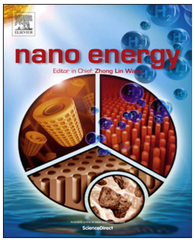
Nano Energy (2015) **17**, 160–170

Available online at www.sciencedirect.com

ScienceDirect

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



RAPID COMMUNICATION

Mechanistic investigation of the graphene functionalization using *p*-phenylenediamine and its application for supercapacitors☆

Xiangning Lu[a,b], **Liyi Li**[b,1], **Bo Song**[b], **Kyoung-sik Moon**[b], **Ningning Hu**[a], **Guanglan Liao**[c], **Tielin Shi**[c], **Chingping Wong**[b,d,*]

[a]*School of Mechanical and Electrical Engineering, Jiangsu Normal University, Xuzhou 221116, PR China*
[b]*School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA*
[c]*Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, Wuhan 430074, PR China*
[d]*Department of Electronic Engineering, The Chinese University of Hong Kong, Shatin, Hong Kong*

Received 30 April 2015; received in revised form 18 July 2015; accepted 22 August 2015
Available online 1 September 2015

KEYWORDS
Graphene;
Supercapacitor;
p-Phenylenediamine;
Functionalization;
Mechanism

Abstract

The *p*-phenylenediamine (PPD) modified graphene oxide (GO)/reduced graphene oxide (rGO) composite materials were synthesized by a facile solution processing with two different routes: 'Reaction first then Reduction' and 'Reduction first then Reaction', which are referred to as GPPDH and GHPPD, respectively. The two composites were employed as active supercapacitor electrode materials, their electrochemical properties were studied, and the mechanism how PPD improves the electrochemical performance is investigated systematically. GPPDH with the PPD molecules incorporated between the graphene sheets demonstrated a loose and crumpled microstructure. However, for GHPPD, the graphene sheets were stacked and cross-linked through PPD molecules. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) also provided quantitative information about the newly formed chemical constituents in the synthesized materials. The specific capacitance values of GPPDH and GHPPD are 316.54 and 249.24 $\mathrm{F\,g^{-1}}$ at 10 $\mathrm{mV\,s^{-1}}$, respectively. The synthesized materials also exhibited an excellent cycling stability as 93.66% (GPPDH) and 87.14% (GHPPD) retentions after 4000 cycles at current density of 2 $\mathrm{A\,g^{-1}}$.The results revealed the role of amine-based

---

☆Electronic supplementary information (ESI) available: TGA test and Electrochemical performance of rGOPPDc.

*Corresponding author.

E-mail address: cp.wong@mse.gatech.edu (C. Wong).

[1] Contribute equally with the first author.

http://dx.doi.org/10.1016/j.nanoen.2015.08.011

organic additives in graphene supercapacitor materials and validated the GPPDH as the electrodes of supercapacitor with an excellent electrochemical performance.

Introduction

Energy storage has become one of the greatest challenges all over the world. As a new promising energy storage device, supercapacitors (SCs) have attracted considerable attention in recent years because of their high power density, long cycle life, short charging time and reversibility [1-3]. Energy storage in SCs is achieved by two different types of capacitive behavior: the electrical double layer (EDL) capacitance through polarization and adsorption of ionic charges on the surface of electrode materials [4,5], and the pseudo-capacitance resulted from fast and reversible surface faradaic redox reactions under certain potentials [6,7]. The performance of the SCs highly depends on the properties of electrode materials, and the surface area of the material plays an important role.

Nano-scale carbon materials with high specific surface area and good electrical conductivity are promising electrode materials for SCs [8]. Graphene, the two-dimensional single-layer sheet of sp^2-hybridized carbon material, is an excellent conductor of both heat and electricity. And it has been intensively studied for SCs applications [9,10] due to its fascinating properties of high specific surface area, good electrical conductivity, light weight and chemical stability [11]. However, the individual graphene oxide (GO) sheets would easily get agglomerated or restacked during the preparing process because of the π-π stacking, which would lead to a dramatic decrease in the accessible surface area of graphene sheets, thus hinder electrolyte ions transport and affect the electrochemical performance of SCs adversely.

A large number of methods have been developed to prevent the aggregation of GO sheets [12,13] and to improve the performance of graphene-based SCs [14,15]. These techniques modulate graphene properties by introduction of fillers or dopants to GO sheets covalently or non-covalently [16-18]. For example, carbon nanotubes [19,20], transition metal oxides [21], heteroatoms [22] and conducting polymers [23,24] were investigated and adopted for surface modification of GO, which would prevent the restacking of graphene sheets and increase the capacitance by serving as spacers and/or adding additional redox-active functional groups. However, the non-covalent approaches have some disadvantages, such as slippage of the molecules, and they are hard to control and unstable compared to the covalent approach [25]. Therefore, the covalent modification strategy is a more promising way for this purpose.

Phenylenediamine has been reported to be a good molecule for GO functionalization and it is effective to improve the performance improvement of SCs [26,27]. It is known that GO has abundant highly reactive groups, which provide the possibility of covalently grafting active small organic molecules onto GO sheets by various reactions [28]. The *p*-phenylenediamine (PPD) with two amine groups ($-NH_2$) on the para-position of benzene rings may react with the functional group of GO layers in certain conditions [29], thus occupying the space between the graphene sheets and prevents the restacking and aggregation. However, many researchers believe that PPD is a good redox mediator and it increases pseudocapacitance of SCs by quick reversible faradaic reactions. Additionally, PPD is also regarded as the precursor of nitrogen doping for capacitance improvement [30]. Herein, we report the PPD modified GO/rGO composite materials using the solution processing and the investigation of the mechanism of graphene functionalizaiton with amine group. PPD functionalizd GO/rGO composite materials were used as the electrodes materials of SCs, exhibiting excellent electrochemical performance.

Experimental

Materials preparation

Natural graphite flakes (99.8%) were obtained from Asbury Company. The *p*-phenylenediamine (PPD), hydrazine monohydrate, nafion solution (5 wt% in ethanol), sulphuric acid (H_2SO_4) and other solvents were purchased from VWR International.

GO synthesis

GO was prepared by the modified Hummers method typically [31]: 1 g of graphite flake (230U from Asbury) was put into a $NaNO_3$ (1 g)/concentrated H_2SO_4 (100 mL) solution in an ice bath. Then 6 g of $KMnO_4$ was slowly added to the solution while maintaining the temperature below 20 °C. The mixture was stirred in the ice bath for 2 h and for another 0.5 h at 35 °C water bath. Next, about 46 mL of 70 °C water was added dropwise into the flask. The reaction-generated exothermic heat raised the solution temperature up to 98 °C. A 140 mL of 70 °C water was then added, followed by a 20 mL of 30 wt% hydrogen peroxide solution to terminate the reaction. The mixture was filtrated and washed with water to remove the excessive acid and inorganic salts. The resulting GO was dried overnight at 55 °C to produce the GO powder.

GO/rGO functionalization using PPD

In a typical surface modification process, ~100 mg of GO was dispersed in 50 mL deionized (DI) water by a water bath sonication for 0.5 h. Then a stable brown GO dispersion (one equivalent) was used for the surface modification. About 100 mg of PPD was dissolved in 50 mL DI water and then added to the GO dispersion slowly in a 250 mL round bottom (RB) flask. After one-hour sonication, the RB flask was placed in an oil bath preheated at ~80 °C and stirred for around