



Temporal-stability of plasma functionalized vertical graphene electrodes for charge storage



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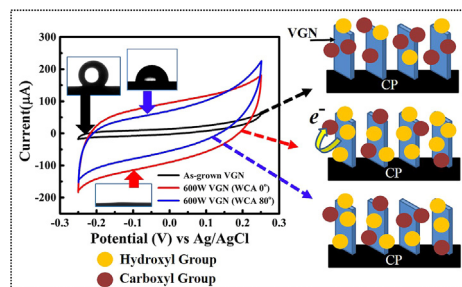
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HIGHLIGHTS

- Superwetting VGN with preferential O₂ groups is achieved without damaging geometry.
- A 10 times enhanced capacitance is apparent in hydrophilic VGN with -OH groups.
- Temporal stability in wettability of VGN is studied & correlated with capacitance.
- A VGN based symmetric coin-type device is fabricated and tested by glowing the LED.

GRAPHICAL ABSTRACT



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ABSTRACT

Vertical graphene is an emerging material for supercapacitor applications. Yet, its inherent hydrophobic nature restricts the interaction with electrolyte ions, which brings in high demand for developing hydrophilic vertical graphene surfaces. Herein, super-wetting vertical graphene nanosheets are achieved by an *in-situ* post-deposition oxygen plasma treatment. The plasma-treated vertical graphene nanosheets electrodes found to exhibit a ten-fold enhancement in specific capacitance. However, the super-wetting nature of the plasma-treated vertical graphene nanosheets transformed back to hydrophobic upon exposure to ambient conditions, yet the rate of transformation is governed by the plasma parameters in-turn the type of oxygen functional group attached. Noteworthy, the analogous effect is persisted in supercapacitor performance too. Furthermore, a correlation between the temporal-stability of wetting nature and supercapacitor performance is established; by measuring the charge storage capacity of vertical graphene surfaces with different water contact angle. A preferential shift in dominant oxygen functionalities from carboxyl type to hydroxyl and carbonyl type with an increase in plasma energy is evident. A symmetric coin-type electrochemical capacitor device using super-wetting vertical graphene nanosheets electrodes is fabricated and demonstrated its performance.

1. Introduction

Electrochemical capacitor or supercapacitor (SC) is a potential substitute to the conventional batteries for energy storage applications, due to their high charge-discharge rate, longer cycle-life and power

density [1–3]. In general, SCs are classified into two categories namely, electrochemical double-layer capacitors (EDLCs) and pseudo-capacitors (PCs). Where, the charge storage mechanism is governed by electric double layer and surface redox reactions at the electrode surface, respectively [4]. Carbon materials with different architectures have been

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extensively studied as EDLC electrodes, due to their remarkable properties such as a large accessible surface area for the electrolyte, high electrical conductivity and electrochemical stability [5,6]. Energy storage in EDLCs determined by the electrostatic interaction between the electrode surface and electrolyte ions [7]. The EDLC has more importance than pseudo-capacitance by virtue of its better chemical stability and electronic conductivity, while a pseudo-capacitor can store ten-to-hundred times more charge than the EDLCs [8–10]. Taking the advantage of EDLC, finding an adaptable and innovative strategy in order to improve their charge storage capacity is the prime focus of recent research.

Vertical graphene or vertical graphene nanosheets (VGN), also known as carbon nanowalls, have drawn significant attention among the research community, due to its intriguing properties [11]. Basically, VGN are well connected vertically standing few-layer graphene sheets of few tens of nanometer thick [12,13]. This unique 3D-geometry bestows a large surface area, inter-connected open porous network with high unsaturated edge density. Thus, VGN structures are found to be potential candidate for a wide range of applications spanning from energy storage devices, field emission, and sensors to memory devices [14–20].

Generally, as-grown VGN is inherently hydrophobic in nature, due its inter-connected porous network and H-terminated edges [21]. The hydrophobic surfaces are most suitable for applications like anti-icing, anti-corrosion, anti-fogging and self-cleaning coatings [22]. Impressively, this hydrophobic VGN exhibited long-term stability without any ageing effects [23]. On the other hand, hydrophilic surfaces are most desired for better wettability of electrode, which improves the interaction with electrolyte and in-turn the energy storage performance [24–26]. Hence, achieving hydrophilic VGN surfaces, while retaining its distinct geometry, is highly demanding for the high performance supercapacitor electrodes. Additionally, the unreacted edges, defects, inter-sheet spacing and surface chemistry play a vital role in deciding the wetting nature of VGN structures [25,27–31].

Recently Vizireanu *et al.* [32] reported the growth of super-hydrophilic carbon nanowalls, in contradictory to the widely reported hydrophobic ones. However, the hydrophilicity of these carbon structures sustained for only 3–6 days and further these structures transformed into hydrophobic. Tuning the wetting properties of nanostructures, by altering the surface chemistry and defect density by chemical etching and plasma exposure is widely reported [30,33]. However, chemical activation is time consuming and high possibility of damaging the morphology [34,35]. Whereas, post-deposition plasma treatment is quite fast, it can be carried out as a part of growth process itself and also ensures retention of the geometry [26]. Sui *et al.* [36] recently found that Ar plasma etching promotes the vertical growth of the structure. Various studies on surface plasma treatment to tune the wetting characteristics of VGN structures, using oxygen, hydrogen, fluorine, argon and nitrogen were reported [27,30]. Amongst, fluorinated VGN possess super-hydrophobic nature and exposure to all other plasmas (hydrogen, nitrogen, argon and oxygen) resulted in hydrophilic nature [26,27,30]. In addition, ageing and surface passivation have a significant impact on their supercapacitor performance, since the electrode surface is the active participant in the formation of EDLC [37]. Several groups have reported on the SC behavior of oxygen plasma-treated VGN and also elucidated the role of surface oxygen groups on capacitance [24,27,38–40]. Comparison of the capacitance for plasma-treated VGN is tabulated in Table 1. Ambiguity on the long-term stability of the wetting nature of carbon structures still exist. Yet, very few studies are only available on detailing the ageing behavior of carbon structures wettability [41,42]. Since the plasma-based surface modification is a non-equilibrium process, studies on the long-term stability of the plasma-induced changes in wettability are need of the hour for potential utilization of the VGN electrodes for supercapacitor applications.

In this study, we attempted to achieve super-wetting VGN structures

Table 1

Comparison of the capacitance values for VGN after the plasma treatment.

Material	Areal Capacitance	Electrolyte	Reference
Vertical Graphene Nanosheets (VGN)	120 $\mu\text{F}/\text{cm}^2$ as-grown	1 M Na Acetate and 1 M MgSO_4	[24]
	962 $\mu\text{F}/\text{cm}^2$ after O_2 plasma		
	167 $\mu\text{F}/\text{cm}^2$ as-grown	1 M Na_2SO_4	[43]
	922 $\mu\text{F}/\text{cm}^2$ after H_2 plasma		
	156 $\mu\text{F}/\text{cm}^2$ as-grown	1 M KOH	Present study
	1646 $\mu\text{F}/\text{cm}^2$ after O_2 plasma		

without distorting the geometry using an *in-situ* oxygen plasma treatment. The significant role of process parameters towards achieving hydrophilic VGN surfaces with long-term stability is brought out. Furthermore, the correlation between type of oxygen functional groups (hydroxyl, carbonyl and carboxyl) with wetting nature, ageing rate of wettability and supercapacitor performance of VGN surfaces is established. We also demonstrated the enhanced charge storage performance of super-wetting VGN structures. Finally, a tandem device of solid-state symmetric supercapacitor was used to light up a light-emitting-diode to demonstrate its practicability.

2. Experimental methods

2.1. Growth of VGN by ECR-CVD

Electron cyclotron resonance chemical vapor deposition (ECR-CVD) technique was employed to synthesis vertical graphene nanosheets on SiO_2/Si and carbon paper (CP) substrates. Ultra high pure CH_4 and Ar precursor gases were used for the growth. The detailed growth process was discussed in our previous work [44,45]. Growth was carried out for 1 h on a $4 \times 4 \text{ cm}^2$ size substrate.

2.2. Plasma exposure studies

An *in-situ* post-deposition oxygen plasma exposure was carried out in the same chamber immediately after the growth. Subsequently after plasma exposure the samples were cooled down to room temperature, without disrupting the vacuum to avoid the contamination by atmospheric absorbents. The plasma exposure studies were carried out using commercially pure (99.9%) oxygen gas, by admitting it at a flow rate of 20 sccm, where the chamber pressure was maintained at about $1.2 \times 10^{-3} \text{ mbar}$. Plasma exposure studies were carried out as a function of (i) exposure time namely 30 s, 2 min, 5 min, 10 min and 15 min at a constant microwave power of 100 W and (ii) microwave power namely 100, 200, 300, 400 and 600 W at a constant exposure time of 2 min.

2.3. Fabrication of electrochemical capacitor device

A symmetric VGN electrodes based coin-type device was prepared by assembling two electrodes of 600 W *in-situ* plasma-treated VGN/CP by sandwiching polyvinyl alcohol (PVA) and KOH based gel polymer electrolyte in between them. The gel polymer electrolyte was prepared by continuous stirring of 1 g PVA in 10 ml DI water at 80°C till it completely dissolved and forms a homogeneous solution. Followed which 10 ml of 1 M KOH was added drop by drop to the solution with continuous stirring and then cooled down to room temperature [46]. The gel electrolyte was used in the coin-type symmetric electrochemical capacitor device. The entire cell is encased in stainless steel (SS) foil and the photograph in supplementary file Fig. S1a and S1b depicts the in-

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