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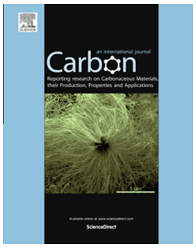

Sustainable process for all-carbon electrodes: Horticultural doping of natural-resource-derived nano-carbons for high-performance supercapacitors

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ABSTRACT

We demonstrate a novel chemical synthesis and functional doping process of vertical graphene nanosheets and other nano-carbons using *natural* precursors. The *all-carbon* electrodes are synthesized *via* the plasma reformation of natural fats and functionalized by microwave-assisted doping using leaf extracts from a variety of horticultural plants such as *bok choy*, *chrysanthemum*, and *spinach*. The resulting nanostructures possess a high loading of electrochemically active dopants and a desirable morphology for energy storage. This combination enables the electrodes to exhibit excellent supercapacitor performance.

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1. Introduction

Recently, nano-carbons have attracted tremendous interest as advanced materials for energy storage and many other functional devices such as sensors, drug delivery systems, water purification membranes, *etc.* [1–6]. However, it remains challenging to grow these nanomaterials (*e.g.*, graphenes, nanotubes, *etc.*) with controlled morphology, structure and property. Such deficiency often leads to unsatisfactory properties and limits their applications. Doping, on the other hand, has been demonstrated as a viable and effective way to improve functional properties of these nano-carbon materials [7–9].

However, the conventional way of chemical doping requires strong acids, hazardous chemicals, and/or long thermal processes with highly purified gases [10,11]. The less commonly used electrochemical or plasma doping often involves dedicated equipment, high cost, and harsh conditions which can potentially damage the nanostructures and impede their mechanical, optical, electronic and electrochemical performance [12–14]. As a result, it is critical to develop both large-scale fabrication and doping methods for nano-carbons in a more sustainable and low cost manner. Thus, exploring means to directly utilise natural precursors with minimal processing are of great interests [15,16].

Here we demonstrate a simple, fast and non-destructive approach to graft nitrogen- and oxygen-containing functional

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groups onto vertically aligned graphene nanosheets (VGNS) which are then integrated into supercapacitor electrodes. This conceptually new approach is inspired by the fact that many horticultural plants possess nitrogen- and oxygen-containing biomolecules [17]. These molecules can be easily extracted through simple techniques (*i.e.*, boiling) as commonly utilised in many culinary practices. The industrialised extraction processes for cultivated vegetables are also well established. We chose VGNS as the platform for doping because of their high surface area, open and porous structure, and excellent structural rigidity. These merits are often critically important to many applications [18,19]. The VGNS was made from butter as they exhibit superior properties as compared to those grown using purified hydrocarbons [4]. Butter consisted of mostly fat which is a long chain of carbons with oxygen groups at the tail. There is also an approximately 20 wt% of water content. Transformation of these precursors into highly ordered structure such as VGNS is a plasma unique process where complex steps of decomposition and reformation take place [20,21].

Supercapacitors are robust energy storage devices which are particularly attractive for portable electronics, hybrid electric vehicles, and integrated renewable energy storage systems as they possess high power density, rapid charge/discharge rate, and long lifespans [22–25]. However, the specific capacitance and energy density of most nanocarbon based supercapacitor electrodes remain low, which is hampering their widespread applications [26,27]. In this work, we aim to solve this problem by doping the nanocarbon structures with a simple “boil and microwave” technique utilising nitrogen- and oxygen-related groups extracted from widely cultivated vegetables (*i.e.*, “horticultural doping”) which significantly enhanced the performance of the electrode. Our process can thus be used to produce high-quality, high-performance, all-carbon based functional nanomaterials suitable for supercapacitor and many other applications.

2. Experimental

The plasma-enabled synthesis and possible scale-up of VGNS are described elsewhere [21]. Briefly, a thin layer of commercially available butter was spread onto the flexible graphite paper substrate. It was then loaded into the radio-frequency (RF) inductively-coupled plasma chemical vapour deposition (ICP–CVD) chamber and placed directly under the plasma generation zone. During the growth, a gas mixture of Ar and H_2 was fed into the chamber at a constant pressure of 2.5 Pa. Even though there was no external heating, the substrate temperature could reach 400–450 °C due to the plasma-heating effect. The VGNS structures were subsequently obtained by exposing the butter laden substrate to a 1000 W plasma for 9 min. The scale-up of VGNS production can be realised by using a larger plasma reactor with a much larger number of samples.

Then the microwave-assisted doping process was performed. First, *Brassica rapa chinensis*, *Chrysanthemum coronarium*, and *Spinacia oleracea*, were bought from the local supermarket and washed with de-ionised water. The solutions containing the leaf extracts were obtained by boiling the leaves in 500 mL of water for 10 min. After allowing the solution to cool to room temperature, they were filtered through porous filter paper to remove any residues. Next, the VGNS samples were soaked in 100 mL of the leaf extracts and treated by a conventional household microwave oven at 1000 W for 1 min. Finally, the doped samples were dried and annealed at 200 °C in vacuum for 30 min.

Field-emission scanning electron microscopy (FE-SEM) images were obtained by Zeiss Auriga microscope operated at 5 keV electron beam energy with an InLens secondary electron detector. Raman spectroscopy was performed using a Renishaw *inVia* spectrometer with a laser excitation at 514 nm (Ar laser) and a probing spot size of $\sim 1\ \mu m^2$. X-ray photoelectron spectroscopy (XPS) spectra were recorded by Specs SAGE 150 with the Mg $K\alpha$ excitation at 1253.6 eV. Both survey and narrow scans of the C 1s, O 1s and N 1s regions were conducted.

The electrochemical measurements were performed in 0.1 M Na_2SO_4 aqueous electrolyte at room temperature in both three- and two-electrode cell configurations. The three-electrode cell setup used the doped VGNS as the working electrode, a piece of Pt foil as the counter electrode, and an Ag/AgCl electrode as the reference electrode; while the two-electrode cell tests used two identical pristine or doped VGNS samples as the electrodes. Cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) measurements were conducted using BioLogic VSP 300 potentiostat/galvanostat. CV tests were performed at scan rates of 10–500 mV s^{-1} in the potential range of 0–0.8 V. Galvanostatic charge/discharge curves were obtained at constant current densities of 200, 400 and 800 $\mu A\ cm^{-2}$. EIS measurements were performed in the frequency range of 0.01 Hz to 100 kHz. The specific capacitance (C_s) based on the three-electrode measurements was calculated from the CV curves by integrating the discharge current against the potential V according to $C_s = \int IdV/\upsilon m\Delta V$, where I is the current, υ is the scan rate (V s^{-1}), m is the mass of VGNS, and ΔV is the operating potential window (0.8 V). For the calculation of cell capacitance in the two-electrode measurements, twice the masses of VGNS ($2m$) were taken into account. The mass loading of the electrode used in this work was 0.12 mg/cm^2 for pristine VGNS and 0.16 mg/cm^2 for the doped samples.

3. Results and discussion

The microwave-assisted doping process of VGNS-based supercapacitor electrodes used horticultural leaf extracts. First, leaves of three widely consumed vegetables, namely, *B. rapa chinensis*, *C. coronarium*, and *S. oleracea*, which are more commonly referred as *bok choy* (BC), *chrysanthemum* (SG), and *spinach* (SP), respectively, are prepared. By using a simple boiling process, the biomolecules containing oxygen and nitrogen functional groups in these leaves were released into the aqueous solution. Next, the VGNS-based electrodes were soaked in the solution and a conventional household microwave oven is used to firmly attach these functional groups to the electrodes’ surface. The final product of doped VGNS is obtained after annealing the samples at 200 °C in vacuum for 30 min.

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