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Three Dimensional Graphitized Carbon Nanovesicles for Highperformance Ionic Liquid-based Supercapacitors

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Three dimensional nanoporous carbon with interconnected vesiclelike pores (1.5-4.2 nm) has been prepared through a low-cost template-free approach from petroleum coke precursor by KOH activation. It is found that the thin pore walls are highly graphitized and consisting of only 3~4 layers of graphene, which endows the material with an unusually high specific surface area (2933 m² g⁻¹) and good conductivity. With such unique structural characteristics, when used as supercapacitor electrodes in ionic liquid electrolytes, the graphitized carbon nanovesicle (GCNV) material displays superior performance, such as high energy densities up to 145.9 Wh

Introduction

Supercapacitors, a class of electric double layer capacitors (EDLCs), can store energy by physically adsorbing opposing electrolyte charges in two closely packed electrodes and deliver significantly higher power density (~10 kW kg⁻¹) than batteries (usually < 1 kW kg⁻¹), which makes them promising as power devices for various portable consumer electronic devices, uninterruptable power supplies, energy efficient industrial equipment, electric and hybrid electric vehicles and power grid applications.^[1-9] However, the energy density (~ 5 Wh kg⁻¹) of supercapacitors is much lower than that of batteries (26-34 Wh kg⁻¹ for lead acid batteries and 100~180 Wh kg⁻¹ for lithium-ion batteries). This limits their applications to those devices requiring both high power and energy. Therefore, current efforts in developing future supercapacitors mainly

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 $\rm kg^{-1}$ and high combined energy-power delivery that an energy density of 97.6 Wh $\rm kg^{-1}$ can be charged in 47 seconds at 60 $^{\circ}\rm C$. This demonstrates that the energy outputs of the GCNV-based supercapacitors are comparable to that of batteries while the power outputs are still one order of magnitude higher. Moreover, the synergistic effect of the GCNVs and IL electrolyte on the extraordinary performance of the GCNV supercapacitors has been analyzed and discussed.

focus on the improvement in energy density while maintaining high power density to match the demand in applications.

Since the electrical energy of EDLC (E) is calculated by the formula: E=1/2 CU^2 (where U is the working voltage. depending on the electrochemical stability of the electrolytes. and C is the capacitance, decided essentially by the properties of the electrode materials),^[10] the strategies for high energy performance are usually via two approaches, i.e. exploiting materials with enhanced capacitance or employing the electrolytes with high electrochemical stability. According to the formula, $C = \varepsilon_r \varepsilon_0 A / 4\pi d$ (ε_r is the electrolyte dielectric constant, ε_0 is permittivity of a vacuum, A is the electrode specific surface area, and d is the effective thickness of the electric double layer), it can be deduced that larger specific surface area of electrodes leads to a higher charge storage capacity. From this viewpoint, a variety of porous carbonaceous materials (AC),^[11-14] including activated carbons mesoporous carbons,^[15-19] carbon aerogels,^[20-21] and carbide-derived carbons^[22-23] have been widely adopted as electrode materials for EDLCs, owing to their advantages of high surface area as well as excellent chemical stability and Usually, relatively low cost. compared with mesoporous/macroporous carbon materials, microporous carbons possess higher specific surface area (SSA) and can achieve higher capacitances. However, these are often realized in aqueous electrolytes, because micropores can only be accessible to small aqueous electrolyte ions.^[4] As a consequence, despite high capacitances, the energy of microporous densities these materials-based supercapacitors are not satisfying because of their narrow electrochemical window (U < 1 V) of aqueous electrolytes. Moreover, due to poor ion transport of narrow micropores, the capacitances as well as energy densities drop sharply at high charge/discharge rate when high power uptake is needed.

On the other hand, as is well known, ionic liquids (IL) are a kind of ideal electrolytes for supercapacitors due to their unique properties such as high thermal stability and non-

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flammability, which can improve the working temperature range and safety of supercapacitors, $^{[24-25]}$ and especially, wide electrochemical windows of 3-4 V, which can contribute greatly to energy density of supercapacitors (E=1/2 CU²). However, when using ILs as the electrolytes for supercapacitors, it requires larger mesopores (2-3 nm) of carbon materials to match IL ions for free access, distortion and insertion/desertion during cycling.^[26] This is usually at the expense of the SSA (A) of carbon materials (SSA < 2000 m² · g⁻¹), ^[26-28] and thereby leads to a low capacitance (C = $\epsilon_r \epsilon_0 A/4\pi d$) and energy density of the system (E=1/2 CU²). Therefore, all things considered, developing new structured carbon materials with IL ion-compatible large pore size and yet high SSA simultaneously is crucial for supercapacitors to obtain both high energy and power density. However, this still remains a great challenge.

In this work, three dimensional (3D) nanoporous carbon consisting of interconnected vesicle-like pores (1.5-4 nm) has been prepared through heat treatment of petroleum coke precursor using KOH as an activation agent. The nanovesicle walls are ultrathin, which are made of 3-4 layers of graphene. In addition, the as-synthesized graphene nanovesicles (GCNVs) exhibit an ultrahigh SSA of 2933 m² g⁻¹, which is about 2 times of normal mesoporous carbon materials (<2000 m² g⁻¹). As expected, the GCNVs display superior performance such as high energy densities of 83 Wh kg⁻¹ at 30 °C and 97 Wh kg⁻¹ at 60 °C that are comparable to batteries, with respective power densities of 15 kW kg⁻¹ and 7.5 kW kg⁻¹ that are one order of magnitude higher, even at a high current density of 9.6 A g⁻¹. To our knowledge, this result is among the best comprehensive performance that has been reported for porous carbon materials-based capacitors. The key to success is ascribed to the structure characteristics of the GCNVs, such as fully accessible high SSA for electrolyte ion adsorption, vesicle-like quasi-mesopores matching IL ion size for direct access of the IL ions, as well as good electronic conductivity for rapid ion transport, which contribute synergistically to the high energy and power densities.

Results and Discussion

A typical scanning electronic microscopy (SEM) image of the GCNV material is shown in Figure 1A. It can be seen that the particle of the GCNV material exhibits an irregular shape with a size of ~15 µm, accompanying with some fragments standing on its surface (Inset in Figure 1A). The high-magnification image shows clearly that the particle surface is very rough, consisting of a layer of densely distributed nanofoams with sizes estimated to be several nanometers. Figure 1B presents a typical transmission electronic microscopy (TEM) image obtained from edge region of a particle, where a number of nanopores with circle-like outlines can be observed, suggesting a porous texture of the material. The electronic diffraction (ED) pattern (Inset in B) corresponding to the observed area in Figure 1B gives a set of diffraction rings that can be readily assigned to (002), (100), (101) and (110) planes, respectively, of hexagonal structure of carbon (carbon, JCPDS 25-0284), revealing that the material is crystalline with graphitized structure. From the high-resolution TEM images shown in Figure 1C and Figure S1, it is observed that the nanopores have sizes mainly less than 5 nm with very thin walls composed of 2-4 layers of graphene, which is well

exemplified by an individual pore whose wall is composed of 4 layers of graphene (Inset of Figure 1C). The structure of multiple layer graphene with curved shape can also be reflected in its corresponding Raman spectrum (Figure 2A). The Raman spectrum shows two prominent peaks, at 1341.3 and 1594.5 cm⁻¹, that well-documented as D and G peaks for graphene materials.^[13b] The broadening of D peak implies considerable bond disorder or defects, which is caused by curved graphene.^[13b] These multiple-wall pores are reminiscent of the well-known vesicles in cell biology, i.e., a kind of ordered assemblies with multiple-layer structure, formed by amphiphilic molecule self-assembly and responsible for efficient intracellular/extracellular mass exchange via their interfaces. The X-ray diffraction (XRD) pattern of the as-prepared GCNV materials (Figure 2B) displays broad diffraction peaks corresponding to (002), (100) and (101) planes, respectively, of graphitized carbon (JCPDS card no. 25-0284), in good agreement with TEM analysis and ED result in Figure 1B. In addition, the Brunauer-Emmett-Teller (BET) measurement (Figure 2C) reveals that the GCNV material is nanoporous with an ultrahigh SSA of 2933 $\mbox{m}^2\mbox{ g}^{\mbox{-}1}$ and a high pore volume of 1.692 m³ g⁻¹ (see Table S1). Importantly, the pore size distribution curve in Figure 2D indicates the nanopores have a



Figure 1. SEM (A), TEM (B) and HRTEM (C) images of the GCNVs. The inset in A is SEM image of the GCNV material in low magnification. The inset in B is the corresponding electronic diffraction (ED) pattern of the observable area in B. The inset in C shows typical structure of a GCNV labeled within the square in C.

narrow size distribution (1.5~4 nm) centered at about 1.8 nm. Evidently, the pores are interconnected throughout the entire material after the GCNV formation, since they are created by KOH activation from the outer surfaces to interiors of the petroleum coke precursor.^[29] Therefore, although with larger quasi-mesopores, the GCNVs exhibit an unusually high SSA, which should be ascribed to the ultrathin pore walls, the quite uniform pore distribution and the high pore population density over the material. We noted that 3D carbon materials with welldefined pore shapes have been reported via different approaches including the template method. For example,

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onion-like carbon from nanodiamonds,^[27] cage-like carbon from MgO templating,^[28] 3D macroporous graphene from PS spheres, [30] ordered mesoporous carbons from soft pluronic F127^[16b] or microporous nanographene via sol-gel polymerization^[13b] and macroporous graphene foams through leavening process.^[18b] These materials obtained are either microporous with high SSA (up to 3000 m² g⁻¹), or meso-/macroporous with low SSA (< 2000 m² g⁻¹). As analyzed above, they are not favorable for high performance supercapacitors from the viewpoint of applications (see more discussion given in S1). In contrast, the 3D GCNV material containing quasi-mesopores and ultrahigh SSA is unusual. It should be pointed out that the structure of the GCNV material depends highly on the synthetic parameters. For example, slight change in KOH amounts or activation temperature in our synthesis will result in the formation of two separate regions of pore distribution and sharp decrease of SSA (see Figure S2 and Table S1). We consider moderately high temperature at appropriate mass ratios (2.5~3.5) of KOH to the precursors is crucial for the guasi-mesopore formation. However, since carbon activation is very complex process, it is difficult to determine a clear correlation between the carbon structure and system parameters.^[9b] To the best of our knowledge, this is the first time that a carbon material possessing a larger pore size (quasi-mesopore) and an ultrahigh SSA with a unique vesiclelike pore structure has been prepared. With optimal combination of pore size and SSA, the GCNV material is expected to serve as a promising electrode material for highperformance supercapacitors, as discussed above.



Figure 2. Raman spectrum (A), XRD pattern (B) and nitrogen adsorption-desorption isotherm (C) with corresponding pore size distribution curve (D) of the GCNV material.

As a kind of classic ionic liquid with respective van der Waals radius of 0.76 nm (cations) and 0.33 nm (anions) and a wide electrochemical window of 3.5 V (see Figure S3), 1-ethyl-3-methylimidazolium tetrafluoroborate ($\rm EMI^+-BF_4^-$) was selected as the electrolyte for the GCNV-based supercapacitors. As shown in Figure 3A, cyclic voltammogram (CV) test with various cutoff voltages is applied to the GCNVs at a scan rate of 20 mV s⁻¹. All the CV curves give rectangular shapes, which indicate that the supercapacitor based on the GCNVs and EMI-BF4 is stable at high operating voltage up to 3.5 V. Therefore, the voltage range of 0 ~ 3.5 V was applied to the research system hereafter. As the sweep rate is increased from initial 20 to 80 mV s⁻¹, the CV curve cycled with the cutoff voltage of 3.5 V still retains nearly rectangular shape (Figure 3B). In Figure 3C, the discharge curves of the GCNV supercapacitor display nearly linear response at different current densities from 0.6 to 9.6 A g⁻¹, with corresponding discharge time from 672 to 19.3 s, respectively. Both of above results imply a typical double layer capacitive behavior and little contribution of pseudocapacitive behavior of the GCNVbased supercapacitor. The small peaks (~1.25 V) in CV and the slight deviations in discharge curves, as well documented, are probably caused by trace amounts of oxygen containing groups on the GCNV surface after activation.^[35] In addition, the GCNV supercapacitor also exhibits very good cycling performance. It should be pointed out that, unlike the pseudocapacitors, EDLCs often have significantly long cycling



Figure 3. Supercapacitor performance of the GCNV material in the EMI-BF₄ electrolyte at 30 °C. (A) Cyclic voltammogram (CV) curves cycled to different maximum voltages (scan rate: 20 mV s⁻¹) and (B) Cyclic voltammogram (CV) curves cycled at various scan rates. Rectangular shapes indicate the capacitive behavior. (C) Galvanostatic discharge curves of the GCNV-based supercapacitor under different constant currents. (D) Charge-discharge performance at 0.9 A g⁻¹.

life (> 100,000 cycles) due to the absence of faradaic redox reactions. As shown in Figure 3D, galvanostatic chargedischarge curves are completely reproducible during the first 10 cycles, and give a high retention of over 98% even after first 2,000 cycles at a current density of 0.9 A g⁻¹ (Figure S4). It can be observed that there is a slight IR drop at the beginning of each discharge, which is resulted possibly from the internal resistance or equivalent series resistance (ESR)^[31,32] of the GCNVs in EMI-BF₄ electrolytes. The ESR of the GCNV material is measured to be 4.0 ohm at the temperature of 30 °C (Figure 4A). This value is comparable to other graphene-based supercapacitor in the presence of organic or high-viscosity IL electrolytes,^[33,34] owing to the high conductivity of assynthesized GCNV shows that capacitance decreases

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sharply by about 80% from 0.03 to 1.3 Hz (Figure 4B). Since mesopores are responsive in this range of frequency, this means the capacitance is mainly contributed by the mesopores. This result also mirrors the BET measurement in Figure 2C and D, indicating the quasi-mesoporous nature of the GCNV material.



Figure 4. (A) Nyquist plots of the GCNV electrodes at 30 $^{\circ}$ C (blue color) and 60 $^{\circ}$ C (red color). ESR was decreased from 4.0 to 1.38 ohm when increasing the temperature from 30 to 60 $^{\circ}$ C. (B) Normalized Bode diagrams of the real part of the GCNV-based capacitance versus frequency at 30 $^{\circ}$ C.

The specific capacitances (C_{ss}) at different current densities can be calculated to be 221.3, 214.3, 209.4, 196.6 and 189.7 F g⁻¹ (see equation 2 in S2) in terms of the discharge curves in Figure 3C, which shows a downward tendency with current density increasing from 0.6 to 9.6 A g⁻¹, as shown in Figure 5A. The corresponding energy and power densities are further calculated out according to the equations 2 and 3 in S2, as shown in Figure 5B, where the energy densities of 94.1, 91.2, 89.1, 83.6 and 80.7 Wh kg⁻¹ are achieved with the corresponding power densities of 488, 978.8, 2,228.7, 5,282.7 and 15,047.2 W kg⁻¹, respectively. It can be concluded that the GCNV-based supercapacitors are capable of storing a maximum energy density of 94.1 Wh kg⁻¹, and retaining a high energy of 80.7 Wh kg⁻¹ at very high cycling rate with the discharge time less than 20 s (19.3 s). The values for energy and power density were calculated according to the mass of the GCNV electrode material. Based on a weight ratio of 30% for the active electrode material in the packaged supercapacitor device, the practical energy density for the large-scale GCNV-based supercapacitor of up to 28.2 Wh kg⁻¹ can be obtained. Compared with other carbon material-based supercapacitors with IL electrolytes, the GCNV supercapacitor is able to deliver higher energies at the same current densities applied. For example, as shown in the inset of Figure 5B, the energy densities of the GCNV supercapacitor are close to or even outperform current graphene supercapacitors,^[33-35] and are more than twice as high as the porous carbon^[31,36] or carbon nanotube-based supercapacitors.^[37,38] Therefore GCNV



Figure 5. The specific capacitance of GCNVs in EMI-BF₄ at different specific current at (**A**) 30 °C and (**C**) 60 °C, Ragone plot for GCNV electrode with 3.5 V cutoff voltages (**B**) and performance comparison between several different energy storage devices (**D**) ^[3]. Inset of B shows performance comparison of energy density *versus* current density between the GCNV and other carbon materials based supercapacitors. The GCNV electrode presented in this study shows higher power densities than batteries and fuel cells (**D**).

supercapacitors do not only have a higher energy output than current graphene-based devices, but also can be fabricated at lower costs. Furthermore, improved performance of the GCNVbased supercapacitor can be obtained at higher operating temperature. Figure 5C demonstrates that by readily elevating the temperature to 60°C, higher capacitances of 343.0, 301.9, 262.8 and 229 F g⁻¹ are obtained at the current densities of 1.2, 2.4, 4.8 and 9.6 A g⁻¹, respectively, which is ascribed to the high thermal stability and resistance decrease of the GCNV supercapacitor (Figure 4A). Consequently, higher energy densities ranging from 145.9 to 97.6 Wh kg⁻¹ can be delivered at the temperature of 60°C, with discharge times of 588 ~ 47 s (Figure S5), which means, for the GCNV-based supercapacitor, a maximum energy density of 145.9 Wh kg⁻¹ can be stored and even an high energy density of 97.6 Wh kg⁻¹ stored can be recharged less than 1 min (47 s). For a packaged cell, the maximum energy density of above 43 Wh/kg⁻¹ can be expected. Figure 5D illustrates the Ragone plots of several main energy including traditional storage devices capacitors, supercapacitors, batteries and fuel cells,^[3] giving an intuitive comparison on their combinative performances. It can be seen

that the GCNV-based supercapacitor can provide high energy uptake approaching that of batteries and even fuel cells, while still remain high power output one order of magnitude higher. The high energy-power output with high operating temperature and electrochemical stability will endow the GCNV-based supercapacitors with an optimistic prospect for many important practical applications.

To further investigate the pore size influence of activated carbons on their electrochemical performance, the two control carbon samples (sample A and B, see Figure S2 and Table S1) with separated pore size distributions in micropore and mesopore regions were adopted as supercapacitor electrodes for comparison. From Figure S2, it can be seen that besides mesopore of around 2 nm, there are smaller micropore (< 1.5 nm) and bigger mesopore (~4 nm) existing in the control samples. The electrodes based on the sample A and B show respective ESR values of 6.2 and 3.7 ohm which are comparable to the GCNV (Figure S6). However, compared with the GCNV, the CV curves of the two electrodes conducted at various voltage scan rate display twisted rectangular shapes (Figure 6 A and B). In addition, as shown in Figure 6 C, the specific capacitances are much lower than the GCNV at the same current densities. Because of lower capacitance, energy densities of the control sample based supercapacitors are greatly decreased to 20-60 Wh Kg⁻¹, which are only 30~60 percent of the GCNV. Notably, excellent power output can also be achieved (Figure 6D) due to the existence of bigger mesopores (~4 nm) that are conducive to the diffusion of the IL ions. The capacitance decrease and energy deterioration are considered to be caused by incompatibility between IL ions and pore sizes of the control samples. As discussed above, the small micropores (< 1.5 nm) may block free entrance of IL ions and the bigger mesopores (~ 4.0 nm) allow more IL ions to get into, which result in the formation of incomplete double layers or disordered multiple layers within the pores rather than EDLs. The high compatibility between pore size and IL ions is crucial for the formation of effective EDLs with a minimal thickness (d) and the full availability of SSA (A), thus allowing the high capacitance (C = $\epsilon_r \epsilon_0 A/4\pi d$) and energy density (E=1/2 CU²).



Figure 6. Cyclic voltammogram (CV) curves of the sample A (A) and sample B (B) cycled at various scan rates, and the specific capacitance of the two control samples in EMI-BF₄ at different specific current at 30 °C (C and D)



Figure 7 illustrates the interaction between IL ions and the GCNVs on the electrode material interface (upper right), where IL ions can freely insert into the electrode material via 3D interconnected GCNV nanopores to form effective EDLs on the interface of the GCNVs. A charged GCNV is tentatively shown as an example to simulate the spherical EDL structure with positive holes on the GCNV walls and negative BF4⁻ ions inside the GCNVs (lower left), respectively. We think the superior performance of the GCNV-based supercapacitor is ascribed to the unique structure of the GCNVs. As illustrated in Figure S7, firstly, the ultrahigh SSA of the GCNVs provides abundant active sites for electrolyte ion adsorption, leading to the high capacitance and energy density. Secondly, the thin graphitized walls with high electronic conductivity are beneficial to IL ion delivery into the full inner surface of 3D GCNVs. This facilitates the ion transport and makes the SSA fully available, which are crucial for both high energy and high power density. Thirdly, the guasi-mesopores of the GCNVs with IL ion-compatible size, [26,39] serve as not only an effective pathway towards the full porous GCNVs, but also local reservoirs for IL ions to form effective monolayers, responsible for the high power and energy density as well. In fact, it had been proposed that, for porous carbon materials small pores (< 1.5 nm) would hinder IL ion insertion and only 2-3 nm or bigger pores guaranteed IL ion monolaver formation.^[26] Furthermore, theoretical simulation



Figure 7. Schematic illustration of interaction between the GCNVs and IL ions on interface of the GCNV electrode. The lower left shows the simulation of a charged GCNV forming a spherical EDL consisting of two layers of opposite charges (positive holes: red, negative BF₄⁻: blue) on the GCNV walls and inside the GCNVs, respectively.

for IL system showed a capacitance increase with pore size increasing from 1.1 to 1.3 nm,[39] indicating an upward tendency of capacitance with pore width increase in the quasimesopore region. These investigations also confirm that our quasi-mesoporous GCNV material is not only appropriate for EDL formation of IL ions, but also feasible to acquire high capacitance. Last, the utilization of ILs endows the device with operating temperature, and high especially, wide electrochemical window, contributing greatly to the high energy density. It should be pointed out that, aside from the points discussed above regarding the influence on the supercapacitor performance, ion behaviors in confined space of nanopores that lead to multiply-layered or incomplete double-layered structure may also be addressed for consideration.^[29] For better understanding of the ion behaviors within carbon nanopores, in situ characterization techniques and computational modeling are required.

Conclusions

In conclusion, 3D interconnected GCNVs have been prepared from the petroleum coke precursor by heating treatment with KOH. The GCNVs exhibit a narrow pore distribution (1.5- 4 nm) centered at 1.8nm and ultrathin graphitized walls with thickness of 2-4 layers graphene, which leads to an unusually high SSA of 2933 m² g⁻¹. Owing to their unique structural advantages, the GCNVs display superior performance as supercapacitor electrodes with neat IL electrolytes, such as ultrahigh capacitance (343.0 F g⁻¹) and energy density (145.9 Wh kg⁻¹), and high combined energy-power outputs, i.e., an energy density of 80.7 Wh · kg⁻¹ stored can be recharged in 20 s at 30°C, and a higher 97.6 Wh kg⁻¹ can be recharged in 47 s at the higher temperature of 60°C. Therefore, the GCNV-based supercapacitors are capable of delivering high energy as batteries and, simultaneously, high power as supercapacitors. The results demonstrate that our high-quality reproducible GCNVs are an improved material for new generation supercapacitors with low cost, high stability, and especially high energy and power density. Moreover, the GCNV material also has great potentials as efficient electrodes for lithium-ion batteries^[40,41] and conductive supports for visible photocatalysis^[42] and sensors,^[43] when loaded with functional counterparts such as metals or metal oxides. These related investigations are under way.

Experimental Section

Preparation of GCNVs. The petroleum coke precursors with pretreatment from Xinjiang Xintai Zhongli Company were firstly ground to about 28 mesh, heated to 400 °C at a ramping rate of 10 °C min⁻¹ and pre-carbonized at this temperature for 1 h in a tubular furnace under N₂ atmosphere. After cooled to room temperature naturally, the pre-carbonized activated carbons were ground to 180 mesh and soaked in KOH solution at certain weight ratio under stirring for 12 h. Then the mixture was dried, heated to 800 °C at a heating speed of 10 °C min⁻¹, and held for 20 min to accomplish the activation process. After washed with 1 mol L⁻¹ HCl, the solution was adjusted to neutral (pH ~ 6-7) with distilled water. Finally, the GCNV product was obtained after the mixture was washed by ethanol and dried at 120 °C for 8 h.

Material Characterizations. The structure of GCNV material was characterized by scanning electron microscopy (SEM, JEOL, JSM-6700F and Hitachi, S-4800), high-resolution transmission electron microscopy (HR-TEM, JEM 2011, 200 kV), power X-ray diffraction using a D/max2550VB3+/PC X-ray diffractometer with Cu Kα radiation with a 1.5418 Å wavelength. The Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) of the powders was analyzed by N₂ adsorption in a Tristar 3000 nitrogen adsorption apparatus at 77K. The Raman spectrum was recorded on a spectrophotometer (XploRA, Horiba Jobin Yvon) with a 532 nm laser.

Device assembly. Ionic liquid of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄) (purchased from Lanzhou Institute of Chemical Physics, CAS) were treated with molecular sieves (4Å) for 2 days before use. The electrodes were prepared by mixing the samples, carbon black and polytetrafluoroethylene (PTFE) in the mass ratio 80:10:10. The mixture was dispersed in ethanol and sonicated adequately to form a slurry. Then it was coated onto a nickel foam current collector (diameter = 10 mm), pressed at 8 MPa, and dried under vacuum at 120 °C for 24 h, forming an active film with a thickness of ~ 100 mm. The final mass on each electrode is 8.1 mg. Prior to cell assembly, the prepared electrodes were soaked in the ionic liquid at 40 ^oC for 12 h under vacuum to enhance the wettability between the electrode materials and ionic liquids. The cells were assembled in an Ar-filled glove box with water and oxygen contents both less than 1 ppm.

Electrochemical testing. The capacitive performance of the samples in the ionic liquid were tested by a symmetric twoelectrode cell and a glass microfiber filter separator (Whatman, (CV), GF/A). Cyclic voltammetry galvanostatic charge/discharge (GC) and electrochemical impedance spectroscopy (EIS) measurements were performed with a CHI 660 workstation (CH Instruments, USA) at ambient temperature. The scan rate of CV was varied from 10 to 100 mV s⁻¹ in the range of 0 ~ 3.5 V. GC measurement was carried out in the current range of 0.1 to 10 A g⁻¹. EIS was recorded by applying open circuit potential and an ac oscillation of 5 mV over the frequencies range of 100 kHz to 0.001 Hz.

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Entry for the Table of Contents

FULL PAPER

Three dimensional interconnected graphitized carbon nanovesicles have been prepared through a low-cost template-free method with quasimesopores (1.5-4.2 nm), ultrathin walls (3~4 layers of graphene) and an unusually high specific surface area (2933 $m^2 g^{-1}$). The unique structure endows the GCNV material-based supercapacitors with superior performance, such as high energy approaching to batteries and simultaneously power output one order of magnitude higher.



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CHEMISTRY & SUSTAINABILITY CHEMISTRY & SUSTAINABILITY

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Supporting Information

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Three Dimensional Graphitized Carbon Nanovesicles for Highperformance Ionic Liquid-based Supercapacitors

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S1. Detailed discussion

Conventional microporous carbon materials can easily obtain high specific surface area (SSA, over 2000 m²/g). However, due to their narrow pore size, they are often applied to aqueous electrolyte (U<1) based supercapacitors, because their narrow micropores can only be accessible to small aqueous electrolyte ions. Therefore, the microporous carbon based supercapacitors are able to deliver high capacitance due to the their high SSA ($C = \varepsilon_r \varepsilon_0 A/4\pi d$), but low energy ($E = 1/2 \text{ CU}^2$). Moreover, due to poor ion transport of narrow micropores, the capacitances as well as energy densities drop sharply at high charge/discharge rate when high power uptake is needed. On the other hand, for meso-/macroporous carbon materials, they have bigger pores (over 2 nm or bigger) but unsually low SSA ($<2000 \text{ m}^2/\text{g}$). Because of their bigger pore sizes that can be accessible to organic or ionic liquid ions, they can be applied to the organic or ionic liquid electrolyte based supercapacitors. Organic and ionic liquid electrolytes have wide electrochemical windows (U: up to 3.0 V for organic electrolytes and 4.0 V for ionic liquid electrolytes), which can contribute greatly to energy of the supercapacitors ($E = 1/2 \text{ CU}^2$) and thereby achieve relatively high energy. However, because the pores are big, it leads to SSA (A) decrease and low capacitance (C = $\epsilon_{t}\epsilon_{0}A/4\pi d$). In addition, if pores are too big, it will lead to sharp decrease of SSA (A), and increase of the effective distance of the ions to the carbon wall surface (d) due to the formation of electrochemical multiple layers in the pores. This often results in a much low capacitance ($C = \epsilon r \epsilon 0 A/4\pi d$), and low energy ($E = 1/2 CU^2$). In a word, the "matching" between the pores and IL ions is very important, which in fact guarantee free ion transport and maintain high power at the cost of minimum loss of SSA, because bigger pores, though can improve ion transport and power, will decrease SSA as well as energy.

Accordingly, for porous carbon materials, to obtain high performance, i. e., both high energy and power density, suitable large pore size compatible with ionic liquid ions and high specific surface area simultaneously are required, which can synergistically contribute to high cell voltage and capacitance, and high energy and power density eventually.

S2. electrochemical calculations.

The specific single capacitance (C, F g⁻¹) of the GCNV-based supercapacitors in GC measurements was calculated by using the following equation:

$$C = \frac{2i\Delta t}{m\Delta v} \tag{1}$$

Where *i* is the discharge current (A), $\Delta v/\Delta t$ is the slope of the discharge curves(V s⁻¹) calculated from upper half of the discharge curves and *m* is the mass (g) of the GCNV material on one electrode, respectively.

Since two-electrode cells were employed in the measurement, the specific energy densities (E_s , Wh kg⁻¹) and the specific power densities (P_s , W kg⁻¹) of the supercapacitors were calculated as follow:

$$E_{s} = \frac{1}{8} CV^{2} \cdot \frac{1000}{3600}$$
(2)
$$P_{s} = \frac{E_{s}}{t} = \frac{1}{8} \frac{CV^{2}}{t} \cdot 1000$$
(3)

Where V and t are the voltage applied (V) and the discharge time (s), respectively.



Figure S1. HRTEM images of the nanoporous carbon showing the typical vesicle-like pore structures (marked within the circles)



Figure S2. Nitrogen adsorption-desorption isotherms (**a**) and pore size distribution curves (b) of two activated carbons prepared at different conditions (see Table S1 for details).



Figure S3. Cyclic voltammograms of EMI-BF₄ ionic liquid with platinum as working and counter electrode, Ag/AgCl as reference electrode (Scan rate: 1 mV s^{-1}).



Figure S4. Cycling performance of the GCNV-based supercapacitor at a current density of 0.9 A g⁻¹.



Figure S5. Galvanostatic discharge curves of the GCNV-based supercapacitor under different constant currents of 1.2, 2.4, 4.8 and 9.6 A g^{-1} at 60 °C.



Figure S6. Nyquist plots of the two control carbon electrodes at 30 $^{\circ}$ C.



Figure S7. Schematic illustration showing synergistic contribution of the GCNV structure coupling with IL electrolyte to performance of the supercapacitors.

Table S1: Brief preparation conditions and textural characteristics of the three activated carbons including the GCNV material

Sample	KOH to precursor ratio	Activation temp. (°C)	$\frac{S_{BET}}{(m^2 \cdot g^{-1})}$	$\frac{S_{ext}}{S_{BET}}$	V_{tot} (cm ³ ·g ⁻¹)
А	3:1	700	1 154	4.33	0.619
В	4:1	850	2 000	7.55	1.157
GCNV	3:1	800	2 933	3.24	1.692

 S_{BET} , BET specific surface area; V_{tot} , total pore volume