Materials Letters 178 (2016) 95–99

Contents lists available at ScienceDirect

Materials Letters

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

# Facile preparation of nitrogen-doped graphene sponge as a highly efficient oil absorption material

Wenlong Yang [a,1], Hui Gao [a,*,1], Yu Zhao [a], Kaiqi Bi [a], Xiaolong Li [b,*]

[a] School of Physical Science and Technology, Key Laboratory for Magnetism and Magnetic Materials of Ministry of Education, Lanzhou University, Lanzhou 730000, PR China

[b] Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, PR China

ARTICLE INFO

*Article history:*
Received 14 December 2015
Accepted 16 April 2016
Available online 22 April 2016

*Keywords:*
Nitrogen-doped graphene
Porous materials
Oil absorption
Carbon materials

ABSTRACT

A superoleophilic and hydrophobic Nitrogen-doped graphene (NG) sponge with three-dimensional (3 D) structure is fabricated through a facile hydrothermal method without further surface pretreatments or modification. The as-prepared NG exhibited a high specific surface area (132 $m^2$/g), low density (0.501 $cm^3$/g) and good porosity. Interestingly, NG demonstrated very strong absorption capacities (up to 200 times as its own weight) in a short time (5 s) for a broad spectrum of oil and organic solvents with a good recyclability of 5 times. The research results suggest that practical application of NG in the field of spilled oil recovery is feasible, cost-effective and scalable.



## 1. Introduction

With the growth of oil production and transportation, oil-spill from industrial accidents or the sinking of oil tankers caused severe environmental and ecological problems [1]. In the past decades, carbon based materials, such as activated carbon, carbon nanotube sponges (CNT sponges), and microporous polymers have been reported for the absorption of oil from water [2]. However, the environmental incompatibilities and high production costs of these absorbents limited their practical applications. Graphene, the ultralarge specific surface area and flat structure [3] provides promising characteristics as an excellent adsorbent for various oil solvent. Herein, we used the nitrogen (N) doping to improve the absorption ability of graphene. Bulk quantities of graphene sheets doped with N atoms were achieved via the reduction of graphene oxide (GO) in the presence of hydrazine hydrate under the hydrothermal environment. The NG had a high efficient absorption capacity of 200 times as its own weight and very fast absorbing speed (within 5 s).

## 2. Experimental

GO solution (15 ml, 2.0 mg/ml) with different amount of hydrazine hydrate (0.2 ml, 0.6 ml, 0.8 ml, 1.0 ml, 1.2 ml), termed as NG-1, NG-2, NG-3, NG-4 and NG-5 were transferred into a Teflon-lined autoclave, and the total volume remained 30 ml. The sealed autoclave was maintained at 180 °C for 9 h in an electric oven. Then the black columns were obtained and then put in the vacuum freeze drier for lyophilization to obtain the NG samples. In order to compare the adsorption ability of NG, we also prepared pristine graphene (G) and nitrogen-doped graphene with different nitrogen resources, remaining the content of nitrogen unchanged, we select different nitrogen sources (pyridine, pyrrole, sodium borohydride, ammonium hydroxide), termed as sample-1, sample-2, sample-3 and sample-4. All samples were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectra (XPS, PHI-5702, Physical Electronics), Raman and Contact Angle Meter, respectively.

## 3. Results and discussion

### 3.1. Morphology and structure of N-doped graphene sponge (NG)

Fig. 1(a) showed the digital photograph of GO (2 mg/ml), NG-4 (hydrogel), NG-4 (aerogel). After doping and reducing process, GO converted to NG (hydrogel). From the hydrogel into the aerogel, water loss rate was about 98.5%, indicating the huge water content involved in the NG. The density of the NG-4 was approximately 5.94 mg/$cm^3$, the whole sample could be placed on the top of dandelion without causing significant deformation. Fig. 1(c) presented the SEM micrograph of NG-4, which formed porous structures with pore sizes of a few tens of nanometers. These

* Corresponding authors.
*E-mail addresses:* hope@lzu.edu.cn (H. Gao), lixiaolong@sinap.ac.cn (X. Li).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.matlet.2016.04.131
0167-577X/

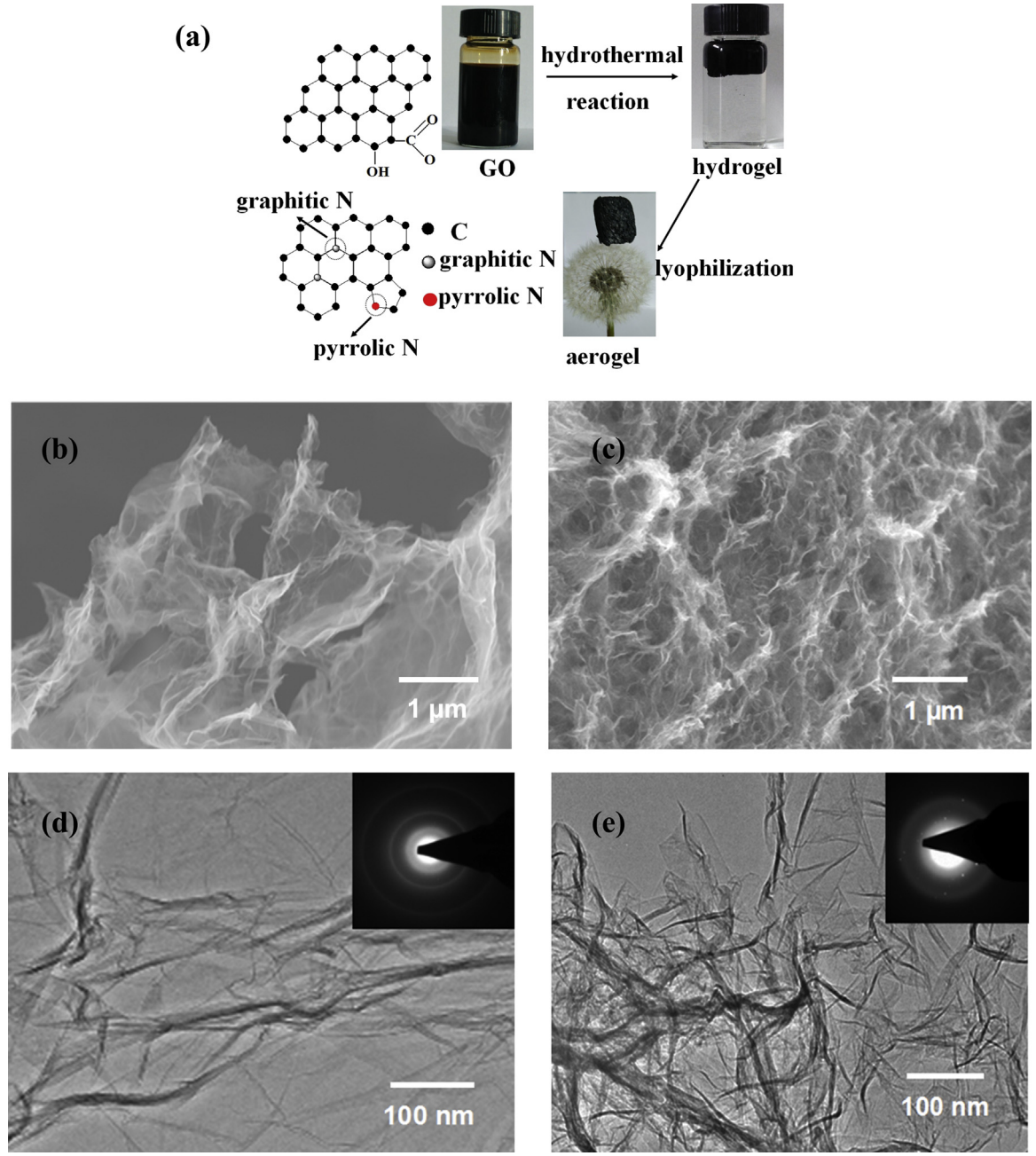


**Fig. 1.** Reaction and structure of NG-4 (a); SEM images of G (b) and NG-4 (c); TEM images and diffraction pattern of G (d) and NG-4 (e).

pores would provide the sufficient space for the storage of absorbed oil or organic solvents. Significantly, NG-4 had more wrinkles on the surface than G (Fig. 1(b)). Fig. 1(e) showed a TEM image of the NG-4, which exhibited a laminar morphology like silk veil waves. The surface of NG-4 had more wrinkles compared with G (Fig. 1(d)). The partially crinkled nature may be originate from the defective structures formed during the fabrication of GO and the N doping processes. The specific surface area of NG-4 was measured to be 132 $m^2/g$ (Fig. S1), larger than that of the freeze dried G (101 $m^2/g$), and the pore volume of NG-4 is 0.501 $cm^3/g$.

The G peaks of G and NG-4 appeared at 1593 and 1580 $cm^{-1}$ (Fig. 2(a)), respectively. The downshift of the G peak in NG-4 may be related to the electron-donating capability of N heteroatoms [4]. The $I_D/I_G$ ratio in G was 1.17 and 1.49 for NG-4. The increased $I_D/I_G$ ratio probably resulted from loss of carbon (C) atoms by the decomposition of oxygen-containing groups and the incorporation of N heteroatoms [4]. XRD patterns of the NG-4 was depicted in Fig. 2(b), diffraction peaks at $2\theta=23^\circ$, indicating the interlayer spacing was about 0.396 nm. While for G, the interlayer spacing was about 0.381 nm (Fig. S2). The decreased interlayer spacing could be attributed to the effective π-π stacking of graphene. The XPS results demonstrated that nitrogen had been successfully doped into the graphene's lattice (Fig. 2(c)). The atomic ratio of N/C is 1.81%. The C 1s peak (Fig. 2(d)) was centered at 284.8 eV. Peak deconvolution showed that there was C=C (52.5%), C=N & C-O (19.3%), C-N & C=O (15.1%), and O-C=O (13.1%). The N 1s spectrum (Fig. 2(e)) could be deconvoluted into two peaks at 399.8 eV and 400.8 eV, which could be assigned to pyrrolic N (42.9%) and graphitic N (57.1%). Moreover, the O 1s spectrum (Fig. 2(f)) could be fitted with two peaks at 532.8 and 536.2 eV corresponding to hydroxyls and absorbed water. Those results were consistent with the schematic structure of NG (Fig. 1(a)). Hydrazine could remove the oxygen from the oxygen functionalities such as carboxyls, epoxides, hydroxyls, etc. During deoxygenation, the reorganization