Carbon 111 (2017) 774–781

Contents lists available at ScienceDirect

Carbon

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

Rational design of reduced graphene oxide for superior performance of supercapacitor electrodes

S. Rasul [a, *], A. Alazmi [a], K. Jaouen [a], M.N. Hedhili [b], P.M.F.J. Costa [a, **]

[a] King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, Thuwal, 23955–6900, Saudi Arabia
[b] King Abdullah University of Science and Technology (KAUST), Imaging and Characterization Laboratory, Thuwal, 23955-6900, Saudi Arabia

ARTICLE INFO

Article history:
Received 30 March 2016
Received in revised form
17 October 2016
Accepted 24 October 2016
Available online 25 October 2016

ABSTRACT

Strategies to synthesize reduced graphene oxide (rGO) abound but, in most studies, research teams select one particular oxidation-reduction method without providing a methodic reasoning for doing so. Herein, it is analyzed how diverse oxidation-reduction strategies commonly used can result in considerable performance differences of rGO for supercapacitor applications. Depending on the graphite oxidation method followed, the surface chemistry analysis of the products confirms that there is a marked disparity in the degree of oxidation and the nature of the oxygen functional groups present. Subsequent reduction of the oxidized graphite (using three different methods) showed that the maximum specific capacitance of rGOs produced from the classical Hummers' method was 128 F g^{-1} whereas an analogous material obtained from an improved Hummers' method reached ~274 F g^{-1} (both via an hydrothermal reduction route). Besides showing that the improved oxidation method results in superior capacitance performance, explained by the higher number of structural defects allied to a surface chemistry where residual hydroxyl and epoxy functional groups predominate, this study highlights the need to rationalize the oxidation-reduction strategies followed when investigating applications of rGO materials.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Electrochemical capacitors, also commonly called supercapacitors, store energy either within the electrochemical double-layer formed at the electrode/electrolyte interface (a.k.a. electrochemical double layer capacitors) or through fast surface-localized redox reactions (a.k.a. pseudo-capacitors) [1–4]. Carbon-based nanomaterials are excellent candidates to integrate the electrodes of supercapacitors due to their high surface area, good electrical conductivity, chemical stability and wide range of operating temperatures [5–8]. Among nanocarbons, graphene stands out as it exhibits exceptional electrical and thermal conductivities and mechanical strength. As a monolayer, graphene has a high specific surface area (~2675 m^2 g^{-1}) which leads to a maximum theoretical capacitance of 550 F g^{-1}, thereby setting an upper limit for all carbon-based electrode materials [9,10]. Still, considering the low mass loading and its accessible surface area, the areal capacitance of single-layer graphene is limited to 21 μF cm^{-2} [9] which renders its device application impractical. This limitation has fueled the search for strategies to enhance the supercapacitor performance of graphene-based materials [11–13].

Much work has been carried out on reduced graphene oxide (rGO) to realize the mass production of graphene-based energy storage devices [14–17]. Among the most popular methods to synthesize rGO flakes is the Hummers' method [18] in which graphite is first oxidized in aqueous medium and subsequently reduced/exfoliated by utilizing, for instance, chemical [19–23], thermal [24], hydrothermal [25], electrochemical [26,27] or microwave-assisted reduction means [28]. The flakes obtained via this or analogous methods are generally several tens of layers thick. Still, the dominant terminology refers to them as reduced "graphene" oxide. The use of the term graphene in rGO, as applied here, is therefore to be understood *sensu lato*.

It is known that the reduction of the graphite/graphene oxide (GO) by different oxidation-reduction routes bears a considerable effect on the structure and chemistry of the final product [29–33]. With the introduction of defects and assorted functional groups, it is plausible to state that a pronounced influence on the non-faradaic EDLC behavior of these materials should also be

* Corresponding author.
** Corresponding author.
E-mail addresses: shahid.rasul@kaust.edu.sa (S. Rasul), pedro.dacosta@kaust.edu.sa (P.M.F.J. Costa).

http://dx.doi.org/10.1016/j.carbon.2016.10.066
0008-6223/© 2016 Elsevier Ltd. All rights reserved.

expected. While there are numerous studies available which describe the supercapacitor performance of rGO-based supercapacitors [4,9,11,15,29], we found that a systematic study describing how different oxidation-reduction strategies may influence the non-faradaic specific capacitance of these materials is missing. In our previous study [34], we synthesized GO by two of the most common synthesis methods, the classical Hummers' [18] and the improved Hummers' [35] methods, subsequently reducing them under thermal, chemical or hydrothermal conditions to obtain six different rGOs (see also tree sample scheme in Fig. 1a). Following up on that first study, here we analyze the complete set of GO and rGO products as we questioned how much influence the oxidation-reduction routes would have on the supercapacitor performance of these materials.

2. Experimental

As previously reported [34], graphite powder was oxidized to obtain GO using either the Hummers' method (HGO) or the so-called improved Hummers' method (IGO). This was followed by dividing each of the GO products into three parts which were then reduced using one of various treatments (thermal, chemical and hydrothermal). In the following, we keep to the notation introduced in Ref. [34] where, for instance, thermally reduced Hummer's graphene oxide (rHGO) in N_2 atmosphere is named rHGO/N_2.

The entire set of samples, from the initial graphite to the rGO, was structurally, chemically and electrochemically characterized. The powder X-ray diffraction (XRD) analysis was performed on a diffractometer (Bruker D8 Advance) with Cu Kα radiation (λ = 1.5418 Å). The morphology of the materials was characterized using an FEI NovaNano scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of ~10^{-9} mbar. The survey and high-resolution XPS spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively. Samples were mounted in floating mode in order to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the aromatic sp^2 hybridized carbon (C=C) peak from the C 1s spectrum set at 284.4 eV.

For the electrochemical characterization, the working electrode was prepared by mixing the active material (5 mg) with 15 μl of Nafion (at 5 wt% in ethanol and water), in a solution of water and ethanol (1 ml, 50% v/v). The use of Nafion as a binder for carbon materials has been discussed previously in the literature [10,36]. The mixture was then ultrasonicated for about 30 min until a fine, homogenous slurry was obtained. The slurry was drop-cast onto the glassy carbon electrode (5 mm diameter) and dried under an incandescent lamp for ~30 min. A three-electrode cell configuration was used in a BioLogic VMP3 electrochemical workstation to evaluate the electrochemical performance of the GO and rGO materials under cyclic voltammetry (CV) and galvanostatic charge-discharge conditions. A platinum (Pt) wire and a saturated calomel electrode (SCE) were employed as counter and reference

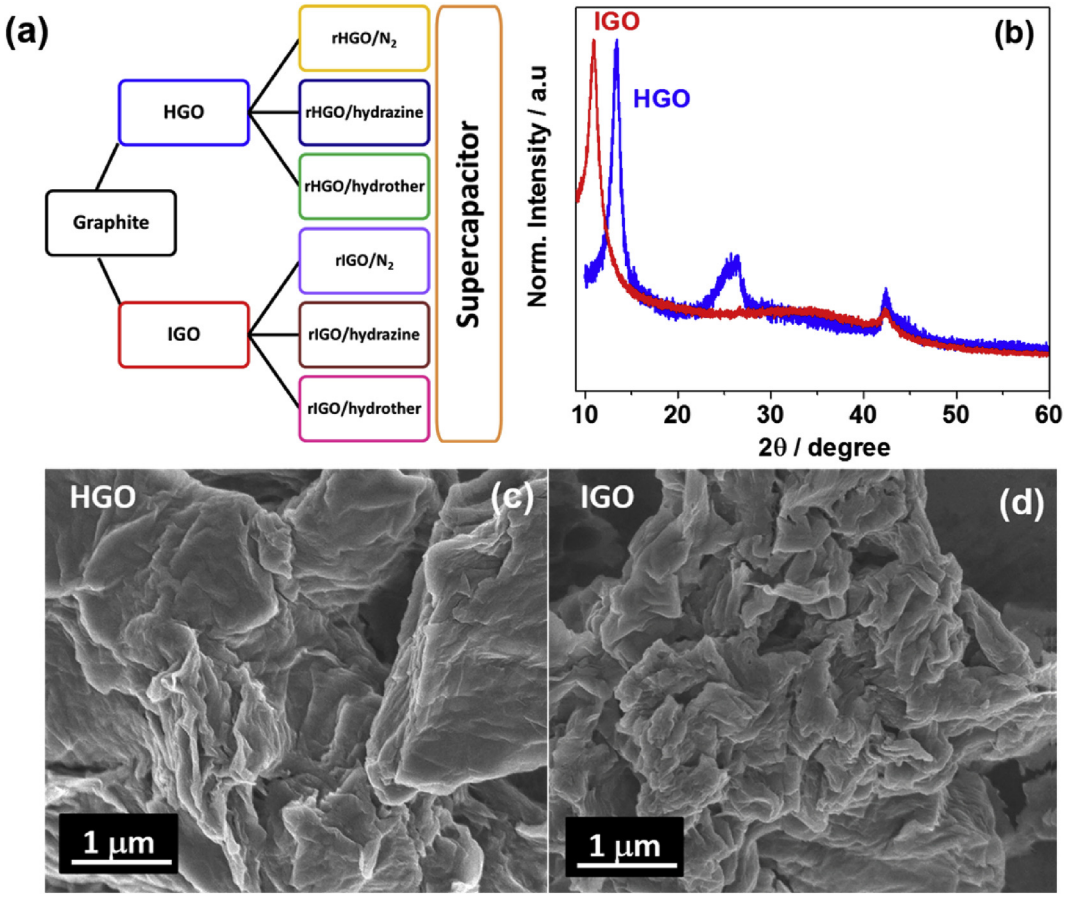

Fig. 1. a) Sample tree diagram of GO and rGO products, b) XRD patterns of HGO and IGO (normalized), c) and d) SEM images of the HGO and IGO products. (A colour version of this figure can be viewed online.)

Download English Version:

https://daneshyari.com/en/article/5432671

Download Persian Version:

https://daneshyari.com/article/5432671

Daneshyari.com