Mesoporous structure favorable for high voltage and high energy supercapacitor based on green tea waste-derived activated carbon

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Abstract

Designing high voltage, high energy, and activated carbon-based supercapacitors has been a long-time wish for meeting various electronic module requirements. This paper focuses on the approach of synthesizing the hierarchical porous activated carbon with dominant mesopores using eco-friendly green tea waste. The desirable ample pore space achieved by changing the weight ratio of KOH activating agent renders more ionic accessibility and space charge distribution. This feature leads to the achievement of a 4 V double layer supercapacitor with a remarkable specific energy of 142 Wh kg\(^{-1}\) and specific power of 3192 W kg\(^{-1}\), respectively using an acetonitrile organic electrolyte. The fabricated cell also exhibits a superior 104% capacitance retention after 25 000 charge-discharge cycles at the working potential of \(\geq 3\) V. Besides, the hierarchical porous activated carbon soaked in an aqueous KOH electrolyte shows a high specific capacitance of 397 F g\(^{-1}\) at 5 mA cm\(^{-2}\), high rate capability of 100 mA cm\(^{-2}\), and excellent cycle life of 116% capacitance retention after 50 000 cycles tested at 200 mA cm\(^{-2}\). The larger Debye length of the diffuse ion layer permitted by the mesopores is proposed to explain the higher voltage window as against low voltage of micropore dominated commercial activated carbon. The present research may pave the way toward the design of high-energy supercapacitors through recycling tea waste.

1. Introduction

In the present society, there is a great requirement for sustainable, renewable, and clean energy storage devices due to the exhaustion of fossil fuels, rapid environmental pollution, fast-growing world population, and increasing market value for modern electronic devices [1, 2]. Supercapacitors have gained a significant research attraction as green energy storage devices due to their exceptional characteristics such as faster charge/discharge rates, high power density, and remarkable cyclic stability [3, 4]. The carbon-based electric double layer capacitors (EDLCs) have been dominating the market value in commercial devices over pseudocapacitors due to their longer cycle and high specific power [5, 6]. However, the specific energy of carbon supercapacitors is limited to \(\sim 5–40\) Wh kg\(^{-1}\), which is still much inferior to lithium-ion batteries (LIBs). Therefore, an enormous research enthusiasm has been focused on simultaneously achieving high specific energy at high cycle life and specific power in a single device. The apparent strategy to enhance the specific energy of the EDLCs is by improving their working voltage window using organic or ionic liquid electrolytes and capacitance, which requires both stability of electrolyte and the accessibility of bigger ions into the pores with compatible size and characteristic structure.

Among the various electrodes, activated carbon (AC) has been regarded as a prominent material due to its excellent electrochemical stability, large surface area, higher porosity, good electrical conductivity, and high packing density [7–9]. Nevertheless, the orthodox commercialized ACs are predominantly micro-porous (<1 nm) in nature, which do not allow high accessibility for bulky ions of non-aqueous electrolytes and fail to present higher electrochemical storage performance at above 2.7 V [10, 11].
Consequently, the search for porous carbon materials exhibiting larger pore space and hierarchical distribution for better ion transfer and accommodation became a great technical effort. Particularly, the AC synthesis using bio-mass waste precursor has emerged as a viable route for hierarchical pore structure, high surface area, and simple synthetic process [12–16]. However, their AC-based cells suffer from the limited electrochemical performance including low specific energy at low voltage aqueous electrolytes and inferior cycle life [17–20]. Alternatively, the green-tea powder is new, economical, and most abundant and available. The global consumption of green tea in 2019 was 2 billion kilograms, which will generate an enormous wastage of resources, and this ultimately enhances the burden on our environment [21, 22]. To the best of our knowledge, there is no study to address the high voltage supercapacitor behavior of green tea waste-derived AC (gtAC) by fabricating a two-electrode symmetric device and the effect of the mesopore dominant carbon structures.

Herein, we report the synthesis of hierarchical activated carbon possessing dual micro- and mesoporous features and their roles for increasing operation voltage and specific energy of 142 Wh kg⁻¹ in their coin cell supercapacitor. We purposely tuned the surface area, mesopore structure, and surface functional groups of the resultant carbon materials during the activation process of carbonized carbon by changing the weight ratio of KOH activating agent. And this has a great influence on the electrochemical properties of the synthesized carbon-based supercapacitors. Therefore, we first performed a three-electrode testing experiment in an aqueous electrolyte to identify the high-performing and optimized electrodes associated with the optimum KOH weight ratio. Then, we designed the coin cell supercapacitor using the optimized electrodes and organic electrolyte, which demonstrates a reliable cyclic retention and a specific energy at a high working voltage (≥3.5 V).

2. Experimental

2.1. Materials
The green tea waste (raw material) was obtained from used Lipton green tea bags (owned by Unilever) purchased from the local supermarket. All chemicals were obtained from Shanghai Macklin Biochemical Co., Ltd and were used without further purification.

2.2. Synthesis of gtACs
First, the green tea powder waste was thoroughly cleaned with DI water followed by ethanol to eliminate the surface impurities before drying at 70 °C for 8 h. Then, it was crushed and sieved under the size of 500 μm. After this, the powder was carbonized at 800 °C (at 5 °C min⁻¹ ramp rate) for 2 h in the presence of Argon gas in a tube furnace. Then, 0.5 g of the obtained powder was impregnated with 0.5 g, 1.5 g, and 2.5 g of KOH (weight ratio of KOH/precursor at 1, 3, and 5), which were then activated individually at 800 °C for 1 h. Afterward, these powders were washed with a 1 M HCl solution followed by DI water to remove the captured potassium compounds and other surface impurities. Drying at 85 °C for 14 h resulted in the porous activated carbons from green tea waste, which were denoted as gtAC-1, gtAC-3, and gtAC-5.

2.3. Characterizations
The surface morphology of the synthesized gtAC samples were investigated by a ZEISS Sigma-500 scanning electron microscope (SEM, Germany). The elemental distribution and mapping were obtained using Energy Dispersive Spectroscopy (EDS, BRUKER XFlash-6130, Germany). The surface elemental composition was evaluated using X-ray photoelectron spectroscopy (XPS) from Thermo Scientific ESCALAB 250Xi, USA, with a monochromed Al Kα as the X-ray source. The N₂ adsorption-desorption isotherm analysis of the samples was done by Quantachrome Autosorb-iQ2-MP (USA) Nova-1000 system at −196 °C. The degassing of the samples was performed at 250 °C for 3 h. The specific surface and pore size distribution were measured using Brunauer–Emmett–Teller (BET) and density functional theory (DFT) methods, respectively. The defects in the synthesized gtACs were obtained from Raman spectroscopy with an Argon ion laser at 514 nm excitation wavelength (HORIBA LabRAM HR Evolution, France).

2.4. Electrochemical performance test
The supercapacitive performance of the synthesized gtAC materials was evaluated in a three-electrode cell using Gamry electrochemical workstation (Interface 1010E, USA). The working electrodes were prepared by homogeneously mixing gtAC (85%), super P carbon black (10%), and polyvinylidene difluoride (5%) in N-methyl-2-pyrrolidinone solution, followed by coating on a 1 cm × 1 cm nickel foam, and subsequent dry in the oven at 100 °C for 9 h. Finally, it was pressed to a dense sheet at 10 MPa to obtain working electrodes. The loaded active mass of gtAC working electrodes was ~10 mg cm⁻². Hg/HgO was used as the reference, and Pt plate was used as counter electrodes. Aqueous 6 M KOH solution was used as the electrolyte. CV measurement was performed at different scan rates from 5 to 100 mV s⁻¹, the voltage window for CV and GCD measurements...
SEM analysis shows the morphologies of the gtACs and their effect of the KOH mass ratio. At lower KOH mass 3.1. Microstructure and surface analysis

The specific capacitance values in the three-electrode system were calculated using GCD curves from the following equation [23]:

\[ C = \frac{I \Delta t}{m \Delta V} \] (1)

Where C denotes the specific capacitance (F g\(^{-1}\)) of the electrode materials, I represents the discharge current (A), \( \Delta t \) is the discharge time (s), m is the mass (g) of active material loaded, and \( \Delta V \) denotes the potential window (V) excluding IR drop.

Symmetrical supercapacitor device was fabricated using CR2032 coin cells to verify the practical applicability of electrode materials. The gtAC-5 was used as both anode and cathode. Aluminum foil of 0.2 \( \mu m \) in thickness was used as a current collector. Organic electrolyte of 1 M TEABF\(_4\)/acetonitrile and cellulose separator were used. The specific capacitance of the supercapacitor cell was evaluated from equation (1). Still, here in the case of m, the total loaded mass (g) of both anode and cathode electrodes is taken into consideration.

The specific energy (E, Wh kg\(^{-1}\)) and specific power (P, W kg\(^{-1}\)) of the supercapacitor device were calculated from the following equations [25].

\[ E = \frac{C \times \Delta V^2}{2 \times 3.6} \] (2)

\[ P = \frac{E \times 3600}{\Delta t} \] (3)

where C denotes the specific capacitance (F g\(^{-1}\)) of the device, \( \Delta V \) describes the potential window (V) excluding IR drop, \( \Delta t \) is the discharge time (s).

3. Results and discussions

3.1. Microstructure and surface analysis

SEM analysis shows the morphologies of the gtACs and their effect of the KOH mass ratio. At lower KOH mass (gtAC-1), there is an irregular bulk morphology with a rough surface (figure 1(a)), which can be attributed to inefficient etching of carbon by the low usage of KOH. When KOH mass increases to further (gtAC-3), the partial etching of rough carbon surface may result in an interconnected sheet-like morphology (figure 1(b)). At the highest KOH mass (gtAC-5), there occurs a severe activation and more etching effect, which wreck the connected sheet structure to form spherically aggregated nanoparticles (figure 1(c)). TEM images of gtAC-5 (figures 1(d) and (e)) show the dominant existence of the abundant mesopores (several nanometers) besides the traditional micropores (<1 nm not see at the current length scale). Such a hierarchical porous structure dominated with mesopores appears to be the unique pore characteristics of bio-mass precursors or N-doped AC powders. They do not cause much loss of capacitance, but shorten the ion diffusion path, which ultimately improves the charge accessibility and storage capacity of the electrodes. The presence of various elements and their distribution in the gtAC samples, for example, gtAC-5, is confirmed by the EDS spectrum (figure 1(f)). It shows that the gtAC-5 consists of elements like carbon, nitrogen, oxygen. The elemental mapping images confirm their homogeneous distribution with minimal aggregation or phase separation.

The specific surface area and pore characteristic structure are pivotal for the electrochemical energy storage application of carbon materials. Figure 2(a) shows the nitrogen adsorption–desorption isotherms of the gtAC-1, gtAC-3, and gtAC-5 samples. All the samples exhibit both Type I and type IV isotherms characterized by a hysteresis effect. The sharp adsorption at a lower relative pressure (0–0.6) and the hysteresis loop at a higher relative pressure (0.4–0.7), respectively reveal the presence of both dual micro- and mesoporous feature. Compared to the gtAC-1 and gtAC-3, the gtAC-5 exhibits a large hysteresis loop, which reveals the presence of the significant mesoporosity.

In general, the activated carbons exhibit H4 type hysteresis loop with slit-shaped pores. The hysteresis loop of N pet N2 adsorption–desorption is correlated with filling of meso pores by capillary condensation (adsorption) at high relative pressure (P/P0) followed by pore emptying by evaporation process (desorption). Capillary condensation represents a phenomenon of gas condensation in pores into a liquid-like phase at a pressure smaller than the saturation pressure, P0, of the bulk fluid [24]. Once condensation has occurred, a meniscus immediately forms at the liquid-vapor interface which allows for equilibrium below the saturation vapor pressure and the curvature of meniscus is assumed to have cylindrical symmetry [25, 26]. As the pressure is increased from zero in the adsorption process, an adsorbed film of nitrogen begins to form on the walls of the pore. The increasing pressure causes the thickening of the film. This process continues until the condensation pressure, P, is reached. At this pressure, the pore fills with a liquid-like condensed phase, resulting in a step
increase in the adsorption isotherm. The capillary condensation pressure is an increasing function of pore size and is related to pore size by the Kelvin equation for large pores. For slit-like mesopores, capillary condensation can be classically described on the basis of the following Kelvin equation [27].

\[
\frac{P}{P_0} = \exp[-2\gamma/RT\rho_1w]
\]

where \(\gamma\) is the liquid-vapour interfacial tension, \(R\) is the gas constant, \(T\) is the temperature, \(\rho_1\) is the density of liquid nitrogen and \(w\) is the width of the pore. A hysteresis loop is considered developed, when capillary condensation occurs at the limit of metastability of the vapor-like state (vapor-like spinodal), and developing, if capillary condensation occurs between the equilibrium and the vapor-like spinodal. The capillary condensation hysteresis occurs for nitrogen at its boiling temperatures at \(P/P_0 \geq 0.4\).

The effect of the weight ratio of KOH during the activation process of carbon on the specific surface area is investigated by BET and pore size distribution by DFT methods. As summarized in table 1, the corresponding
values for the gtAC-1, gtAC-3 and gtAC-5, synthesized at KOH weight ratio of 1, 3, and 5 have shown specific surface area of 1354, 1843 and 1966 m² g⁻¹ along with a pore volume of 0.532, 0.896 and 1.023 cm³ g⁻¹, respectively. This dataset indicates that the specific surface area and pore volume are enhanced prominently upon increasing the KOH weight ratio.

The pore size distribution curve (figure 2(b)) of the gtAC samples shows the broad distribution of pores between 0.5 nm to 5.5 nm in size, which indicates the presence of a hierarchical porous structure with micro (<1 nm) and mesopores (2–6 nm). With the increase in KOH ratio, the number of mesopores increases and the sub-nanometer pores decreases. Comparatively, AC derived from coconut shell such as commercial YP-50 only possesses 1281 m² g⁻¹, 0.73 cm³ g⁻¹, and about 80% of micropores less than 1 nm in diameter [28]. Therefore, the increased mesopore structure derived from tea-waste in this work should play a vital role in enhancing the diffusion of electrolyte ions, which benefits the charge accumulation via an electrical double layer configuration. This ought to ultimately result in the enhanced capacitance, potential window, and energy storage performance of the supercapacitors using either organic electrolyte or ionic liquid of larger ions [29, 30].

Raman spectra also reveal the advantage of the synthetic gtAC samples through changing the KOH weight ratio according to the degree of graphitization. As shown in figure 3(a), Raman spectra of the gtAC-1, gtAC-3, and gtAC-5 exhibit two prominent bands. The one at ~1348 cm⁻¹ is D-band, which represents the disordered

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**Table 1.** Specific surface area and pore characteristics of the synthesized gtAC samples obtained from BET and DFT methods.

| Sample | S_{BET} (m² g⁻¹) | V_{meso} (cm³ g⁻¹) | V_{micro} (cm³ g⁻¹) | D_{meso} (nm) | D_{micro} (nm) |
|--------|------------------|---------------------|---------------------|---------------|----------------|
| gtAC-5 | 1966             | 0.360               | 1.023               | 2.977         | 0.567          |
| gtAC-3 | 1712             | 0.176               | 0.896               | 2.975         | 0.555          |
| gtAC-1 | 1354             | 0.154               | 0.532               | 2.967         | 0.542          |

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**Figure 2.** (a) nitrogen adsorption-desorption isotherms, (b) pore size distribution of gtAC.
or defective structure. The other at ~1590 cm\(^{-1}\) is G-band, which represents the E\(_{2g}\) phonon vibration of the graphitic sp\(^2\) hybridized carbon atoms. The intensity ratio of the D band to the G band \((I_D/I_G)\) reveals the degree of graphitization \([31]\). The \(I_D/I_G\) ratios of the gtAC-1, gtAC-3, and gtAC-5 are found to be 0.943, 1.004, and 0.872, respectively. This indicates their disordered structure due to defects and edges. Although gtAC-5 has disordered (or defected) structure, its defective nature is smaller than the gtAC-3. The defects on the surface of the carbon are mainly originated from oxygen functionalities introduced during the KOH activation process. Few authors described that, the \(I_D/I_G\) ratio of activated carbons follows two trends with the increase in KOH mass. In the first category, for example, Zhimin \textit{et al}\([32]\) observed that, there is a continuous increase in the \(I_D/I_G\) ratio and oxygen wt% with the increase in the KOH mass from 1 to 3\% (1, 2, and 3\%). Different from the first observation, in the second category, Shaokui \textit{et al}\([33]\) noticed that, there is an increase followed by a subsequent decrease in the \(I_D/I_G\) ratio, when increasing the KOH mass from 1 to 5\% (1, 2, 3, 4, and 5\%). Here, they have observed that, the sample with 4\% KOH shows the highest \(I_D/I_G\) value and more oxygen functionalities.

Figure 3. (a) Raman spectra of gtAC-1, gtAC-3, and gtAC-5. (b) XPS survey spectra of gtAC-5, the inset shows the elemental atomic\% of gtACs. (c), (d), and (e) high-resolution C1s, N1s, and O1s XPS spectra of gtAC-5, respectively.
In our case, the second category change is noticed, as \( \frac{I_{2}}{I_{1}} \) ratio is increased from gtAC-1 to gtAC-3, however, it decreased from gtAC-3 to gtAC-5. This behavior is similarly attributed to the introduction of higher wt\( \% \) (17.2\%) of oxygen functionalities as defects in gtAC-3, which is revealed from XPS surface chemical analysis. when comparing with gtAC-1 (11.6\%) and gtAC-5 (12.8\%). However, after the peak point of oxygen loading is reached, there is no further increase in the oxygen wt\( \% \) with increasing the KOH mass. This transition may be understood in the following. At relatively higher KOH mass, the oxygen functionalities are trapped in the smaller pores in the activation process of carbon. At very high KOH mass, the pores become larger and the trapped oxygen are more free to be released during the subsequent washing process.

The gtAC-5 sample also comprises normal surface elemental composition, as revealed by XPS (figure 3(b)). The gtAC-5 is mainly composed of C (85.4 atomic\%), O (12.87 atomic \%) with a small amount of N (1.6 atomic\%). The high-resolution deconvoluted C1s spectrum (figure 3(c)) shows three peaks at 284.4, 285.3, and 288.6 eV, which are characteristic of C–C, C–O, and COOR, respectively [34]. The high resolution N1s spectra were deconvoluted into three peaks, corresponding to pyridinic nitrogen (398.2 eV), pyrrolic nitrogen (400.05 eV), quaternary nitrogen (401.2 eV) [34]. This high intensity quaternary nitrogen can facilitate electron transfer rate and enhances the conductivity of carbon electrodes, which ultimately enhances the charge storage property of a supercapacitor. Whereas, the pyrrolic nitrogen enhances the amplitude performance of carbon based electrodes [35]. Likewise, the deconvoluted O1s spectrum (figure 3(d)) shows three peaks corresponding to three oxygen-based components such as C=O (~531.4 eV), C–O (~532.8 eV), and COOR (534.5 eV) [36]. The presence of O and N along with the hierarchical pore distribution can be an advantageous functionality for electrochemical cyclic performance.

3.2. Electrochemical performance measurements

Before designing symmetrical coin cell supercapacitors in an organic electrolyte, we first measured the electrochemical performance of the bare green tea-derived carbon (gtC) before KOH activation and electrodes (gtAC-1, gtAC-3, and gtAC-5) using aqueous 6 M KOH electrolyte in a 3-electrode setup to identify the optimized electrode. Their capacitive performance was investigated by CV and GCD techniques within a working potential of −1 to 0 V. Figure 4(a) shows the comparative CV curves of the gtACs at a scan rate of 50 mV s\(^{-1} \). Here gtC shows lower CV current compared to gtACs. The integral area under CV curves gradually increases with the increase in the KOH weight ratio from 1 to 5. This confirms that the gtAC-5 electrode has the highest capacitive behavior than others. Figure 4(b) shows the CV curves of gtAC-5 electrode at different scan rates (5 to 100 mV s\(^{-1} \)). It is observed that the quasi-rectangular shape of the CV curves is well-maintained even at a scan rate of 100 mV s\(^{-1} \), demonstrating the high rate capability and faster ion diffusion. As shown in figure 4(c), all the gtAC electrodes exhibit symmetrical and triangular-shaped charge-discharge curves at the current density of 5 mA cm\(^{-2} \), which feature a typical EDLC behavior.

The gtAC-5 delivers a longer discharge time and less internal resistance (IR) drop than the gtC, gtAC-1 and gtAC-3, which reflects its high charge storage capacity and high conductivity. The excellent reversible electrochemical behavior of the gtAC-5 electrode is further confirmed by its good symmetrical shape GCD curves at different current densities from 5 to 100 mA cm\(^{-2} \) (figure 4(d)), where IR drop is enhanced slightly with the enhancement of current density.

The comparative specific capacitances of the gtAC electrodes at different current densities are shown in figure 4(e). At 5 mA cm\(^{-2} \) current density, the specific capacitance of the gtAC-5, gtAC-3, gtAC-1, and gtC electrodes are 397, 304, 250, 146 F g\(^{-1} \), respectively. Even at a higher current density of 100 mA cm\(^{-2} \), the gtAC-5 exhibits a high rate capability with 78.7\% capacitance retention (312 F g\(^{-1} \)), whereas gtAC-3 and gtAC-1 exhibit lower rate capability with 74\% (226 F g\(^{-1} \)) and 67\% (168 F g\(^{-1} \)) specific capacitance retention, respectively. The high specific capacitance of the gtAC-5 electrode can be ascribed to its high specific surface area, high micro and mesopore volume, and enhanced wettability. These factors significantly reduce the ion transport resistance and provide more spaces to absorb ions from electrolyte during the charge-discharge process [37].

Electrochemical impedance spectroscopy (EIS) is further employed to study the electrochemical reaction kinetics and conductive nature of the gtAC electrodes. Figure 5(a) shows the Nyquist plot of the gtC, gtAC-1, gtAC-3 and gtAC-5 electrodes in the frequency range from 10 kHz to 0.01 Hz. The small semicircle in the high-frequency region indicates the charge transfer resistance \( (R_s) \) at the interface. In the low-frequency region, the linear part represents the ions’ diffusion process towards the electrode surface. The gtAC electrodes show vertical curves at the low-frequency region nearly close to the imaginary axis, which reveals their EDLC behavior [38]. The intercept with the \( Z' \) axis in the high-frequency region denotes the equivalent series resistance \( (R_s) \) [39].

The equivalent circuit model used to fit the impedance data is shown as an inset of figure 5(a). Here CPE indicates constant phase element, which is an imperfect capacitive behavior of the diffusion layer. At the same time, \( Z_m \) is the Warburg resistance for the diffusion of electrolyte ions towards the porous network of the
The Rct values of gtAC-5, gtAC-3, gtAC-1, and gtC electrodes after fitting the data were found to be 0.12, 0.14, 0.24, and 0.32 $\Omega$, respectively, indicating their low resistance for the ion migration at the interface and better conductivities, which are consistent with the IR drop observed at the beginning of discharge curves in GCD curves. The smallest Rct of gtAC-5 is attributed to its hierarchical pore structure with abundant micro- and mesopores as well as high pore volume. This reduces the electrolyte ions’ diffusion path length, thereby facilitating their faster migration. Rs values are almost similar in the range of 0.13–0.135 for all the gtAC samples. The phase angles of gtAC-5, gtAC-3, and gtAC-1 electrodes from the Bode plot (figure 5(b)) were found to be 82°, 80°, and 84° respectively, which are close to 90° at low frequencies, suggesting their ideal capacitive behaviour, whereas gtC exhibits a lower phase angle of 77°.

The cycle life of gtAC-5 electrode, the best performing electrode, is measured using galvanostatic charge-discharge (GCD) for 50 000 cycles at ultra-high current density of 200 mA cm$^{-2}$ (figure 5(c)). Interestingly, the gtAC-5 electrode shows an exceptionally high capacitance retention of 116% from 100% up to 50 000 GCD cycles. The continuous increase in the capacitance retention during prolonged charge-discharge cycles is attributed to the activation of the electrode’s specific surface area through wettability [41]. This results in the enhanced migration of electrolyte ions into the micro- and mesopores, thereby improving the charge storage capacity. The cycle life performance and specific capacitance obtained in this work are much superior to most of electrode [40].

Figure 4. Electrochemical performance of gtC and gtACs. (a) Comparative CV curves of the gtC, gtAC-1, gtAC-3 and gtAC-5 at a scan rate of 50 mV s$^{-1}$. (b) CV curves of gtAC-5 at various scan rates from 5 to 100 mV s$^{-1}$. (c) GCD plots of the gtC, gtAC-1, gtAC-3 and gtAC-5 at 5 mA cm$^{-2}$ current density. (d) GCD plots of gtAC-5 at current density from 5 to 100 mA cm$^{-2}$. (e) Specific capacitance of the gtC, gtAC-1, gtAC-3 and gtAC-5 at various current densities.
the earlier reports about bio-waste-based AC supercapacitors, as shown in table 2. Besides, the gtAC-5 also shows a stable Coulombic efficiency value of 100% during the prolonged cycling process, which means the excellent reversibility of the electrodes.

Designing high specific energy supercapacitors require both higher voltage window and AC electrode’s hierarchical pore structure. Using organic electrolytes instead of aqueous electrolytes can fulfil the high potential and thereby superior specific energy. The electrochemical properties of the high-performance gtAC-5 electrode is further evaluated by designing symmetrical coin cell supercapacitors having 1 M TEABF₄/acetonitrile electrolyte. As shown in figure 6(a), the gtAC-5 symmetrical supercapacitor shows the stable CV voltage window between 0 to 3 V, 0 to 3.5, and 0 to 4 V without any decay in the current at a scan rate of 25 mV s⁻¹. Figure 6(b) shows the CV curves of the gtAC-5 based high potential window (4 V) symmetrical supercapacitor working at various scan rates ranging from 5–100 mV s⁻¹. The supercapacitor shows a quasi-rectangular shaped CV curve. Even at a high scan rate of 100 mV s⁻¹, the shape of the CV curves is well-maintained, demonstrating its excellent rate capability and high capacitive nature. The good reversibility is also confirmed by the symmetrical
shaped GCD curves at various current densities (figure 6(c)). As shown in figure 6(d), the specific capacitance values of this supercapacitor at various current densities are much more superior than those of commercial YP-50F that only has nanometer sized pores inaccessible to organic electrolyte ions.

Evaluation of the supercapacitor’s cycle life at high voltage is crucial for realizing the real application of energy storage devices. The cycle life test of the symmetrical supercapacitors is performed between 0 to 3 V at a high current of 100 mA (figure 7(a)). The device exhibits a remarkable cyclic stability with 104% capacitance retention even after 25 000 GCD cycles and high Coulombic efficiency. The inset of figure 7(a) shows that the shape of the GCD cycle is similar before and after the cycle life test, which implies no degradation of the material. Furthermore, a slight increase in the IR drop after cycling occurs. Inspired by this result, we have endeavored to further study its cycle life at an increased voltage window of 0–3.5 V (figure 7(b)). Interestingly, even at this higher voltage window, the device maintains 99% capacitance after 5000 cycles. The high cycle life of the coin cell supercapacitor might be associated with the stable voltage window of the organic electrolyte interfacing with

| Biomass          | Activating agent | Specific capacitance (F g⁻¹) | Cyclic stability | Electrolyte | References |
|------------------|------------------|------------------------------|------------------|-------------|------------|
| Onion peel       | H₃PO₄           | 127                          | 109% after 2000 cycles | 1 M H₂SO₄   | [42]       |
| Quinoa           | KOH             | 330                          | 93% after 10 000 cycles | 6 M KOH     | [43]       |
| Pine nut shell   | KOH             | 324                          | 94% after 10 000 cycles | 6 M KOH     | [44]       |
| Tea waste        | KOH             | 167                          | 96% after 16 000 cycles | 1 M Na₂SO₄  | [45]       |
| Flax seed        | KOH             | 369                          | 98% after 10 000 cycles | 6 M KOH     | [46]       |
| Blueberry peel   | KOH             | 324                          | 99.9% after 20 000 cycles | 6 M KOH     | [47]       |
| Coconut shell    | K₂CO₃           | 92                           | 85.1% after 5000 cycles | TEMABF₄/PC  | [48]       |
| Tree bark        | ZnO             | 286                          | 88.9% after 5000 cycles | 6 M KOH     | [49]       |
| Rice waste       | KOH             | 153.2                        | 87% after 10 000 cycles | TEMABF₄/PC  | [50]       |
| Walnut shell     | KOH             | 262                          | 93.7% after 3000 cycles | 6 M KOH     | [50]       |
| Green tea waste  | KOH             | 397                          | 116% after 50 000 cycles | 6 M KOH     | This work  |

Table 2. Comparison of the electrochemical performances of porous carbon electrodes derived from different biomass sources.

Figure 6. Electrochemical performance of the gtAC-5 based symmetrical two-electrode supercapacitor in 1 M TEABF₄/acetonitrile organic electrolyte. (a) CV curves at different working potential windows. (b) CV curves at various scan rates under 4 V operating potential (c) GCD curves at various current densities. (d) Comparison of the specific capacitance values with commercial YP-50F at different current densities.
the hierarchical porous AC. The presence of abundant surface functionalities at the pore walls of the gtAC as revealed by XPS led to the enhanced wettability of the organic electrolyte at the pore walls. This may enable the better accessibility of the large TEA$^+$ and BF$_4^-$ ions towards the mesopores resulting in the higher charge storage capacity during the long-term charge-discharge process. The effective diffusion behavior of TEA$^+$ and BF$_4^-$ towards the surface of the porous gtAC during the long-term cycling process is also supported by the impedance behavior. As shown by the Nyquist plot in figure 7(c), the $R_{ct}$ value of the symmetrical supercapacitor before cycling test is 9.3 $\Omega$. However, 25 000 GCD cycles of charge-discharge decreases the $R_{ct}$ value to 7.8 $\Omega$. The decrease in the $R_{ct}$ is ascribed to gradual surface activation and wettability of the porous gtAC during the charge-discharge process. Thus, the ion diffusion path length reduces and facilitates faster ion transport between electrolyte and surface of the electrode. The $R_s$ value after cycling test is slightly higher than the measured one before the cycle test, which is consistent with the IR drop observed in GCD curves. These results are supported by the prior theoretical work of Rica et al [51] who found the electro-diffusion of ions in activated carbon porous electrodes become faster when the macroporosity is larger due to the larger paths for diffusion. In addition, the favorable role of large pores and their dispersity for the higher voltage window was investigated by Kondrat et al [52] using the grand-canonical Monte Carlo simulations. Larger optimal pore size was found to be related to higher operating voltage for the case of pore size below 2 nm. Yes, it is still not understood why high operating voltage can be obtained when mesoporous AC of 1–6 nm are used for supercapacitor cell. It is known that the voltage withstanding capability of a parallel plate capacitor is proportional to the distance and the breakdown strength of the dielectric. For an electric double layer (EDL) capacitor, the critical distance between a carbon electrode and the equivalent diffuse charge in the electrolyte is typically defined by the Debye length ($\lambda_D$) which is much larger than Stern thickness. This value is related to the dielectric constant ($\epsilon_r$), the concentration of electrolyte, and the operating temperature. Besides, it can also be altered by the accumulation of ions against the carbon electrodes depending on the ionic accessibility that can be limited by the pore size.

Figure 7(d) schematically shows two cases of ionic accumulation at the charge stage (small and large pores). For large mesoporous activated carbon, diffuse layer thickness $\lambda_D$ is large but still remains within the boundary of the mesopore. And the mesopore is large enough to host more ion crowding toward the AC electrode surface.
On the other hand, the Debye length for the case of micropores becomes shortened and limited by the boundary of the smaller micropores, which only allows limited ion crowding towards the carbon surface (lower drawing). According to the Gouy–Chapman–Stern model, the total voltage drop across the EDL is the sum of voltage at diffuse layer ($V_D$) and Stern layer ($V_{Ss}$). $V_D$ is described by the Gouy–Chapman surface charge–voltage relationship below for small surface charge [53]:

$$V_D \sim -Q \lambda_D / \varepsilon_1 \varepsilon_0$$

where $Q$ is the total charge per unit surface in the diffuse region of the EDL. The voltage drop in the diffuse layer of the double layer electrolyte increases when Debye length or the charge ($Q$) increases. Therefore, one expects to reach higher operating voltage window when using mesopores–dominant AC electrodes rendering large space for more charges.

The specific energy and specific power of the device calculated using charge-discharge data is presented in the Ragone plot (figure 8(a)). The device delivers a remarkable specific energy of 142 Wh kg$^{-1}$ at a specific power of 630 W kg$^{-1}$. Even at a high specific power of 3192 W kg$^{-1}$, it retains a specific energy of 95.5 Wh kg$^{-1}$. The achieved specific energy is almost 4-fold higher than the device reported in recent literature and commercial YP-50F based capacitors [42, 43, 46, 54–59]. Such a high voltage performance of the capacitor using green tea waste-derived hierarchical AC exhibits practical applicability to a modern electronic device, as shown in figure 8(b), where a 4 V and 20 mA green LED was powered up for 7 min by a single coin cell after charging for 45 s.

4. Conclusions

Hierarchical porous activated carbons comprising of micro- and mesoporous features are derived using green tea waste, an abundant biomass as the precursor. The optimal performance of gtAC electrodes is identified by a three-electrode experiment using the aqueous electrolyte. A stable 4 V symmetrical coin cell supercapacitor is...
designed from the hierarchical porous gtAC-5 electrode that is obtained by carefully controlling the KOH weight ratio during the activation process. The designed supercapacitor cell exhibits a remarkable specific energy and specific power of 142 Wh kg$^{-1}$ and 3192 W kg$^{-1}$, respectively, in 1 M TEABF$_4$/acetonitrile organic electrolyte. Especially, the achieved specific energy is $\sim 20 \times$ higher than the current EDLC using commercial YP-50F. The newly fabricated cell shows a superior cycle life at the working potential of $\geq$3 V with 104% capacitance retention $\geq$25 000 GCD cycles. Even upon further increasing the potential window to 3.5 V, it shows 99% capacitance retention at 5000 GCD cycles. The good electrochemical performance of the supercapacitor in the organic electrolyte is mainly attributed to the presence of optimum number of mesopores in gtAC and also the enhanced wettability of electrolyte at the mesopore walls. Thus, the large TEA$^+$ and BF$_4^-$ ions of the organic electrolyte get more accessibility towards the mesopores and increase the Debye length of diffuse layer due to more ion crowing in front of the carbon electrodes, which ultimately increases the charge storage capacity and the voltage window. The additional benefit of the enhanced voltage from green tea waste-derived hierarchical activated carbon promises a new way to for next-generation high voltage and high energy supercapacitor devices.

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Conflicts of interest

The authors declare no conflict of interest.

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