Unusual Interconnected Graphitized Carbon Nanosheets as the Electrode of High-Rate Ionic Liquid-based Supercapacitor

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Abstract

A type of unusual interconnected graphitized carbon nanosheets (GCNS) was fabricated from biomass waste, *i.e.*, inner shaddock skins using a facile combined method of simultaneous carbonization-activation and post-vacuum-annealing processes. The obtained GCNS has an optimized integration of a cage-like high-aspect-ratio nanosheet structure (~ 8 nm thickness), a large surface area of $2327 \text{ m}^2 \text{ g}^{-1}$ and hierarchical meso/micropore systems (82.3% mesopore volume). Given the effect of post-vacuum-annealing process, enhanced graphitization degree and excellent electronic conductivity (7.9 S cm^{-1}) were obtained for the GCNS. The enhanced graphitization degree not only effectively improves electronic/ionic-transport kinetics in favor of rate capability but also prevents electrolyte degradation thus benefitting cyclic life. The ionic liquid-based supercapacitors assembled with symmetric GCNS electrodes exhibited an ultrahigh rate capability of 87% at current density of 100 A g^{-1} (holding 132 F g^{-1}) and a long cyclic life of 97.6% capacitance retention after 10,000 cycles. The excellent rate capability resulted in an integrated high energy-power property at an energy density of 56 Wh kg^{-1} (29.2 Wh L^{-1}), corresponding to a power density of 93 kW kg^{-1} (48.4 kW L^{-1}).

1. Introduction

Supercapacitors or electrochemical double layer capacitors, assembled by carbon (*e.g.*, graphene, activated carbons and carbon nanosheets) electrodes and ionic liquid (IL) electrolytes, have been dramatically developed during the past years [1-11]. This development is mainly ascribed to the integrated effects of carbon electrodes and IL electrolytes. The large specific surface area and high porosity of carbonaceous nanomaterials can be in favor of charge storage [12, 13]; furthermore, the high electrochemical stability, good ionic conductivity and non-flammability of ILs can provide large operating voltage window and wide operating temperature range even at an extreme aerospace environment [11, 14]. Such advantages make these supercapacitors suitable for the power sources of portable electronics, uninterruptable power supplies, hybrid electric vehicles, regenerative braking systems, grid applications, *etc.* [7, 10, 15].

In principle, the energy storage mechanism of supercapacitors is the non-Faradaic electrostatic sorption on the solid-fluid interface of electrode-electrolyte, which leads to a limited energy storage capacity. Thus, many concept designs and experimental strategies were explored to enhance the energy density of supercapacitors without sacrificing originally high power density and long cyclic life. These are based on the energy density (E , equaling to $\frac{1}{2}CV^2$) that is linear with the capacitance (C) and quadratic with the voltage window (V). For example, first, optimizing geometric parameters of carbon electrodes with a high specific surface area and matched pore size for electrolyte ion can generate sufficient interface charge storage for high double-layer capacitance [16]. Second, enhancing graphitization degree of carbon materials not only possibly improves the electrical conductivity to accelerate charge transfer in favor of a high rate performance, but may also increase the charge carrier density to boost charge screening at electrode-electrolyte interface resulting in high quantum capacitance [17]. Third, formation of novel IL electrolyte systems to balance the charge capacity of symmetric electrodes can expand the operating voltage window and increase the ability to screen charges for electro-adsorbing more electrolyte ions [18].

Regarding to the advanced supercapacitor electrode materials, two-dimensional (2D) carbonaceous material with abundant sp^2 hybridization and/or heteroatom doping is very promising because of its short ionic transport pathways and rich interface active sites compared with that of the activated carbon particles [4, 19, 20]. For example, as typical 2D carbonaceous materials, graphenes and MXenes have been intensively developed as supercapacitor electrodes with excellent capacitive performances. However, manufacturing these 2D carbonaceous materials is a complex process and requires high-cost feedstock. Currently, some 2D graphene-like carbon nanosheets have been prepared using eco-friendly and low-cost methods from waste biomass, such as silk [8], shrimp shells [11], hemp [4], gelatin [21], cornstalk [22] and coffee grounds [9]. These sustainable carbon nanosheets have thin thickness of less than 30 nm and high specific surface areas, which can potentially substitute the graphene for supercapacitor electrodes used. This possibility opens a door to create advanced carbon nanosheet electrodes for high-performance supercapacitors. However, most of the biomass-derived carbon nanosheet electrodes exhibit low-rate capability in organic and/or IL electrolyte systems, leading to inferior energy retention at high power output. This result mismatches the demand for devices requiring both high energy and high power.

In this study, a type of unusual interconnected graphitized carbon nanosheet (GCNS) material was prepared from waste biomass, *i.e.*, inner shaddock skins (ISSs), by using a facile combined method of simultaneous carbonization-activation and post-vacuum-annealing processes. The as-obtained GCNS presents good integration of a cage-like high-aspect-ratio nanosheet structure, hierarchical meso/micropore systems, large surface area and excellent electronic conductivity, which is different from the usual biomass-based activated carbons. These integrated characteristics render an excellent electrochemical performance for GCNS electrodes in the IL-based supercapacitor assembly.

2. Experimental

2.1 Materials

The inner shaddock skins (ISSs) were obtained from the shaddocks (*citrus grandis*) grown in the south of China. The N,N-dimethylacetamide (DMAC), zinc chloride (ZnCl_2), ferric trichloride (FeCl_3) and hydrochloric acid (HCl) were purchased from Beijing Chemical Works. 1-ethyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide (EMI TFSI) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI BF_4) were purchased from Sigma-Aldrich. All reagents used are analytically pure.

2.2 GCNS fabrication

The GCNS materials were synthesized as follows. The ISSs were firstly rinsed with distilled water and then dried. The dry ISSs were milled into powders in a hammer mill and then the powders underwent ultrasound-assisted pretreatment in DMAC. The suspension was vacuum-filtered, washed with ethanol and dried at 50°C . The pretreated ISSs powders were mixed with ZnCl_2 by a mass ratio of 1:2 (ISS: ZnCl_2), and then put into 3 M FeCl_3 solution at a solid loading of 5 wt.% (a mass ratio of the ISSs to the FeCl_3 solution). The mixtures were continuously treated by ultrasonic for 3 h and then were dried thoroughly at 80°C in a conventional oven. The pre-treated carbon precursors were carbonized at 900°C for 2 h with a ramp rate of 2°C min^{-1} in a tubular furnace under Ar flow of 100 mL min^{-1} . The resulting dark char was washed with 1 M HCl solution to remove the inorganic impurities, then rinsed several times with deionized water to pH around 7 and dried at 110°C for 10 h. The obtained material was denoted as CNS, and the yield of CNS was 28.2 wt.% based on the weight of dry ISSs powders. Then, the CNS underwent a post-vacuum-annealing in a tubular furnace under about 0.1 Pa at 1200°C for 1 h, and the final product was obtained and named as GCNS. The control samples of GCNS-1 and GCNS-2 were prepared under the same procedures used to prepare the GCNS except for the different vacuum-annealing temperatures at 1000 and 1400°C , respectively. The carbon yield was 7.9 wt.% for GCNS, 13.7 wt.% for GCNS-1 and 3.4 wt.% for GCNS-2, respectively, based on the weight of dry ISSs powders.

2.3 Characterization

Field emission scanning electron microscopy (FESEM) was carried out on the microscope S-3400N, Hitachi. Field emission transmission electron microscopy (FETEM) was examined on the JEM2100F, JEOL. X-ray diffraction (XRD) patterns were obtained on the X-6000, Shimadzu, using Cu K α radiation at 40 kV with 2θ steps of 0.2°. Raman spectra were determined on the spectrometer LabRAM, HR800, at a laser wavelength of 514 nm. The chemical compositions were measured on X-ray photoelectron spectroscopy (XPS) of Escalab 250, Thermo. The electrical conductivity was tested by a four-point probe method on the Jandel, RM3 with a pin-distance of about 1 mm. The powder samples were pressed at room temperature between two plungers into a hollow stainless-steel cylinder at a pressure of 15 MPa for 30 s. The obtained disc-like samples with a diameter of 13 mm and a thickness of 0.8 mm, were measured at three different positions. The average values were acquired within an error range of $\pm 1\%$. N₂ adsorption-desorption isotherms were obtained on the Quantachrome Instrument to measure the specific surface areas and pore size distributions of samples, based on the multipoint Brunauer-Emmett-Teller (BET) and non-local Density Functional Theory (NLDFT) model using slit model, respectively.

2.4 Electrochemical testing

Two-electrode symmetrical cells were used to characterize the supercapacitive performances of our samples. The electrodes were prepared by pasting a slurry including 95 wt.% GCNS and 5 wt.% polyvinylidene difluoride (PVDF) binder without conductive additive onto the current collector of conducting carbon-coated aluminium foils (MTI Technologies). The as-prepared electrodes were dried at 100°C for 12 h in vacuum oven and then were pressed at 10 MPa with a thickness of $\sim 95\ \mu\text{m}$. The final mass loading on one electrode is around $5\ \text{mg cm}^{-2}$ with a packing electrode density of $0.53\ \text{g cm}^{-3}$. A glass-fiber membrane (Whatman) was used as the separator, and an IL mixture of EMI TFSI and EMI BF₄ with volume ratio of 80:20 was used as the electrolyte. Finally, the symmetrical cells were assembled in an argon-filled glove box. For the symmetrical cells, the cyclic voltammetry (CV) curves, galvanostatic charge/discharge voltage profiles and electrochemical impedance

spectroscopies were measured on a CHI660D electrochemical workstation. The specific capacitance C (F g^{-1}) was calculated from the upper part of discharge curves after voltage drops, according to $C = 2I/[(dV/dt)m]$ where I (A) is the discharge current, dV/dt is the slope of discharge curves in the range of $V_{\max}$ to $V_{\max}/2$ and m (g) is the mass of active electrode material of one electrode. The energy density E (Wh kg^{-1}) and power density P (W kg^{-1}) were calculated from $E = CV^2/(8 \times 3.6)$ and $P = E/t$, respectively, where V (V) is the discharge voltage and t (h) is discharge time.

3. Results and discussion

3.1 Physicochemical characterization

Figure 1 highlights the morphology characterization of the GCNS. Numerous interconnected nanosheets with high-aspect-ratio graphene-like structures could be observed from the FESEM (Figure 1a and b) and FETEM images (Figure 1c). The incompactly crumpled and folded nanosheets assembled a mass of cage-like structures that can act as ion-buffering reservoirs to enhance ion transport kinetics during the electrochemical process [10]. The high-resolution FETEM image (Figure 1d) highlights the single nanosheet of GCNS consisting of several graphene-like layers, with thickness of approximately 7.5 nm. The selected area electron diffraction image (inset of Figure 1d) presents the hexagonal patterns corresponding to the reflections of the graphene plane [23]. This finding indicates that the conjugated sp^2 graphitic domains were successfully constructed in the GCNS.

The unique interconnected graphitized carbon nanosheet structures of GCNS could be attributed to the combined effect of the intrinsic fiber structures of the biomass precursor ISSs and the synthesis strategy of the simultaneous carbonization-activation and post-vacuum-annealing process. Figure S1 illustrates the schematic of the synthesis process of GCNS. A 2D laminated structure was observed from the ISSs after the ultrasound-assisted pretreatment in DMAC. With their main composition of lignocellulose, terpene, phenolic, nootkatone, *etc.* [24], the ISSs could be converted into chars during the simultaneous carbonization-activation process at 900°C . Synchronously, a rapid contraction

occurred in all the dimensions of the chars, leading to the generation of the thinner nanosheet structures than that of the precursors. However, this contraction could be partly prevented by the ZnCl_2 and FeCl_3 that had been impregnated in the precursor interiors before carbonization. The ZnCl_2 further acted as the template and activation agents in favor of constructing the high specific area and hierarchical micro/mesopores [7, 25]. Furthermore, FeCl_3 can act as the iron catalyst to promote the formation of carbon nanosheet structures [25-27]. During the carbonization process, the iron catalyst can form the 2D carburized phase of Fe_3C layers when the temperature increasing to 600°C [26, 27]. Then the carburized phase could be transformed to $\alpha\text{-Fe}$ layers as the temperature rising to 800°C [26]. The $\alpha\text{-Fe}$ layers may synchronously act as an in situ self-template to build nanosheet structures by means of depositing carbon atoms exuded from Fe_3C and residual carbon atoms from the frameworks onto this self-template surface [26, 28]. The carbon nanosheet (CNS) was obtained by rinsing out inorganic impurities from chars. To obtain CNS structures successfully, these factors play key roles in the process, such as laminated structure of the ISSs having spatial confinement effect for the formation of 2D carburized phase, a high concentration of Fe^{3+} constructing the dense array in laminated ISSs which are then transformed carburized phase [26], and a high pyrolysis temperature needed. Then, the CNS underwent the post-vacuum-annealing process at 1200°C to further enhance the graphitization degree for the final product of GCNS. The final GCNS presents an obviously high electronic conductivity of 7.9 S cm^{-1} compared with 4.6 S cm^{-1} for CNS (Table 1), which is well comparable with 8.6 S cm^{-1} of Super P [19]. Notably, the CNS has the similar nano-morphology with the GCNS but without apparently ordered graphitic structures even at the edge of the nanosheets (Figure S2). This finding suggests that the post-vacuum-annealing treatment can successfully construct the partially ordered graphitic structures, which was used as a universal tool to tailor the graphitization degree of carbon electrodes in spite of a high energy demand [10, 17].

Figure 2a depicts the Raman spectra of the samples. Two characteristic peaks of D-band at 1355 cm^{-1} and G-band at 1598 cm^{-1} were observed, which are assigned to the breathing modes of C sp^2 atoms in rings, and the bond stretching of C sp^2 atoms in both chains and rings [29], respectively. The integral I_G/I_D ratio of GCNS (1.23) is significantly higher than that of CNS (0.94), demonstrating less number of defects and larger graphitic domain length L_a in GCNS than that in CNS [29]. The Raman spectroscopy of GCNS also appears the second-order 2D peaks caused by the second-order zone boundary phonons [30], further indicating that the GCNS has a more ordered graphitic structure than that of the CNS [31]. The graphitization degree of our samples is further surveyed through the XRD analyses (Figure 2b). Two peaks corresponding to graphitic domains of the graphene layer stacking (002) and ordered hexagonal graphitic structure (100) are observed [8, 31]. The average interlayer distance d calculated from the central position of (002) peaks is 0.38 nm for GCNS and 0.40 nm for CNS, which are higher than that of the functionalized graphene (0.37 nm) [32]. The related calculation could be found in the supporting information. The high interlayer spacing may result from the formations of graphite lattice through nucleation or growth from biomass-based precursors as well as 2D carburized phase instead of reordering of the existing graphene layers. A bit low average interlayer distance of GCNS compared with that of CNS could result from the post-vacuum-annealing process. Based on the (100) peak, the obtained L_a of GCNS is up to 7.28 nm larger than that of CNS (2.36 nm) [33], which further confirms a high graphitization degree of the former that is in good agreement with their Raman analyses.

The textural characteristics of the samples were investigated by N_2 adsorption-desorption at -196°C . The hybrid I/IV-type isotherms are observed from Figure 2c, indicating the existence of a hierarchical pore size distribution. The pore size distribution of GCNS calculated by the NLDFT method mainly consists of bimodal mesopore systems around 3.3 and 6.4 nm (accounting for 82.3% of total pore volume) and a small amount of micropore at 1.2 nm (Figure 2d). The outcome is attributed to the combined effect of the ZnCl_2 activation that is beneficial to the development of

small mesoporosity [34] and the post-vacuum annealing process. Remarkably, the high mesoporosity can provide efficient ion-transport ways for matched IL electrolyte ions (EMI^+ of 0.43-0.79 nm, TFSI^- of 0.29-0.76 nm, and BF_4^- of 0.45 nm [11]) in the electrochemical process. The specific surface area of GCNS is up to $2327 \text{ m}^2 \text{ g}^{-1}$ based on the BET method, which is mainly attributed to the ZnCl_2 activation creating a mass of micro/mesopores on the surface of nanosheets. As shown in Table 1, the GCNS has slightly lower specific surface area and micropore volume but higher mesopore volume than those of CNS, which are attributed to the post-vacuum annealing graphitization process that leads to the collapse of some micropore structures as well as the widening of pre-existing mesopores [35].

XPS was used to investigate different bonding states and surface functionalities of the samples, considering its high surface sensitivity in the range of less than 10 nm [17, 36]. Notably, the surface chemical composition and C/O ratio of the samples obtained from XPS (Figure 2e) are consistent with those of the elemental analyses (Table 1). Compared with the CNS, the GCNS presents low oxygen content (2.7 wt.%) and high C/O ratio because of the added elimination of the surface oxygen groups through the post-vacuum-annealing process. The oxygen content of GCNS is lower than those of Na- NH_3 -reduced graphene (5.6 wt.%) [37], thermal-reduced graphene (4.96 wt.%) [32] and commercial activated carbon for supercapacitor (Norit, 4.5 wt.%) [23]. The high C/O ratio of GCNS is in favor of the electrochemical stability, particularly in non-aqueous electrolyte systems [12]. The high-resolution C 1s spectrum of GCNS (Figure 2f) was deconvoluted by five peaks, including $\text{sp}^2 \text{ C}$ (284.6 eV), $\text{sp}^3 \text{ C}$ (285.7 eV), C-O (286.8 eV), C=O (287.9 eV) and O=C-O (289.5 eV) [8, 10, 32]. A smaller shoulder toward the high binding energy region obtained for GCNS suggests a higher content of sp^2 hybridized component compared with that of CNS. The sp^2/sp^3 ratio of 5.5 was achieved for GCNS higher than that of 2.8 for CNS (Table 2). These results further demonstrate the higher graphitization degree in GCNS than that in CNS, which is consistent with the above analyses.

3.2 Electrochemical performance

To demonstrate the supercapacitive performance of our samples, two-electrode symmetric coin-type supercapacitors (denoted as GCNS-SC and CNS-SC) were assembled using the IL mixture electrolyte, *i.e.*, EMI TFSI and EMI BF₄ with a volume ratio of 80:20 [11, 18]. As shown in Figure 3a and b, the CV curves of GCNS-SC still exhibit nearly rectangular shapes at a scan rate ranging from 100 to 4000 mV s⁻¹, indicating the formation of pure supercapacitor behavior with small equivalent series resistance (ESR) even at high rates [19]. Although the CV curves of CNS-SC similarly show the quasi-rectangular shapes at a low scan rate of 100 mV s⁻¹, they distort severely at the scan rates up to 1000 mV s⁻¹ (Figure 3a and Figure S3). These observations are due to a low mesopore volume and small conductivity of CNS, leading to a large ESR for CNS-SC compared with that of GCNS-SC. Figure 3c and d highlight the charge/discharge voltage profiles of GCNS-SC, which still display linearly triangular forms with smaller voltage drops at a current density ranging from 1 to 100 A g⁻¹ compared with the case for CNS-SC (Figure S3). These outcomes signify the efficient formation of a reversible capacitive behavior with an excellent rate performance in GCNS-SC [38, 39].

Figure 3e displays the rate performances of our devices, *i.e.*, specific gravimetric capacitances calculated from the upper part of discharge curves, in the wide current density range of 1-100 A g⁻¹. The GCNS-SC has a specific capacitance of 152 F g⁻¹ at 1 A g⁻¹, holding an ultrahigh rate capability of 87% initial capacitance at 100 A g⁻¹ compared with that of CNS-SC (40%). Based on the packing electrode density of 0.53 g cm⁻³, the volumetric capacitance is up to 80.6 F cm⁻³ (Figure S4). The outcomes are in agreement with their CV and charge/discharge evaluation. More importantly, only 4% loss was found for the specific capacitance of GCNS-SC in a current density range of 1-20 A g⁻¹. The surface area normalized capacitance for GCNS-SC is up to 6.8 μF cm⁻². These results are in good agreement with the charging/discharging kinetic analyses (Figure 3f). The electrode specific capacitance C could depict the form of $k_1 + k_2 t^{1/2}$, where k_1 represents a rate-independent factor

attributed to a reversible electrical double-layer capacitance, and $k_2 t^{1/2}$ stands for a diffusion-limited factor controlled by the charge/discharge time t (s) [40]. k_1 was extrapolated at the $t = 0$ intercept with the vertical axis. Noticeably, the rate-independent factor k_1 for GCNS-SC is 145 F g^{-1} , which is obviously higher than that of CNS-SC. The ultrahigh-rate performance of GCNS could be attributed to the effect of post-vacuum annealing treatment, which creates unique graphitized cage-like high-aspect-ratio nanosheet structures with higher graphitization degree and better conductivity leading to a smaller ESR, and higher mesopore volume providing more efficient ion-transport ways compared with CNS.

To further understand the high-level performance of GCNS-based electrodes, electrochemical impedance spectroscopy (EIS) was applied to reveal the ionic/electronic transport process (Figure 4a). In the low-frequency region GCNS-SC displays a more vertical curve than that of CNS-SC, manifesting a nearly ideal supercapacitor behavior with a smaller diffusion resistance in the former. As shown the insert of Figure 4a, the total cell resistance of GCNS-SC obtained by extrapolating the vertical portion to the real axis is $2.71 \text{ } \Omega$, which is obviously smaller than that of CNS-SC ($8.79 \text{ } \Omega$). The different total cell resistances primarily originate from the shorter Warburg Region and the smaller charge transfer resistance R_{ct} ($1.7 \text{ } \Omega$) of GCNS-SC than those of CNS-SC (R_{ct} , $3.72 \text{ } \Omega$) because of the higher mesopore volume in the former leading to the more efficient charge transport process [38]. R_{ct} was calculated from the diameter of the semicircle in the high- to medium-frequency region. The ESR of GCNS-SC (obtained from the first intercept of the plots with the real axis in high frequency region) is $0.27 \text{ } \Omega$ lower than that of CNS-SC ($0.77 \text{ } \Omega$), which is ascribed to the higher conductivity of GCNS. The outcomes are consistent with their CV and charge/discharge analyses.

The Bode plots of the frequency response are shown in Figure 4b. The phase angle of our devices is close to -90° at the low-frequency region, further indicating an ideal supercapacitor behavior [39]. The characteristic frequency f_o at a phase angle of -45° is 0.93 Hz for GCNS-SC while

0.51 Hz for CNS-SC, providing the relaxation time constant τ_o ($1/f_o$) of 1.08 s for the former shorter than 1.96 s for the latter. The small relaxation time constant of GCNS-SC is superior to those of advanced carbon electrodes in ionic liquid electrolytes, such as activated graphene (1.67 s) [38], hemp-derived carbon nanosheets (1.61-2.77 s) [4], carbide-derived carbon aerogel (~5 s) [41] and bamboo-derived beehive-like carbon (1.64 s) [10]. The outcome further confirms that the graphitized cage-like high-aspect-ratio nanosheet structure can provide a short relaxation time for ion transport and be in favor of fast-rate capability [30]. Nonetheless, not very high charge propagation and a high drop of capacitance at 1 Hz observed from the Bode plot (Figure 4b) may be attributed to the intrinsic structure of GCNS with partially ordered graphitic structures, more than 5 nm thickness and a small amount of micropore. It is worth mentioning that the drop of capacitance for GCNS-SC at 1 Hz is considerably comparable to or less than those of previously reported high-rate ionic liquid-based supercapacitors with biomass-based carbon electrodes, such as algae-derived porous carbons [42], lignin-derived porous carbon [43], shrimp shells-derived nitrogen-doped carbon nanosheets [11], hemp-derived carbon nanosheet [4] and reed-derived porous carbon nanosheets [44].

GCNS-SC also displays an excellent cyclic stability of 97.6% capacitance retention after 10,000 cycles at 10 A g⁻¹ (Figure 5a and b), whereas CNS-SC only displays 89% at the same test condition (Figure S5). After a long cycle test, the GCNS-SC still holds a small cell resistance that only increased by 9.2% of the initial value, whereas that of CNS-SC increased by 62.7% (Figure 5c). Moreover, the GCNS-SC still holds high Coulombic efficiency (~100%) and high energy efficiency (>93%) from initial to final cycle. These outcomes indicate that GCNS-SC has a state-of-health at the operating voltage window of 3.5 V [15]. These findings are ascribed to the higher graphitization degree and better conductivity of GCNS than those of CNS, which resulted in less degradation of electrolyte on the interface between electrode and electrolyte [10]. As shown in Table S1, the supercapacitive performance of GCNS is clearly known to stay at the state-of-the-art level for carbon

nanosheets and even advanced graphenes in non-aqueous electrolytes [21, 26, 30, 38, 44, 45].

The Ragone plots (Figure 6) are used to evaluate the energy and power characteristics of our devices based on the active electrode materials. The max energy density was obtained of 64.7 Wh kg⁻¹, *i.e.*, 33.6 Wh L⁻¹ (Figure S6) for GCNS-SC. The high-rate capability of GCNS-SC results in an excellent energy density retention of 56.1 Wh kg⁻¹ (29.2 Wh L⁻¹) even at high power density of up to 93.1 kW kg⁻¹ (48.4 kW L⁻¹), while CNS-SC only holds 26.9 Wh kg⁻¹ (13.9 Wh L⁻¹). These results highlight that GCNS-SC presents integrated high energy-power properties compared with CNS-SC. The energy and power characteristics of GCNS-based electrodes are also compared with those of the state-of-the-art biomass-derived carbon nanosheet electrodes from hemp [4], silk [8], coffee grounds [9], shrimp shells [11] and reed [44], biomass-derived porous carbon electrodes from soybean root [46], algae[42] and cellulose nanofibril [47], graphene-based electrodes such as N-doped reduced graphene oxide aerogel [48] and S, P-codoped porous graphene aerogels [49], and other advanced carbon electrodes such as carbon nanosponge [50] and carbon nanofiber[51] in ionic liquid electrolytes.

To extrapolate the practical performances of the assumed packaged cells, the normalized energy and power densities based on the total device can be inferred from a fourth of the values based on the electrode material [1, 8, 38]. The normalized energy densities of our assembled devices are 14-16 Wh kg⁻¹, which can potentially compare against lead-acid batteries and nickel metalhydride (Ni-MH) batteries. The normalized power densities are 1.1-23.2 kW kg⁻¹, which are one order of magnitude higher than those of Ni-MH batteries. Thus our devices can be well compared with those of commercial energy storage devices (Figure 7) [40].

The outcomes demonstrate that the GCNS-SC has excellent rate capability, fast frequency response, high cyclic stability and integrated high energy-power property. The high-level supercapacitive performances of GCNS are attributed to the synergism of these distinct characteristics as follows. First, the special cage-like structures with thin walls and high mesopore

volume can provide short diffusion distances for rapid ionic transport with limited diffusive resistance even at high discharge rates. Second, the high-aspect-ratio nanosheet with high specific surface area and hierarchical micro/mesopore systems can generate large surface charge storage because of the abundantly ion-accessible surface and active sites for high areal stack capacitances. Third, the high graphitization degree and excellent conductivity not only possibly accelerate electronic transfer kinetics, leading to small charge transfer resistance and high rate/power property, but also provide abundant charge carriers for more charge screening that generates a high capacitance value.

To further evaluate the effect of post-vacuum-annealing process on the electrochemical performances, two control samples of GCNS-1 and GCNS-2 were prepared at different vacuum-annealing temperatures of 1000 and 1400°C, respectively. As shown in Figure S7, the GCNS-1 has a low rate capacity compared with GCNS, which could be due to the low vacuum-annealing temperature of 1000°C that leads to low graphitization degree and inferior conductivity. However, the GCNS-2 exhibits a better rate property but a lower capacitance response than that of GCNS. This outcome is a result of an excessively high vacuum-annealing temperature of 1400°C, generating an excellent conductivity but simultaneously causing a significant amount of collapse of the pre-existing pore systems (Figure S7c and Table S2). Thus, the post-vacuum-annealing process at 1200°C is a good trade-off. Notably, other synthetic conditions (ISSs/ZnCl₂ ratio and activation temperature) of the samples were also optimized based on their electrochemical performances (Figure S8).

4. Conclusions

Sustainable GCNS has been successfully prepared using inner shaddock skins as carbon source. High-rate ionic liquid-based supercapacitors based on the GCNS electrodes have been constructed. The device exhibits an excellent rate capability of 87% initial capacitance at 100 A g⁻¹, an integrated high energy-power property at energy density of 56 Wh kg⁻¹ (29.2 Wh L⁻¹) corresponding to a high

power density of 93 kW kg⁻¹ (48.4 kW L⁻¹), and a long cyclic life of 97.6% capacitance retention over 10,000 cycles in the IL mixture electrolyte. These outcomes are attributed to the synergistic effect of the characteristics of GCNS electrodes, such as cage-like ultrathin nanosheet structure (~8 nm thickness), large surface area (2327 m² g⁻¹), hierarchical micro/mesopore systems (82.3% mesopore volume), high graphitization degree (graphitic domain length L_a of 7.28 nm and sp²/sp³ ratio of 5.5) and excellent electronic conductivity (7.9 S cm⁻¹). Simultaneous carbonization-activation and post-vacuum-annealing processes are extremely important for the preparation of GCNS. The post-vacuum-annealing strategy can be used as a facile tool to enhance the graphitization degree for biomass-based carbon electrodes, which can effectively improve the rate capability coupled with the energy and power property especially in IL electrolytes.

Supporting Information

Supporting Information is available from the Online Library or from the author.

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Figure Captions

Figure 1. (a, b) FESEM, (c) FETEM and (d) high-resolution FETEM images of the GCNS. Inset of (d) is the selected area electron diffraction pattern.

Figure 2. (a) Raman spectra, (b) XRD patterns, (c) N₂ adsorption-desorption isotherms and (d) pore size distribution, and (e) XPS survey spectra and (f) C1s spectra of GCNS and CNS.

Figure 3. (a) CV curves of GCNS-SC and CNS-SC at scan rates of 100 and 4000 mV s⁻¹, (b) CV curves of GCNS-SC at different scan rates, (c) charge/discharge voltage profiles of GCNS-SC and CNS-SC at current densities of 1 and 100 A g⁻¹, (d) charge/discharge voltage profiles of GCNS-SC at different current densities, (e) specific capacitances at different current densities, and (f) specific capacitance versus square root of discharge time of GCNS-SC and CNS-SC.

Figure 4. (a) Nyquist plots and (b) Bode plots of phase angle versus frequency of GCNS-SC and CNS-SC.

Figure 5. (a) Cycling stability and the Coulombic efficiency, and (b) first and final charge/discharge voltage profiles of GCNS-SC at 10 A g⁻¹. (c) Nyquist plots of GCNS-SC and CNS-SC after 10,000 cycles.

Figure 6. The Ragone plots (upper) of GCNS-SC and CNS-SC, and the performance of GCNS-SCs compared to those of the state-of-the-art reported advanced supercapacitors (down).

Figure 7. The Ragone plots of packaged GCNS-SC based on total-device mass and the performance comparison with several standard devices (Data from ref. 40).

Table 1. The physical and chemical parameters of GCNS and CNS.

Sample	Conductivity [S cm ⁻¹]	Carbon structure ^a			Textural property					XPS [wt.%]			Element analysis	
		I_G/I_D ^[a]	d ^b	L_a ^c	S_{BET} ^d	S_{DFT} ^e	V_t ^f	V_{micro} ^g	V_{meso} ^h	C	O	C/O	C	O
GCNS	7.9	1.23	0.38	7.28	2327	2156	1.56	0.27	1.29	97.3	2.7	36	97.1	2.9
CNS	4.6	0.94	0.40	2.36	2513	2308	1.68	0.69	0.99	84.3	15.7	5.4	83.9	16.1

^a I_G/I_D is integral ratio of G-band peak and D-band peak. ^b d is the average interlayer distance. ^c L_a is the average graphitic domain width. ^d S_{BET} is the specific surface area calculated by Brunauer-Emmett-Teller (BET) method. ^e S_{DFT} is the specific surface area calculated with density functional theory (DFT) method. ^f V_t is the total pore volume. ^g V_{micro} is the micropore volume. And ^h V_{meso} is the mesopore volume.

Table 2. Data from XPS on the binding state of GCNS and CNS.

Functional group	sp^2 [%]	sp^3	sp^2 / sp^3	C-O	C=O	C=O-O
B. E. [eV]	284.6	285.7	--	286.8	287.9	289.5
GCNS	76.1	13.9	5.5	5.4	1.2	3.4
CNS	55.1	18.2	2.8	13.2	3.2	10.3

Figure 1

Figure 2

Figure 3

Figure(4)

Figure 4

Figure(5)

Figure 5

Figure(6)

Figure 6

Figure(7)

Figure 7