Accepted Manuscript

Title: Facile synthesis of nitrogen-doped graphene aerogels functionalized with chitosan for supercapacitors with excellent electrochemical performance

Authors: Yong Zhang, Jia-Yi Zhu, Hong-Bo Ren, Yu-Tie Bi, Lin Zhang

PII: S1001-8417(17)30046-3
DOI: http://dx.doi.org/doi:10.1016/j.cclet.2017.01.023
Reference: CCLET 3972

To appear in: *Chinese Chemical Letters*

Received date: 2-12-2016
Revised date: 2-1-2017
Accepted date: 18-1-2017

Please cite this article as: Yong Zhang, Jia-Yi Zhu, Hong-Bo Ren, Yu-Tie Bi, Lin Zhang, Facile synthesis of nitrogen-doped graphene aerogels functionalized with chitosan for supercapacitors with excellent electrochemical performance, Chinese Chemical Letters http://dx.doi.org/10.1016/j.cclet.2017.01.023

Original article

Facile synthesis of nitrogen-doped graphene aerogels functionalized with chitosan for supercapacitors with excellent electrochemical performance

Yong Zhang [a,b,c], Jia-Yi Zhu [b,*], Hong-Bo Ren [b], Yu-Tie Bi[b], Lin Zhang [a,b,c,*]

[a]*Department of Physics, University of Science and Technology of China, Hefei 230026, China*
[b]*Joint Laboratory for Extreme Conditions Matter Properties, Southwest University of Science and Technology and Research Center of Laser Fusion, Mianyang, 621010, China.*
[c]*Science and Technology on Plasma Physics Laboratory, Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang 621900, China*

ARTICLE INFO

Article history:
Received 4 December 2016
Received in revised form 2 January 2017
Accepted 16 January 2017
Available online

Keywords:
Nitrogen-doped graphene aerogels
Hierarchical porous structure
Carbonizing temperature
Supercapacitors
Energy storage and conversion

ABSTRACT

Three-dimensional porous nitrogen-doped graphene aerogels (NGAs) were synthesized by using graphene oxide (GO) and chitosan *via* a self-assembly process by a rapid method. The morphology and structure of the as-prepared aerogels were characterized. The results showed that NGAs possessed the hierarchical pores with the wide size distribution ranging from mesopores to macropores. The NGAs carbonized at different temperature all showed excellent electrochemical performance in 6 mol/L KOH electrolyte and the electrochemical performance of the NGA-900 was the best. When working as a supercapacitor electrode, NGA-900 exhibited a high specific capacitance (244.4 F/g at a current density of 0.2 A/g), superior rate capability (51.0% capacity retention) and excellent cycling life (96.2% capacitance retained after 5000 cycles).

1. **Introduction**

Supercapacitors, which have been widely used in various areas, such as memory back-up, electric vehicles, power quality management, battery improvement, high performance energy storage/conversion devices and renewable energy applications, have attracted growing attention owing to their ultrahigh power density, fast charging, long-life cycle and excellent safety properties [1,2]. A variety of materials have been used to build high-performance supercapacitors to obtain high energy storage capability [3-8]. Because of its well-developed microstructure, high specific surface area and relatively high packing density, porous carbon material is one of the most well-studied and widely used as a supercapacitor electrode material. With unique three-dimensional (3D) structure and outstanding electrochemical properties, graphene aerogels have promised potential applications for energy storage. Recently, much research had been focused on enhancement of the electronic properties of graphene materials through doping nitrogen element by using various reducing agents such as pyrrole, dopamine, thiocarbohydrazide, phenylenediamine, melamine, amino acids and urea [9-22]. The obtained N-doped graphene aerogels showed improved excellent electrochemical performance. However, the environmental destructiveness of preparation, high cost of raw materials and complicated manufacturing limited its further applications in the market. Chitosan (CS) was produced through the deacetylation of chitin, which was one of the most abundant and renewable natural polymers, and was biocompatible and biodegradable [23,24]. In addition, the chitosan consisted of a large number of amino-groups that could be used to synthesize N-doped carbon aerogels with excellent supercapacitor performance [25].

Herein, we used the chitosan as the nitrogen-doped agent to fabricate the nitrogen-doped graphene aerogels (NGAs) by a rapid method. The synthesized NGAs could have the surface area as large as 692 m^2/g. Especially, it was found that the porous structure and specific capacitance of NGAs could be adjusted by the change of the carbonizing temperature. The prepared NGAs exhibited a high specific capacitance and outstanding cyclability due to the high specific surface area and hierarchical pore size and distribution.

2. Results and discussion

As shown in Fig. 1a and b, a good-formability black hydrogel with a cylinder shape was formed by using chitosan as functionalizing agents in GO aqueous solution in a vacuum oven at 90 °C for 6 h. In the contrast experiment, GO suspension could not form hydrogels in the same conditions (90 °C for 6 h), indicating GO suspension and chitosan were indispensable in the formation of hydrogels and chitosan was conducive to self-assembly of GO nanosheets to form three-dimensional hydrogels acting as a binder. After supercritical CO_2 drying, NGOAs would be obtained. Then, the NGOAs were carbonized at 900 °C in nitrogen atmosphere for 4 h and the NGAs

* Corresponding authors.
E-mail address: zhuyu416my@sina.com (J.-Y. Zhu), zhlmy@sina.com (L. Zhang).