Applied Surface Science 393 (2017) 144–150

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Synergistic effect of Nitrogen-doped hierarchical porous carbon/graphene with enhanced catalytic performance for oxygen reduction reaction

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ARTICLE INFO

Article history:
Received 14 August 2016
Received in revised form
15 September 2016
Accepted 4 October 2016
Available online 5 October 2016

Keywords:
Oxygen reduction reaction
Waste biomass
N-HPC/RGO
Synergistic effect
Valuable functional products

ABSTRACT

Developing efficient and economical catalysts for the oxygen reduction reaction (ORR) is important to promote the commercialization of fuel cells. Here, we report a simple and environmentally friendly method to prepare nitrogen (N) –doped hierarchical porous carbon (HPC)/reduced graphene oxide (RGO) composites by reusing waste biomass (pomelo peel) coupled with graphene oxide (GO). This method is green, low-cost and without using any acid or alkali activator. The typical sample (N-HPC/RGO-1) contains 5.96 at.% nitrogen and larger BET surface area (1194 m^2/g). Electrochemical measurements show that N-HPC/RGO-1 exhibits not only a relatively positive onset potential and high current density, but also considerable methanol tolerance and long-term durability in alkaline media as well as in acidic media. The electron transfer number is close to 4, which means that it is mostly via a four-electron pathway toward ORR. The excellent catalytic performance of N-HPC/RGO-1 is due to the synergistic effect of the inherent interwoven network structure of HPC, the good electrical conductivity of RGO, and the heteroatom doping for the composite. More importantly, this work demonstrates a good example for turning discarded rubbish into valuable functional products and addresses the disposal issue of waste biomass simultaneously for environment clean.

1. Introduction

With the increase in global pollution and exhaustion of fossil fuel, to develop an energy supply with environmentally friendly, high energy density, and excellent sustainable performance is urgent [1,2]. Fuel cells (FCs) are one of the most appealing electrochemical energy conversion and storage devices by virtue of its low emissions and high energy conversion efficiencies [3–5]. And in FCs, the oxygen reduction reaction (ORR) in cathode plays a crucial role [6,7]. However, the high loading of Pt in electrodes caused by the sluggish kinetics of ORR has hindered the commercial development of the FCs [8–10]. According to earlier reports, precious metal [11], metal alloys [12], transition metal oxides [13,14], metal-nitrogen-carbon nanostructures [15,16], and metal-free carbon materials [3,17,18], have proven to be efficient catalysts toward ORR. And among the catalysts mentioned above, metal-free carbon materials due to their low-cost and environment friendly characteristics, were considered to scalable and economical materials to replace Pt. Therefore, intensive efforts have been committed to developing the metal-free catalysts for accelerating the large-scale application of FCs.

As an extensively available, renewable and entirely green carbon precursor, biomass derived carbon have caused the extensive concern of the researchers [19]. However, there are still some problems to overcome before the commercial application. The performance of most biomass derived carbon toward ORR remains lower than that of Pt/C catalysts [20–22]. And researchers have proved that biomass derived carbon carbonized at higher temperature (such as at or over 1000 °C) [23,24] or couple with transition metal [25,26] are effective methods to improve the electro-catalytic activity of biomass derived carbon close to Pt/C, which are not economical and green strategies for the large scale application of FCs.

RGO with large surface area and excellent electrical property is an ideal candidate as a catalyst supports material. Nevertheless, RGO itself does not exhibit satisfying performance toward ORR, which mainly due to the serious aggregate in the process

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http://dx.doi.org/10.1016/j.apsusc.2016.10.019
0169-4332/

of preparation [27]. In previous reports, different approaches have been designed for preparing a high performance catalyst based on graphene, for instance, graphene coupled with carbon nanotube [28], metal nanoparticles [29], metal oxide composites [10], etc. These nanocomposites not only prevent RGO from aggregation of RGO during the preparation, but also utilize the separate outstanding characteristics of the two substances at the same time, and take advantage of the synergy between them. Hence, preparation of a composite based on GO and low-cost material to overcome the shortcomings of each other, take full use of their strengths and exhibit efficient and durable catalysis toward ORR still remains a great challenge.

Pomelo peels as environmental waste are abundantly available and constantly renewable sources, which have not been effectively re-used and then became rubbish, polluted the environment. Lu and co-workers [30] successfully prepared fluorescent carbon nanoparticles (CPs) by using pomelo peels as carbon source and this CPs can act as probes for sensitive and selective detection of Hg^{2+} ions for the first time and the detection limit as low as 0.23 nM. This work inspired us that some functional materials can be prepared by using the waste biomass as carbon precursor. Here, a novel composite containing a highly active nitrogen-doped hierarchical porous carbon by employing the waste pomelo peel as biomass derived carbon precursors coupled with slight of GO was prepared by a facile strategy. This method was green, low-cost and without using any acid or alkali activator. The results exhibit that typical sample N-HPC/RGO-1 has efficient and steady catalysis toward ORR both in alkaline media and acidic media. This work displays a good example for turning waste into valuable products, and is very meaningful in low-cost development of new materials and environmental cleaning. And prepared composites may be used in other areas, such as lithium ion batteries, and so on.

2. Experimental section

2.1. Materials

Pomelo peel was recycled from a local market, washed with distilled water and then cut into pieces. Graphene Oxide (GO) was prepared via a modified Hummers' method [31]. NH_3 (99.9%) was purchased from Shang Yuan Company (Nanjing, P.R. China). Methanol (CH_3OH), ethanol (C_2H_5OH), potassium hydroxide (KOH) and concentrated sulphuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, P.R. China). All reagents are analytically pure and without further purification.

2.2. Synthesis of N-HPC/RGO

As illustrated in Scheme 1, 4 g of pomelo peel and different volume of GO solution (4 mg/mL) mixed with 30 mL of distilled water were placed into a 50 mL Teflon-lined autoclave, then heated at 180 °C for 12 h. After freeze-dried for 2 days, the samples were placed in the furnace and carbonized at 900 °C in NH_3 atmosphere. The obtained products were marked as N-HPC/RGO-X, where X stands for the volume of GO solution (0.5 mL, 1 mL, 1.5 mL, 2 mL, respectively). Control sample N-HPC and RGO were also synthesized according to the method mentioned above without adding the GO solutions and pomelo peel, respectively.

2.3. Characterization

The phase analysis of the as-synthesized products was carried out using X-ray diffraction (XRD, DX-2700) with Cu-Kα radiation (λ = 1.54 Å). The morphologies of samples were examined by field emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan). Transmission electron microscopy (TEM) images were obtained using a JEM-2100 instrument. BET surface area was gotten on a TrstarII3020 analyzer. Raman spectra were performed on a focusing Raman spectrometer (Renishaw inVia) with a 532 nm laser excitation. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an X-ray photoelectron spectrometer (ESCALAB 250Xi).

2.4. Electrochemical measurements

For electrochemical measurements, 10.0 mg of the product was dispersed in the 5.0 mL of ethanol solution and sonicated to form homogeneous ink. 10 μL of the ink was dropped onto the glass carbon (GC) disk electrode and adhered by using Nafion solution (10 μL, 0.05 wt%). The electrochemical measurements were performed on a typical three-electrode cell using CHI 852C electrochemical workstation in a Pine electrochemical system controlled at room temperature.

For rotating disk electrode (RDE) tests, a GC disk with a diameter of 5 mm served as the substrate for the working electrode, and the counter electrode was platinum wire. Hg/HgO and Ag/AgCl was used as a reference electrode in alkaline and acidic media, respectively.

For rotating ring-disk electrode (RRDE) tests, a GC disk with a diameter of 5.61 mm surrounded by Pt ring served as the substrate for the working electrode. A platinum wire and an Hg/HgO electrode were applied as counter and reference electrodes, respectively. The electron transfer numbers (n) and peroxide yield (% H_2O_2) can be obtained from the RRDE curve using the Eqs. (1) and (2), respectively [7,32].

$$n = 4 \times \frac{I_d}{I_d + I_r/N} \quad (1)$$

$$\%H_2O_2 = 200 \times \frac{I_r/N}{I_d + I_r/N} \quad (2)$$

where I_r is the ring current, I_d the disk current, and N is the current collection efficiency of the Pt ring (N = 0.37).

3. Results and discussion

The XRD patterns of the N-HPC and N-HPC/RGO-X (X = 0.5, 1, 1.5, 2) are presented in Fig. 1a. A broad band located around 23° can be clearly observed, indicating that the amorphous nature of carbon with disordered nanocrystalline structures in these catalysts [26,32]. The other peak about 44° for these catalysts is indicative of small domains of ordered graphene sheets [33]. Fig. 1b shows the Raman spectra of N-HPC, N-HPC/RGO-X (X = 0.5, 1, 1.5, 2). Two strong carbon characteristic peaks are observed approximately at 1342 cm^{-1} and 1594 cm^{-1}, which are ascribed to the defects and disordered structures (D band) and sp^2-hybridized graphitic carbon atoms (G band) respectively [9]. The intensity ratio of D peak to G peak (I_D/I_G) is a commonly used to estimate the degree of defects and disordered structures [34]. The I_D/I_G ratios increased gradually from 0.927 for N-HPC to 0.970 for N-HPC/RGO-2, with different initial volume (X) of GO solution in N-HPC/RGO preparation. The result indicates that the biomass derived carbon successfully coupled with GO during the hydrothermal treatment. The nitrogen adsorption and desorption isotherms of the samples are shown in Fig. 1c and Fig. S1 (see Supporting information). Among these samples, N-HPC/RGO-1 exhibits the highest surface area (1194 m^2/g) compared with N-HPC (972 m^2/g) and the other composites (1139 m^2/g, 947 m^2/g and 774 m^2/g for N-HPC/RGO-0.5, N-HPC/RGO-1.5 and N-HPC/RGO-2, respectively). The reason for this is that when the volume of GO solution was no more than 1 mL (the mass ratio of pomelo peel to GO is 1:1, g/mg), the RGO sheets can distribute on the composite uniformly, and by virtue of RGO's large surface area,