Scalable, large-area synthesis of heteroatom-doped few-layer graphene-like microporous carbon nanosheets from biomass for high-capacitance supercapacitors

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High-capacitance electrochemical supercapacitors are promising devices due to their long-term stability and simple device construction. Unlike available reports on biomass-derived carbon as supercapacitor electrodes, in this paper, we report novel few-layer graphene-like microporous carbon nanosheets obtained from a single biomass precursor, which yield very high specific capacitance. A simple, ultra-low cost, one-step activation-free approach yields few-layer graphene-like microporous carbon nanosheets in the presence of heteroatoms by using ginger root as a biomass precursor. Suitable heteroatom content combined with porous graphene-like carbon nanosheet structure enhances the specific capacitance. The as-prepared carbon nanosheets from ginger roots possessing few-layer graphene-like structures are confirmed by X-ray diffraction and transmission electron microscopy, and the presence of few heteroatoms is confirmed by energy dispersive spectroscopy. The electrochemical measurements reveal that the ginger root-derived carbon electrode exhibits very high specific capacitance of 390 F g$^{-1}$ at 1 A g$^{-1}$ of current density. The ginger-derived carbon electrode also has 93.3% capacitance retention until 3500 charge/discharge cycles. This approach indicates great potential to achieve sustainable, low-cost, simple and large-scale production of renewable biomass-derived carbon materials for efficient energy storage applications in the future.

1. Introduction

Supercapacitors, known as electrochemical capacitors (ECs), have been an attractive alternative energy storage technology for the past few years. Compared to the existing fossil fuel and intermittent-based energy systems, lithium-ion batteries (LIB) and supercapacitors provide sustainable energies. The critical issue however is to meet the commercial energy requirements delivered by the fossil fuel technology.$^1$ Supercapacitors/ultracapacitors have numerous advantages compared to LIBs such as high power density, safer technology, several thousands to millions of charge/discharge cycles and faster charge/discharge cycles.$^2$ The only major drawback of supercapacitors is their low energy density due to the electrostatic charge storage. Currently, many new electrode materials are under investigation for achieving better energy density without losing their other operational advantages. Among them, carbonaceous materials have advantages such as natural abundance, high electrical conductivity, tunable surface area, chemical stability and biocompatibility.$^3-^4$ However, these carbon materials suffer from low energy density (5–8 W h kg$^{-1}$), which leads to low specific capacitance; recently, attempts have been made to increase this by developing porous materials having high surface areas. Several nanostructured carbon-based electrode materials, such as carbon fibers,$^5$ graphene,$^6$ carbon nanotubes,$^8$ carbon aerogels,$^9$ and porous and mesoporous carbons,$^{10}$ have been extensively used for supercapacitors. Although the synthesis of these carbon materials is easily achieved at the lab scale, they cannot be used for commercialization due to the complex synthetic approaches and expensive carbon precursors involved.$^{11}$ Thus, developing environmental friendly and more efficient methods with low-cost precursors is an interesting field of research.

Biomass-based compounds serve as a sustainable source for carbon materials. Some of the biomass precursors used as supercapacitor electrodes are derived from coffee beans,$^{12}$ peanut shells,$^{13}$ coconut shells,$^{14}$ cellulose,$^{15}$ etc. These precursors are either pyrolyzed directly or combined with activation agents to produce functionalized and porous carbon. The main challenges are controlling/tuning the pore size distribution, surface

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chemistry and morphology. Activated carbons derived using chemical and physical activation provide control over porosity and surface of the carbon. However, these activation methods have limitations due to the complex process of addition/removal of these activating agents such as KOH, ZnCl₂, and H₃PO₄, thereby making them cost ineffective also.¹⁶ On the other hand, self-activation is a process that contains two mechanisms: one that utilizes the gas emitted during pyrolysis of biomass and other that makes use of inorganic materials existing in the biomass precursor.¹⁷ Compared to the conventional activation approach, self-activation using inorganic materials, such as K+, that already exist in the biomass precursor is more environment friendly and cost effective.¹⁸ Some of the reported biomass-derived self-activated carbon sources are cellulose,¹⁷ kenaf,¹⁹ and pokeweed.²⁰ Therefore, a new biomass precursor that is accessible, cheap and has potential to create significant economic valorization is required.

Here, we employ ginger with a fleshy and fibrous structure as the carbon precursor to develop a simple, one-step and facile method for large-scale synthesis of few-layer graphene-like porous carbon nanosheets (FLG-CNs) in the presence of heteroatoms. Ginger, also known as Zingiber officinale, is a widely consumed condiment both as spice and medicinal herb worldwide and is known for its antioxidative and anti-inflammatory properties.²¹,²² Raw ginger is composed of major minerals such as potassium (415 mg), magnesium (43 mg), phosphorous (34 mg), calcium (16 mg), sodium (13 mg) and other minerals per 100 g of quantity with water content of 79 g.²³ During pyrolysis, these minerals create porous nature that increases the surface area suitable for EDLC performance. Therefore, ginger is a propitious carbon precursor due to its natural abundance, low cost and sustainable biological resource to produce FLG-CNs with heteroatoms. To the best of our knowledge, this study is the first demonstration of the synthesis of novel few-layer graphene-like porous carbon nanosheets in the presence of heteroatoms via direct pyrolysis of a ginger root as a biomass precursor and its demonstration for high-capacitance supercapacitor application.

2. Experimental procedure

2.1. Preparation of ginger-derived carbon

Fresh Ginger root was purchased from a local supermarket. It was peeled, cut into slices and washed in deionized water to remove impurities for further processing. A schematic of the synthesis of carbon from ginger is illustrated in Scheme 1. In a typical synthesis procedure, the peeled and washed ginger was subjected to complete drying in an oven at 240 °C overnight. The pre-treated ginger samples were then carbonized at different temperatures of 600 °C, 800 °C and 900 °C for 1 h at a heating rate of 5 °C min⁻¹ under argon atmosphere. The dark black solid product obtained was crushed and ground to a fine powder. This powder was then washed with ethanol and deionized water by centrifugation to eliminate further impurities and larger particles. The ginger-derived carbon (GC) samples obtained were denoted as GC600, GC800 and GC900. These GC samples having few-layer graphene-like carbon nanosheets are denoted as FLG-CNs.

2.2. Fabrication of electrodes for three-electrode cell

A three-electrode cell configuration was constructed with a glassy carbon electrode (GCE) as the working electrode on which active materials was coated for testing. Platinum wire and Ag/AgCl were used as counter and reference electrodes, respectively. The active material paste was prepared by mixing 80 wt% of GC samples as active material, 10 wt% conductive carbon black and 10 wt% polyvinylidene difluoride (PVDF) grounded with an appropriate amount of N-methyl-2-pyrrolidone (NMP). The paste was then coated onto GCE (≈0.1 mg) of 3 mm diameter and dried in oven at 70 °C to obtain the active material-modified GCE.

2.3. Fabrication of coin cell-type symmetric supercapacitor electrodes

The symmetric supercapacitors were constructed using CR2032-type coin cells. The electrodes were prepared by uniformly coating active material paste onto stainless steel foil (10 mm dia) as a current collector (0.16 g) and then dried at 80 °C overnight. The loading mass of active material onto substrates was maintained to be 2 mg in total with 1 mg on both symmetric electrodes. The two symmetrical electrodes were assembled with a glass fiber as a separator (12 mm) sandwiched between them wetted with 1 M H₂SO₄ as aqueous electrolyte.

2.4. Material characterization

The surface morphologies of the samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The microstructure, surface functionalities and degree of disorders

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**Scheme 1** Schematic of FLG-CN synthesis from ginger root.
were obtained by an X-ray diffraction spectrometer (XRD, Cu Kα radiation), Fourier transform infrared spectrometer (FTIR) and Raman spectrometer, respectively. The surface area and elemental composition of the samples were analyzed by Brunauer–Emmett–Teller (BET) using nitrogen adsorption–desorption at 77 K and electron diffraction spectroscopy (EDS), respectively. The atomic composition and bonding state of the samples were analyzed using X-ray photoelectron spectroscopy (XPS).

2.5. Electrochemical characterization

All electrochemical measurements were carried out on a CHI 660E electrochemical workstation at room temperature. The electrochemical properties of GC samples were analyzed by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) curves. The electrochemical performances of ginger-derived carbon electrode materials were analyzed both in three-electrode and in two-electrode configurations using 1 M H₂SO₄ as the aqueous electrolyte. For three-electrode measurements, ginger-derived carbon electrode materials coated on GCE, Ag/AgCl, and platinum wire served as a working electrode, reference electrode, and counter electrode, respectively.

The symmetrical supercapacitor device (two electrode system) was prepared using two uniformly weighed carbon-coated electrodes separated by an ion permeable layer (porous glass fiber membrane). The device assembly was made using coin cell-type units with 1 M H₂SO₄ as the electrolyte. The gravimetric specific capacitance (C, F g⁻¹) was calculated from charge/discharge and cyclic voltammetry (CV) plots from the following equations:

\[
C = \frac{I}{m(dV/dt)} F \text{ g}^{-1} \text{ (three-electrode set-up)} \tag{1}
\]

here, \( m \) is the mass of carbon material loaded, \( I \) is the applied current, and \( dV/dt \) is the slope of the charge/discharge curve.

\[
C_{\text{cell}} = \frac{2I}{m(dV/dt)} F \text{ g}^{-1} \text{ (two-electrode set-up)} \tag{2}
\]

Here, \( m \) is the mass of active material on each electrode, \( I \) is the applied current, and \( dV/dt \) is the slope of the charge/discharge curve. The energy density (\( E, \text{ W h kg}^{-1} \)) and power density (\( P, \text{ W kg}^{-1} \)) were calculated based on the following equations for a two-electrode cell assembly with \( C_{\text{cell}} \) representing the specific capacitance of the symmetric supercapacitor:

\[
E = \frac{1}{2} \times \frac{C_{\text{cell}} dV^2}{3600} \text{ W h kg}^{-1} \tag{3}
\]

\[
P = \frac{E}{dt} \times 3600 \text{ W kg}^{-1} \tag{4}
\]

3. Results and discussion

FLG-CNs derived from ginger were prepared by one-step pyrolysis under argon atmosphere. As discussed earlier, minerals such as potassium, magnesium, phosphorous and silicon are major constituents of a ginger root. The thermal decomposition of dried ginger roots (that contains gingerol as the major compound) under inert atmosphere at various temperatures results in the formation of carbon nanosheets with a micro-porous structure without any activating agents. The morphologies and the microstructure were analyzed in brief as follows.

3.1. Morphology and microstructure analysis

The FESEM images of FLG-CNs obtained at different carbonization temperatures of 600 °C, 800 °C and 900 °C are given in Fig. 1(a–c), respectively. The images exhibit carbon nanosheets with kinked and wrinkled nature of micron size. As the carbonization temperature increases from 600 °C to 800 °C, there is formation of a porous structure due to the decomposition of carbonaceous precursor material and presence of natural minerals (K, Mg, etc.) acting as porogens. The GC800 sample shows porous nature compared to the other two samples, and this temperature of 800 °C was used as the optimized parameter to yield a high surface area and capacitance, which is explained in later sections. The presence of heteroatoms in GC800 sample was exhibited using EDS spectrum (Fig. 1(d)) with major heteroatoms such as potassium, magnesium and phosphorous of 1.14%, 0.34% and 0.34% atomic weights, respectively. As the temperature increases to 900 °C, there is reduction of heteroatoms attached to carbon with only 0.14% atomic weight of potassium along with the reduction of pore size formation. The increase in temperature leads to the loss

![Fig. 1 FESEM images of (a) GC600; (b) GC800 and (c) GC900; (d) EDS spectrum of GC800; (e) TEM image of GC800; inset-high magnification TEM images of GC800 and (f) HRTEM image showing interlayer distance.](image-url)
of impurities and volatile agents and reduction in the functional groups attached to the carbon surface.

The porous nature of GC800 can be seen in the TEM image in Fig. 1(e), which shows the porous nanosheet structure with wrinkled morphology. The inset in Fig. 1(e) shows the high-magnification TEM images of GC800 sample with the presence of clear wrinkled ultrathin nanosheets. Fig. 1(f) shows the HRTEM image of the few-layered graphene-like carbon nanosheets at the edges with interlayer distance of 0.363 nm, which corresponds to the (002) plane of XRD. The GC800 carbon nanosheets exhibit amorphous nature; after increase in temperature to 900 °C, the nanosheets exhibit graphitic nature, as explained in the following section.

The crystalline, structural and compositional information of the GC samples was obtained using XRD, FTIR, Raman and XPS, respectively. Fig. 2(a) shows the XRD spectrum of all the GC samples at various carbonization temperatures. All samples show two diffraction peaks centered at 2θ = 11.4° and 24.5°, corresponding to the (001) and (002) planes. The peak at 11.4° confirms the formation of a graphene oxide structure with large oxygen functionalities attached to the carbon surface with d_{(001)} = 0.77 nm, implying combination of turbostatic and

![Fig. 2](image-url)
graphitic stacking.\textsuperscript{26,27} The (002) plane of GC600 and GC800 shows a broad peak intensity, which indicates the amorphous form of carbon nanosheets corresponding to coherent and parallel stacking of graphene-like sheets. It can also be observed that there is peak shift of (100) and (002) planes towards larger angles as the temperature increases, which indicates that the interlayer spacing is larger for GC600 compared with that for GC800 and GC900. This signifies that the carbonization at higher temperature results in a more intact graphitic structure.\textsuperscript{28} When the carbonization temperature increases to 900 °C, the intensities of (002) and (101) planes at 2\theta = 24.5 and 43° increase. The presence of the (100) plane indicates the formation of higher degree of graphitic carbon structure with good crystalline nature of the GC900 sample.\textsuperscript{27}

In agreement with the XRD spectra, Raman spectra represent graphene-like nature of the GC samples (Fig. 2(b)). Two distinctive peaks are observed; the D band at \sim 1345 cm\textsuperscript{-1} indicates disordered sp\textsuperscript{2}-hybridized carbon atoms or the defect sites of graphite and G band at \sim 1597 cm\textsuperscript{-1} indicates the in-plane phonon mode vibration of sp\textsuperscript{2}-bonded carbon atoms.\textsuperscript{29} As can be seen in Fig. 2(b), the \textit{I}_D/\textit{I}_G ratio is used to measure the degree of disorder in the graphitic structure. The decrease in the values of GC900 from GC800 indicates an increase in the graphitic order of carbon, which is consistent with the XRD patterns. However, the Raman spectrum of synthesized carbon samples does not show a 2D peak due to very low formation of graphitic carbons. Reports have shown that there is reduction in peak intensity and broadening after doping (here, it is the presence of heteroatoms) and in the presence of structural defects in the graphitic carbon.\textsuperscript{30,31} Also, it is reported that the intensity of the 2D band increases with the carbonization temperature above 900 °C. Thus, the plausible reason for no 2D active band for our synthesized carbon samples is the low carbonization/graphitization temperature, presence of heteroatoms and structural defects (amorphous nature). Fig. 2(c) shows the FT-IR spectra of all GC samples and exhibits the analysis of functional groups on the surface of carbon. As seen from the spectra, the bands between 3600 and 3700 cm\textsuperscript{-1} correspond to O–H stretching vibrations. The observed bands at 1730 and 1540 cm\textsuperscript{-1} correspond to C=O and C–C stretching vibrations.\textsuperscript{32} Other transmission bands at 2333, 1030 and 550 cm\textsuperscript{-1} are ascribed to the aliphatic C–H, C–O–C and \sim C–H stretching vibrations, respectively.\textsuperscript{33}

In continuation of surface functionalities, the bonding nature of the elements and their composition are determined by using XPS. Fig. 2(d) shows the complete survey spectrum of the GC800 sample, which displays 81.3 at% carbon and 18.7 at% oxygen with no other elements. Since the heteroatom percentages in GC samples were very less, as indicated in EDS spectrum, they could not be detected in the scan area of XPS survey. The C 1s and O 1s spectra of GC800 were deconvoluted into several peaks using Gaussian–Lorentzian curve fitting, as given in Fig. 2(e and f). The peaks at binding energies 284.4 and 284.6 eV corresponded to the sp\textsuperscript{2}-bonded (C=C) and sp\textsuperscript{3}-bonded carbons (C–C). The other peaks at 286.7 and 288.9 corresponded to C=O and O=C–O bonded carbons.\textsuperscript{29} Similarly, the deconvoluted O 1s spectrum depicts the peaks at binding energies of oxygen functional groups bonded to carbon atoms.

The textural structure of the obtained GC samples was investigated by N\textsubscript{2} adsorption at 77 K, as shown in Fig. 3(a). It is observed that all GC samples indicate an H\textsubscript{4}-type adsorption–desorption isotherm with hysteresis loop at the relative pressure from 0.4 to 0.9, revealing the existence of mesopores in the samples.\textsuperscript{34} The specific surface areas of GC600, GC800 and GC900 are 12.96, 320.67 and 166.70 m\textsuperscript{2} g\textsuperscript{-1}, respectively. The BET surface area increases with an increase in temperature from 600 to 800 °C due to evaporation of mineral salts, which leaves mesopores in the sample. The surface area decreases with increase in temperature from 800 to 900 °C due to loss of functional groups and structural damage to the carbon nanosheets, resulting in more stable graphitic nature. To further analyze the pore structures of GC samples, pore-size distribution curves were acquired using Barrett–Joyner–Halenda (BJH) model, as shown in Fig. 3(b). It is observed that GC800 has pore radius of 2 nm, which lies within the mesopore range of 2–50 nm.

![Fig. 3](image-url) BET analysis of all GC samples: (a) nitrogen adsorption–desorption isotherms; (b) pore size distribution with BJH model.
These 2 nm pores that lie in the meso and micropore range provide important factors such as developing electrical double layer surface on the electrode to obtain high capacitance, better charge propagation with low resistance and faster ion diffusion to improve the supercapacitor performance.\textsuperscript{28} Thus, the property of 2D nanosheet structure with porous nature and high surface area with optimum and uniform pore distribution of GC800 sample resulted in better capacitive performance compared to that of other GC samples.

3.2. Electrochemical performance

To evaluate the characteristics of the GC samples, electrochemical testing of CV and GCD was performed using three-electrode cell configuration in 1 M H\textsubscript{2}SO\textsubscript{4} aqueous electrolyte. Fig. 4(a–c) show the CV profiles of GC600, GC800 and GC900 samples, respectively, measured at different scan rates from 10 to 200 mV s\textsuperscript{-1} between 0 and 1 V. All the CV profiles in Fig. 4 showed a well symmetric rectangular shape, indicating the dominant behavior of EDLC, which is based on ionic adsorption and desorption mechanism. As the scan rate increases, the CV curve gets broader while retaining its rectangular shape even at higher scan rates, which is ascribed to facile charge movement.\textsuperscript{28} Furthermore, Fig. 4(d) shows the comparison of CV curves for all the GC samples at 100 mV s\textsuperscript{-1} scan rate, which reveals that GC800 has a larger area under the CV curve compared to other GC samples. Unlike GC600 and GC900, which have only graphitic nature, GC 800 has optimized pore size and surface functionalities for obtaining higher capacitance values.

To further evaluate the capacitance performance, GCD was carried out, as shown in Fig. 5. Fig. 5(a–c) display the GCD profiles of all the three GC samples with different current densities. These curves exhibit triangle symmetry, demonstrating the ideal EDLC behavior. The discharge times of the GC samples were longer compared to that of other GC samples at both low and high current densities, which is in well agreement with CV profiles. The specific capacitance comparison between the GC800 and GC900 samples is given in Fig. 5(d) at different current densities. The highest specific capacitance achieved was 390 F g\textsuperscript{-1} for GC800, whereas the capacitance achieved by the GC900 sample was 86.3 F g\textsuperscript{-1} at the same 1 A g\textsuperscript{-1} current density. This is because GC800 has a higher surface area with uniform pore size distribution that facilitates faster ion movement, which in turn increases specific capacitance.

With such outstanding electrochemical performance of GC800 sample, the real-time performance in terms of two-electrode cell configuration was tested. In accordance with the three-electrode configuration.
cell configuration, GC800 exhibits excellent EDLC behavior, as shown in the CV profile in Fig. 6(a) at different scan rates from 30 to 200 mV s\(^{-1}\). It is observed that the rectangular symmetry is maintained even at a higher scan rate of 200 mV s\(^{-1}\), which indicates the fast transport of electrons and ions in the GC800 electrode. Fig. 6(b) shows the GCD curves of GC800 at different current densities that exhibit perfect isosceles triangle shapes with negligible resistance. This shows a reasonable capacitance of 70 F g\(^{-1}\) at 0.1 A g\(^{-1}\) current density. To determine the efficiency of the prepared supercapacitor device, stability was measured for 3500 cycles at higher current density of 2 A g\(^{-1}\), as shown in Fig. 6(c). The capacitance retention remains at 93.3% at 3500 cycles of charging and discharging for GC800 sample, thus confirming its long-term electrochemical stability. The inset figure for the first and last ten charge/discharge curves indicates that even at the 3500th cycle, the triangular shape is maintained, exhibiting good EDLC stability. A Ragone plot, which shows the variation of energy density against power density, is the most determining factor for electrochemical performance of supercapacitors in practical applications. Fig. 6(d) shows the Ragone plot of GC800 sample, which exhibits a reasonable energy density of 9.67 W h kg\(^{-1}\) with power density of 200 W kg\(^{-1}\).

To evaluate our electrode material performance, a comparison with the capacitance performance of other biomass-derived carbon materials is shown in Table 1. It can be observed that the GC800 sample exhibits better capacitance performance compared to other reported biomass-derived electrodes. The reported willow leaf-derived activated carbon material with ZnCl\(_2\) activation for supercapacitor achieves 216 F g\(^{-1}\) at 0.1 A g\(^{-1}\) current density\(^{18}\). Another report on rice straw-derived activated carbon with high energy supercapacitor has specific capacitance of 332 F g\(^{-1}\) in a three-electrode cell\(^{39}\). Although these reported biomass-derived carbon materials exhibit good capacitance performance, they require additional activation agents for improving the capacitance. The main disadvantages of the chemical and physical activation processes used for the biomass carbon are low carbon yield, complexity of the synthesis process and enhanced cost\(^{16}\). This study reports the self-activation of the biomass-derived carbon during one-step pyrolysis, which utilizes the inorganic materials that already exist in the biomass. This self-activation method uses the gases emitted during carbonization process to etch the carbon material, which is more environment friendly and cost effective. Hence, the reported study on one-step self-activating biomass-derived carbon from ginger that contains heteroatoms with easy availability of raw materials paves way for commercialization and offers better solutions for new electrode materials for green energy applications.

![Fig. 5 GCD profiles of (a) GC600, (b) GC800, and (c) GC900. (d) Specific capacitance comparison between GC800 and GC900 samples.](image-url)
4. Conclusion

In summary, few-layer graphene-like carbon nanosheets from ginger root biomass have been successfully synthesized using a simple, low-cost, activation agent-free, one-step direct pyrolysis strategy. Benefitting from the presence of minerals and organic compounds in the ginger roots, the obtained FLG-CNs at 800°C possessed microporous nature and ultrathin nanosheet structure, respectively. Remarkably, the GC800 electrode exhibited outstanding specific capacitance of 390 F g⁻¹ at current density of 1 A g⁻¹, demonstrating great potential as a candidate for energy storage electrode. Moreover, the symmetric coin cell supercapacitor device in aqueous electrolyte exhibited a long cyclic life suitable for practical applications. This synthetic strategy of graphene-like carbon structure from renewable biomass opens ways for future high-performance energy storage applications.

Conflicts of interest

There are no conflicts to declare.

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