Energy Storage Materials 14 (2018) 297–305

Contents lists available at ScienceDirect

Energy Storage Materials

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

Plasma-tuneable oxygen functionalization of vertical graphenes enhance electrochemical capacitor performance

Gopinath Sahoo[a,*], S.R. Polaki[a,*], Subrata Ghosh[a,1], N.G. Krishna[b], M. Kamruddin[a], Kostya (Ken) Ostrikov[c,d,*]

[a] Surface and Nanoscience Division, Materials Science Group, Indira Gandhi Centre for Atomic Research, Homi Bhabha National Institute, Kalpakkam, Tamil Nadu 603102, India
[b] Corrosion Science and Technology Division, Metallurgy and Materials Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India
[c] School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, QLD 4000, Australia
[d] Joint CSIRO-QUT Sustainable Processes and Devices Laboratory, P.O. Box 218, Lindfield, NSW 2070, Australia

ARTICLE INFO

Keywords:
Vertical graphene
VGN
Plasma nanotechnology
Electrochemical capacitor
Supercapacitor
Ultracapacitor

ABSTRACT

Vertical Graphene Nanosheets (VGN) is one of the most promising energy storage materials in particular for electrochemical capacitor electrode applications. Yet, the intrinsic hydrophobic nature of VGN impedes electrode-electrolyte interaction and necessitates VGN surfaces to be hydrophilic to enhance the charge storage performance. This work not only demonstrates the improved effectiveness of surface modification through oxygen plasma exposure to transform the inherent hydrophobic VGN surfaces into super-hydrophilic ones, but also fills the existing knowledge gap about the specific oxygenated functionalities that cause this transition. Here we use an innovative combination of *ex-situ* or *in-situ* exposures to reveal and quantify the specific oxygenated functionalities on VGN surfaces. In particular, a preferential increase in hydroxyl and carbonyl type functional groups is demonstrated at higher plasma powers. In this way, the super-hydrophilic VGN electrodes reveal a ten times increase in the areal capacitance over the inherent hydrophobic ones. Moreover, a significant difference in capacitance amongst the samples treated in *ex-situ* and *in-situ* manner under the same plasma power is also demonstrated. The observed variation in the capacitance is related to the type and relative presence of the oxygenated functional groups. This simple and scalable approach elucidates the critical role of surface chemistry and the possibility of decorating VGN structures with preferential functional groups to achieve superior specific capacitance.

1. Introduction

Vertical Graphene Nanosheets (VGN), a derivative of graphene, have drawn a significant attention of research community, due to their remarkable physical and chemical properties [1–4]. Basically, VGN are ensemble of interconnected three-dimensional vertically standing few layer graphene sheets of few tens of nanometer thick [5,6]. This unique geometry bestows a large surface area and high density of sharp edges with non-stacking morphology, thus VGN structures being considered as an emerging material for wide range of applications spanning from energy storage devices, field emission, and sensors to memory devices [2,7–13]. Additionally, VGN can also be used as a mechanical backbone for variety of hetero-atom/structures, to improve their performance and extend their utilization in the area of surface enhanced Raman scattering (SERS) and fuel cells [14–16].

The 3D interconnected porous network of VGN structures offers an easy access to its surfaces on both sides of the sheets for the electrolyte ions to interact with, a big boon for its utilization as an electrode material [2,17]. Further increase in surface area of VGN can be achieved by varying the inter-sheet spacing and producing secondary walls [18,19]. Controlled structure and morphology of VGN is essential to attain better capacitor performance [2,20]. In general, as-grown VGN is hydrophobic in nature due its jagged structure resulted by interconnected porous 3D network as well as its hydrogen terminated edges [21–23]. Conversely, hydrophilic surfaces are most desired for energy storage applications [24,25]. Because, the energy storage capacity of electric double layer capacitors (EDLCs) is greatly depends on the electrostatic interaction between electrode and electrolyte [26]. Whereas the hydrophobic nature restricts the electrolyte access to entire surface area for EDL formation. Hence, transformation of VGN

---

* Corresponding authors.
E-mail addresses: gopinathsahoo5@gmail.com (G. Sahoo), polaki@igcar.gov.in (S.R. Polaki), kostya.ostrikov@qut.edu.au (K.K. Ostrikov).

[1] Presently at Department of Chemical Engineering, Chungbuk National University, Chungbuk-28644, Republic of Korea.

https://doi.org/10.1016/j.ensm.2018.05.011
Received 28 December 2017; Received in revised form 1 May 2018; Accepted 10 May 2018
2405-8297/

surface to hydrophilic, while retaining its unique geometry is in high demand for high performance electrochemical capacitor (EC) applications. The nature and density of defects, inter-sheet spacing and surface functionalization play a vital role in deciding the wetting nature of VGN structures [23,25,27–32]. Surface modification methods like chemical activation and post-plasma treatment were widely adopted to tune the wetting properties of nanostructures, by altering the nature of defects and surface functional groups [26,31,33]. However, chemical activation is time taking and there is a high possibility of damaging the morphology [34,35]. In addition, it is very difficult to achieve super-hydrophilic surfaces through chemical activation process [35,36]. Whereas, post deposition plasma treatment is quite fast and it also helps in preserving the geometry.

In recent past, the post deposition plasma treatment of carbon nanostructures gained a lot of attention for surface functionalizations. Post deposition exposure under different plasma mediums like oxygen, hydrogen, fluorine, argon and nitrogen were studied to tune the wetting characteristics of VGN structures [28,31]. Amongst, surface fluorination makes VGN super-hydrophobic and exposure to all other plasmas (hydrogen, nitrogen, argon and oxygen) mostly results in hydrophilic nature. A recent study by Vizireanu *et al.* [37] reported the growth of super-hydrophilic carbon nanowall which is somewhat different to the most commonly reported intrinsic hydrophobic nature. However, the hydrophilicity of these carbon structures prevailed for only a short period of time (3–6 days), beyond which those structures transformed into highly hydrophobic. Furthermore, few studies confirm the oxygenated functionalization improves the electrochemical capacitor performance [38,39]. Yet, recent study by Belova *et.al.* showed that the oxygen surface functionalization causes low discharge current densities and poor cyclability for battery operation to several cycles only [40]. It is attributed to the slow oxygen reduction and evolution reaction kinetics and complex multistep reaction pathways. However, O_2 reduction on graphite is found to be influenced by the nature and concentration of active surface groups [41]. Additionally, there are reports on attachment of specific type of oxygenated functional groups (hydroxyl and carbonyl) found to enhance the EC performance of graphene sheets [38]. Nevertheless, no specific studies on tailoring VGN surfaces with selective oxygenated groups (hydroxyl or carbonyl) and evaluation of their capacitor performance exists. Although surface modification through post-deposition plasma treatment is well studied, no literature is available on detailing the plausible method of tuning the type of oxygenated functional groups attached to carbon nanostructures and correlation with specific capacitance.

In this study, we endeavor to transform the intrinsic hydrophobic VGN structures into super-hydrophilic, while preserving its unique geometry using post deposition oxygen plasma exposure process. This study demonstrated the significance role of oxygen plasma treatment and the manner (*ex-situ* or *in-situ*) it is carried out, to obtain VGN structures with preferentially functionalized by specific type of oxygenated groups, towards achieving enhanced specific capacitance. Furthermore, the correlation between oxygenated functional groups (epoxy/ether, carbonyl) with super hydrophilic nature and enhanced EC performance of VGN surfaces is established. A simple, well controlled and easily scalable approach for preferential oxygenated functionalization of VGN surfaces towards achieving super-hydrophilicity and enhanced specific capacitance is demonstrated.

2. Experimental methods

2.1. Growth of VGN by ECR-CVD

Vertical Graphene Nanosheets were synthesized on SiO_2/Si and carbon paper (CP) using plasma enhanced chemical vapor deposition (PECVD). Ultra high pure CH_4 and Ar gases were used as hydrocarbon source and dilution, respectively. The detailed growth process is discussed in our previous report [33,42]. Growth was carried out on a 2×2-inch size substrate for 4 hours.

2.2. Post-synthesis plasma treatment

Post deposition plasma treatment was carried out in two ways (i) *ex-situ* and (ii) *in-situ* manner. In case of *ex-situ* plasma treatment, the samples after the growth are exposed to ambient conditions for few days before the plasma exposure. Whereas, *in-situ* means plasma treatment has been carried out immediately after the growth without exposing the samples to ambient. It is to avoid the contamination of the samples by atmospheric absorbents on exposing to ambient conditions. Plasma treatment was carried out by admitting the commercially pure (99.9%) oxygen gas into the vacuum chamber at a flow rate of 20 sccm, where the chamber pressure was maintained at about 1.2×10^{-3} mbar. Plasma exposure studies (both *ex-situ* and *in-situ*) were carried at 100 W, 300 W and 600 W microwave power (plasma power) at constant exposure time of 2 minutes. The optimum treatment time of 2 min was chosen because it is the minimum treatment time allowing an effective change in VGN surfaces to super-hydrophilic behavior without any significant reduction in height, which is prominent at longer treatment duration or plasma powers. The samples are named as 100 W *ex-situ*, 100 W *in-situ*, 300 W *ex-situ*, 300 W *in-situ*, 600 W *ex-situ* and 600 W *in-situ*.

2.3. Characterization

Field Emission Scanning Electron Microscope (FESEM, Supra 55, Zeiss, Germany) was used to obtain the morphology and vertical height of VGN structures. The High-Resolution Transmission Electron Microscope (HRTEM; LIBRA 200FE, Zeiss) was employed to obtain the microstructure of the graphene sheets as well as number layers a sheet consists of. The structural properties like defects and disorderness were evaluated by micro-Raman spectroscopy (Renishaw in-Via, UK) with 514.5 nm laser excitation. The wetting property was analyzed by measuring water contact angle using a telescope-goniometer (APEX, Acam D1N01, India) by half angle method and approximately 1μl volume of water was used. Liquid drop analysis (LB-ADSA) from ImageJ software was used to measure the water contact angle (WCA). X-ray Photoelectron Spectroscopy (XPS, Surface Nano Analysis, SPECS, GmbH) was employed to evaluate the surface chemistry and chemical bonding of as-grown and plasma treated VGN. Electrochemical capacitor performance of as-grown as well as plasma treated VGN was investigated in three electrode system using Metrohm-Autolab electrochemical work station (model PGSTAT302N, Netherlands). Pt foil was used as the counter electrode and 1 M KOH was chosen as electrolyte. Accordingly, these findings are mainly for the aqueous electrolyte based electrochemical capacitor. The current-voltage behaviors were recorded *versus* Ag/AgCl (3 M KCl saturated) reference at scan rates ranging from 0.1 to 0.5 V/s.

3. Results and discussion

3.1. Morphology

Fig. 1a-c illustrates the morphology of as-grown as well as oxygen plasma treated VGN 600 W *ex-situ* and *in-situ*, respectively. The insets depict respective cross-sectional FESEM images. The preservation of morphology after high energy oxygen plasma exposure is clearly evident except a reduction of height from 1.9 µm to 1.1 µm after the plasma treatment for both *ex-situ* and *in-situ* cases.

The morphology and cross-sectional SEM images of VGN samples treated at 100 and 300 W *ex-situ* and *in-situ* are given in Supplementary File Fig. S1. It also confirmed that no change in morphology occurs except a height reduction. The reduction in height is due to chemical etching of graphene by highly reactive oxygen species. However, the morphology of VGN is preserved after the oxygen plasma treatment, which is vital for its utilization as electrochemical capacitor electrode material. The inter-sheet distance generally con-