D graphene materials are developed as a highly efficient metal-free electrocatalyst toward oxygen reduction reaction (ORR). Electrochemical analysis reveals that the as-prepared sample shows comparable catalytic activity, better tolerance to methanol crossover effect as well as higher stability than those of commercial Pt/C. For the first time, we find that C=O bonds on 3D graphene display a vital role in catalytic kinetics toward ORR, of which the C=O bonds might influence the adsorption type between oxygen molecule and catalytic active sites on graphene surface. Meanwhile, the unique porous structure of 3D graphene materials are able to trap oxygen molecules, contributing to decrease in diffusion resistance while enhance electrolyte-electrode accessibility for fast mass transport. This work offers a highly efficient metal-free ORR catalyst obtained by a universal approach, and the prepared 3D graphene materials could be further utilized in other energy conversion/storage fields.

Introduction

The research and development of sustainable energy conversion and storage technologies have attracted a great deal of interest owing to the exhausting conventional fossil fuels [1–3]. Fundamentally, the performance of those systems is closely related to the material properties and various materials that can directly convert or store renewable energies are being extensively studied [4,5]. Carbon materials are of great interest owing to their high conductivity, environmental acceptability and corrosion resistance [6–8], making them extremely attractive as electrode materials in electrochemical energy devices [9–12]. Graphene consists of a flat monolayer of sp2 bonded carbon atoms into a two-dimensional honey comb lattice discovered in 2004 for the

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first time by Geim and co-workers [13,14]. In recent years, it has attracted tremendous attention due to the large surface areas, superior electrical conductivity, high mechanical, thermal and chemical stability [15,16]. This unique nanostructured material also obtained widespread applications in many technological fields such as nanoelectronics, sensors, nanocomposites, batteries, supercapacitors and hydrogen storage [17–20]. It is believed that 3D graphene materials which are composed of cross-linked graphene nanosheets, have great potential towards these applications [21]. Our group demonstrated that the thermal treated hierarchical graphene materials significantly enhance hydrogen storage capacity [22], and the thermal treated 3D graphene materials are expected to have broad application in other energy conversion/storage systems.

Fuel cells, as a device for direct conversion of the chemical energy from fuel to electricity by electrochemical reactions, have brought the technology close to pre-commercial viability with high energy conversion efficiency, low emissions, and simplicity in device fabrication [23,24]. However, the commercialization of fuel cells are still hampered by the high cost, poor tolerance crossover effect and limited natural reserves of platinum (Pt) catalyst [25–27]. In this respect, a broad range of alternative catalysts based on nonprecious metal or metal oxides, macrocyclic complexes and conducting polymers have been developed [28–30], but the stability of those alternatives is often not as good as Pt. Recently, nitrogen-doping graphene based materials have been extensively studied [31,32]. Unfortunately, harsh conditions for doping graphene based materials result in high cost which limits their practical widespread application. Therefore, it is highly desirable to develop a universal method to produce large-scale catalysts with high electrocatalytic performance and long-time stability. Herein, thermal treated 3D graphene materials are developed as efficient metal-free catalyst toward ORR, exhibiting comparable catalytic activity and better tolerance to methanol crossover effect as well as long-term stability than those of commercial Pt/C.

Results and discussion

Characterization of materials

Typically, three-dimensional structure of 3DG-25, 3DG-200, 3DG-400 and 3DG-600 materials were observed in Fig. 1(a–d) with the pore sizes ranging from 30 to 100 nm, respectively. However, for 3DG-800 materials, it is hard to keep their original hierarchical and macroporous structure (Fig. 1e), suggesting that the skeleton of the 3D graphene materials collapsed due to thermal treatment under too high temperature. The SEM image of 3DG-600 materials in Fig. S1 proves that their hierarchical and macroporous structure could be kept in the preparation of catalyst ink. The transmission electron microscopy (TEM) image shown in Fig. 1f indicates that the 3DG-600 materials are made up of ultrathin sheets due to their transparent nature, and the Fig. 1f (inset) describes the photograph of 3D graphene materials which appears highly loose powder. Nevertheless, the HRTEM images of 3D graphene show that it is hard to tell the obvious changes of microstructure after various thermal treatments (Fig. S2).

The N_2 adsorption-desorption isotherms in Fig. 2a show that 3DG-800 has high specific surface area up to 893.4 $m^2\ g^{-1}$, which is larger than that of 3DG-25 (423.2 $m^2\ g^{-1}$), 3DG-200 (465.8 $m^2\ g^{-1}$), 3DG-400 (503.6 $m^2\ g^{-1}$) and 3DG-600 (581.9 $m^2\ g^{-1}$). Obviously, the specific surface area of thermal treated 3D graphene materials increase with the treated temperature enhanced from 20 °C to 800 °C and the pore size distribution of all the thermal treated 3D graphene materials pronounced mesoporosity centered at 4 nm (Fig. 2a inset). It is worthy of a note that the obtained 3DG-600 presents the highest specific surface area among the recent state-of-art carbon based catalysts such as CBLs (399.6 $m^2\ g^{-1}$) [33], g-C_3N_4/C (97.0 $m^2\ g^{-1}$) [34] and N-GNP$_3$ [35]. Combining with pores sizes ranging from 30 to 100 nm observed from SEM characterizations shown in Fig. 1d, the 3DG-600 materials indeed have a series of meso- and macropores, which potentially offer low resistance to fluid flow and ensure efficient mass transfer during the reaction process [21,36–39]. The Fig. 2b presents the FTIR patterns of various 3D graphene materials recorded in the range of 900–2400 cm^{-1}. The bandings at 1200 cm^{-1}, 1563 cm^{-1},1728 cm^{-1} are attributed to C–O, C–C, and C=O [40], respectively. Interestingly, the value of C=O peaks gradually disappears when the temperature up to 600 °C, which might due to the bonds were broken under the thermal treatment. The chemical status of elements was further investigated by X-ray photoelectron spectroscopy (XPS). Fig. S3a and Fig. 2c presents typical elemental composition of 3DG-25 and 3DG-600 materials, respectively. The high resolution spectrum C1s of 3DG-25 was deconvoluted into four peaks, i.e., C–C (284.6 eV), C–O (286.0 eV), C=O (287.4 eV) and O–C=O (288.6 eV) (Fig. S3b). While for 3DG-600 as in Fig. 2d, the high resolution spectrum C1s was deconvoluted into only two peaks, i.e., C–C (284.6 eV) and C–O (286.0 eV), and no obviously groups of C=O was detected. Those results concurs with the FTIR analysis as in Fig. 2b.

Electrochemical characterization

Electrochemical behaviors of the prepared different 3D graphene materials were investigated by cyclic voltammetry (CV) firstly. Fig. 3a showed that 3DG-600 electrocatalyst has obviously quasi rectangular shape in N_2 saturated 0.1 M KOH solution due to capacitor effect [33,41]. In contrast, a well-defined peak potential occurred at about −0.17 V (vs Hg/HgO) in the presence of O_2 saturated solution, indicating distinct ORR ability. Thermal treated 3D graphene materials under various temperatures were also tested and compared under the same conditions, and Fig. 3b told that the peak current density of 3DG-600 (1.03 mA/cm^{-2}) electrocatalyst was significantly higher than that of 3DG-25 (0.79 mA/cm^{-2}), 3DG-200 (0.81 mA/cm^{-2}), 3DG-400 (0.94 mA/cm^{-2}) and 3DG-800 (0.92 mA/cm^{-2}) under the same mass loading, demonstrating that the 3DG-600 had the most catalytic active sites towards ORR.

To further investigate the ORR catalytic activity of thermal treated 3D graphene materials, Liner potential sweep (LSV) curves were measured in O_2 saturated 0.1 M KOH solution at a very lows can rate of 0.5 mV s^{-1} in order to achieve a steady-

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