Journal of Colloid and Interface Science 488 (2017) 317–321

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

Regular Article

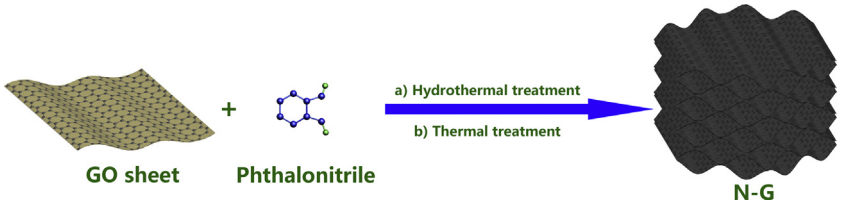
Hierarchically porous nitrogen-doped graphene aerogels as efficient metal-free oxygen reduction catalysts

Zongsheng Hou [a,1], Yeqing Jin [b,1], Xin Xi [b], Tao Huang [a], Dongqing Wu [a,*], Peimin Xu [b], Ruili Liu [c,*]

[a] School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Dongchuan Road 800, 200240 Shanghai, PR China
[b] Department of Chemical Engineering, School of Environment and Chemical Engineering, Shanghai University, Shangda Road 99, 200444 Shanghai, PR China
[c] National Engineering Lab for TFT-LCD Materials and Technologies, Department of Electronic Engineering, Shanghai Jiao Tong University, Dongchuan Road 800, 200240 Shanghai, PR China

GRAPHICAL ABSTRACT

Nitrogen-doped graphene aerogels with hierarchically porous architectures (N-Gs) are fabricated through the co-assembly of graphene oxide and *o*-phthalonitrile in a solvothermal process and the thermal treatment of the obtained composites at different temperatures. The structural characterizations indicate that both mesopores and macropores exist in the monolithic N-Gs. More importantly, the architectures, porosities and compositions show obvious dependence on the thermal treatment temperature. As the metal-free catalysts for oxygen reduction reaction in basic media, the sample thermally treated at 750 °C shows the best catalytic performances among the three N-Gs, which is owing to its advantages in the surface areas and content of active N species.



ARTICLE INFO

Article history:
Received 27 August 2016
Revised 2 November 2016
Accepted 2 November 2016
Available online 3 November 2016

Keywords:
Nitrogen-doping
Graphene aerogel
Oxygen reduction reaction
Metal-free catalyst

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1. Introduction

As the cathodic electrochemical process in fuel cells and metal-air batteries, oxygen reduction reaction (ORR) is of great importance in determining the performance of these energy conversion devices [1–4]. However, platinum (Pt) based electrocatalysts for ORR in present fuel cells have unavoidable disadvantages such as the high price and low nature abundance [5–7]. Moreover, the application of Pt catalysts has to confront the time-dependent drift and the deactivation caused by carbon monoxide, which severely limits the massive commercialization processes of fuel cells. Therefore, the development of novel ORR catalysts with low cost, high activity and good stability has become a hot topic for material sci-

* Corresponding authors.
E-mail addresses: wudongqing@sjtu.edu.cn (D. Wu), ruililiu@sjtu.edu.cn (R. Liu).
[1] These authors make equal contribution to this work.

http://dx.doi.org/10.1016/j.jcis.2016.11.008
0021-9797/

entists in the last few years [8–10]. Along with the research efforts in pursuing the substituent for Pt, a new class of metal-free ORR catalysts, which are majorly based on heteroatom-doped carbon materials, has received intensive attention since Dai's group found that vertically aligned nitrogen-doped carbon nanotube arrays manifested higher electrocatalytic activity and better long-term operational stability for ORR than commercially available Pt/C catalyst [11]. Besides their excellent electrocatalytic behaviors and easy accessibility, the metal-free ORR catalysts also exhibited good tolerance for methanol and carbon monoxide and outstanding durability, which thus made them appealing candidates to replace Pt in fuel cells and other relating energy conversion devices [12–19].

Among the metal-free ORR catalysts, nitrogen-doped graphene aerogels are highly attractive since they can provide three-dimensional (3D) graphitic scaffolds with interconnected macropores for the efficient transportation of charge carriers and the sufficient penetration of electrolytes. In the monolithic aerogels, the stacking of nitrogen-doped graphene sheets can also be avoided, thus allowing the fully exposure of their active sites for ORR. However, to obtain nitrogen-doped graphene aerogel with excellent ORR catalytic performance, the previously reported fabrication processes generally require either multiple steps or harsh conditions, which inevitably reduce the possibility of their practical applications [15,20–22]. In this work, a facile fabrication strategy toward hierarchically porous nitrogen-doped graphene aerogels (N-Gs) was developed via a co-assembly of graphene oxide (GO) and o-phthalonitrile and following thermal treatment of the resulting composites. The obtained monolithic N-Gs contain large amount of mesopores on the wall of the interconnected macropores, and such hierarchically porous structures can lead to high surface areas and pore volumes. As the metal-free catalysts toward ORR in alkaline electrolyte, the N-G composites manifest excellent electrochemical activity and much better durability in comparison with commercial Pt/C catalyst.

2. Results and discussion

The overall procedures for the fabrication of N-Gs are shown in Fig. 1. Firstly, GO and *o*-phthalonitrile were homogeneously

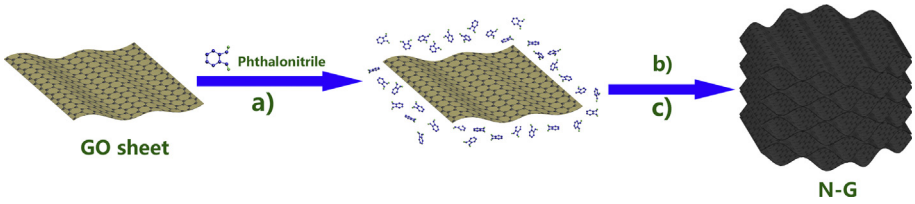

Fig. 1. Schematic illustration for the fabrication process of nitrogen-doped graphene aerogels. (a) Mixing GO with *o*-phthalonitrile; (b) Solvothermal treatment of the resulting mixture; (c) Thermal treatment of the composites from step (b).

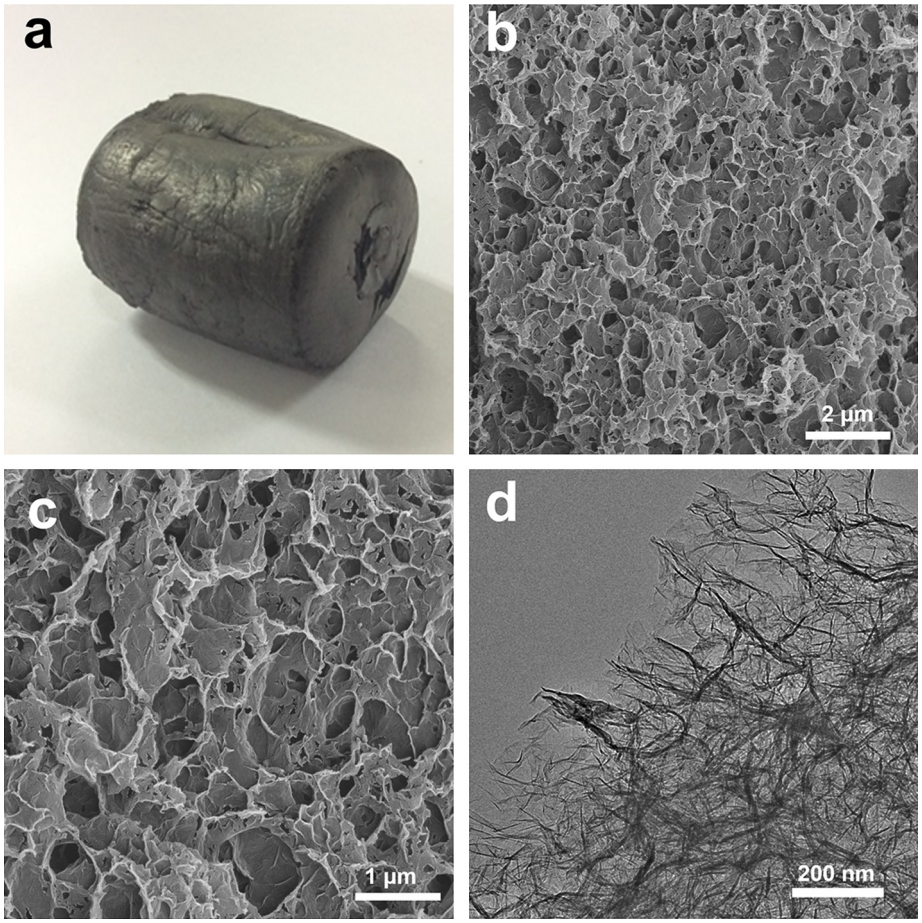

Fig. 2. (a) Digital photograph of N-G_{750}; (b) and (c) SEM images of N-G_{750}, (d) TEM image of N-G_{750}.