Enlarging ion-transfer micropore channels of hierarchical carbon nanocages for ultrahigh energy and power densities

Jin Zhao^{1,2}, Hao Fan¹, Guochang Li¹, Qiang Wu¹, Lijun Yang¹, Yanwen Ma², Xizhang Wang^{1*} and Zheng Hu^{1*}

ABSTRACT Increasing the energy density of supercapacitor without sacrificing its high power is an everlasting pursuit in energy storage. Using ionic liquid electrolyte with high operating voltage can increase the energy density but usually at the expense of power density due to the large ion size, low ionic conductivity and high viscosity. Herein we demonstrate a simultaneous increase of the energy and power densities with ionic liquid electrolyte (EMIMBF₄) mainly by enlarging the ion-transfer micropore channels of the electrode material, i.e., the unique hierarchical carbon nanocages (hCNC). Boudouard reaction is adopted to tune the micropore size while remaining the hierarchical framework of hCNC. Meanwhile, the specific surface area, pore volume and conductivity are also increased under optimal activation temperature. Such a unique modification boosts the large-sized ion transfer, leading to the obvious decrease of equivalent series resistance and the dramatic increase of supercapacitive performance thereof. The optimized product exhibits an energy density up to 153.8 W h kg⁻¹ at the power density of 1.8 kW kg⁻¹, and maintains 54.0 W h kg⁻¹ even at an ultrahigh power density of 480.1 kW kg⁻¹. This study demonstrates an effective way to explore advanced electrode materials by the fine regulation of micropores and related properties.

Keywords: supercapacitors, ultrahigh energy and power densities, hierarchical carbon nanocages, micropore enlarging, ionic liquid electrolyte

INTRODUCTION

Advanced energy storage with both high energy and power densities is of vital importance to address the en-

ergy demands and promote the development of portable electronics and electric vehicles. Supercapacitors are known far superior to batteries in terms of power density and cycling stability, but inferior in energy density. Hence the application of supercapacitors is usually restricted in the fields only needing high power. To broaden the applications, increasing the energy density without sacrificing the power density becomes a challenging topic [1–5]. The energy and power densities of a supercapacitor are given by the formulas of $E=CV^2/2$ and $P=V^2/4R_{\text{ESR}}$, respectively. Accordingly, exploring the high-capacitance (C) electrode materials with small equivalent series resistance (R_{ESR}) and expanding the device operating voltage (V) are crucial to acquire both high E and P . As known, ionic liquid electrolyte has high operating voltage up to 4 V, and hence is usually used to enhance the energy density of supercapacitors. However, the use of ionic liquid electrolyte will lead to large R_{ESR} due to the large ion size, low ionic conductivity and high viscosity, thus resulting in a lower power density in comparison with the case in aqueous electrolyte [6–10]. The pore structure of the electrode material strongly influences the rate capability and the power density of a supercapacitor [11–16]. Consequently, optimizing the pore structure should be an effective way to compensate the power deterioration in the case of ionic liquid electrolyte.

In the past decade, abundant carbon-based materials in diverse forms and dimensions have been explored as supercapacitor electrode materials [17–22]. Our group reported the novel 3D hierarchical carbon nanocages (hCNC) featuring large specific surface area (SSA), co-

¹ Key Laboratory of Mesoscopic Chemistry of MOE and Jiangsu Provincial Lab for Nanotechnology, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

² Jiangsu Key Lab for Organic Electronics and Information Displays & Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing 210023, China

* Corresponding authors (emails: zhenghu@nju.edu.cn (Hu Z); wangxzh@nju.edu.cn (Wang X))

existing micro-meso-macropore structure, high conductivity and tunable wettability. Specifically, the nanocages interconnect to form the micrometer-sized nanosheets, which further assemble into three-dimensional (3D) sphere-like particles. The micropores penetrating across the shell have the small pore sizes of ca. 0.6 nm [4,23,24]. Such unique features result in the high supercapacitive performance, but still with the energy densities far below the batteries' [25–27]. We noticed that hCNC has the good wettability to ionic liquid of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) with the operating voltage up to 4 V, which is favorable for high energy density (Fig. S1) [27,28]. However the micropore channels of ca. 0.6 nm of hCNC is relatively small for the ion transfer of EMIMBF₄ with the EMIM⁺ ion size of 4.3 Å × 7.6 Å. In this study, Boudouard reaction, i.e., C + CO₂ = 2CO, was applied to enlarge the micropore size by activating (etching) the hCNC material. With the optimal activation temperature, all the important parameters for supercapacitors such as the pore size distribution, pore volume, SSA and electron conductivity of hCNC are improved, leading to the much enhanced energy storage capability in EMIMBF₄. The supercapacitor based on the activated hCNC (a-hCNC) at 900°C exhibits an ultrahigh energy density of 153.8 W h kg⁻¹ at the power density of 1.8 kW kg⁻¹, and maintains 54.0 W h kg⁻¹ even under an ultrahigh power density of 480.1 kW kg⁻¹, which locates at the top-level for carbon-based electrode materials.

EXPERIMENTAL SECTION

Preparation of samples

hCNC was prepared at 800°C by *in situ* MgO template method as described in our previous study [26]. In a typical procedure, basic magnesium carbonate (4MgCO₃·Mg(OH)₂·5H₂O) (4 g) with a 3D hierarchical structure was placed into a quartz tube in a vertical furnace. For the growth of hCNC, the furnace was heated up to 800°C in Ar at the flow rate of 100 sccm and heating rate of 10°C min⁻¹. Then benzene was introduced into the tube at the feeding rate of 65 μL min⁻¹ by a syringe pump for 12 min. During the growth, the sample was remixed by a flash of high-rate Ar flow of 1200 sccm with the interval of 1 min. The reactor was thus naturally cooled down to room temperature. The as-prepared sample was first stirred in 6 mol L⁻¹ HCl aqueous solution for 48 h to remove the MgO template and repeatedly washed with deionized water. Finally, the hCNC was obtained after drying at 80°C for 24 h. For a-hCNC preparation, 50 mg of obtained hCNC was placed into a quartz tube in a

horizontal furnace. The furnace was first flushed with Ar for 20 min and then heated to the designated activation temperatures of 800, 900 or 1000°C, respectively, at a rate of 10°C min⁻¹ and maintained for 1 or 2 h in 50 vol.% CO₂/Ar gaseous mixture at the flow rate of 100 sccm. After activation, the reactor was spontaneously cooled down to ambient temperature to obtain the products.

Structural characterizations

The morphologies and structures of the samples were characterized by scanning electron microscopy (SEM, Hitachi S4800 at 10 kV), transmission electron microscopy (TEM, JOEL JEM-2100F operated at 200 kV), Raman spectra (Witec alpha 300 SR with an excitation laser of 488 nm), X-ray photoelectron spectroscopy (XPS, Kratos AXIS Supra X-ray photoelectron spectrometer) and Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer 100 FTIR spectrometer). N₂ adsorption/desorption isotherms were measured on Thermo Fisher Scientific Surfer Gas Adsorption Porosimeter at 77 K. Before measurement, the sample was degassed at 300°C for 6 h. The SSA was calculated using the BET (Brunauer-Emmett-Teller) method based on the adsorption data in the linear relative pressure (p/p_0) range of 0.05–0.3. The pore size distribution was calculated from the corresponding adsorption branch of N₂ isotherm by Horvath-Kawazoe method for micropore and Barrett-Joyner-Halenda method for meso- and macro-pore. The conductivity was measured by a four-wire method using a source measure unit (Keithley 6430) [26,29].

Dynamic contact angle measurements

The sample was first wetted with ethanol and then rolled into sheet on aluminum foil. After drying at 80°C for 12 h, the evolution of the contact angle was recorded by the contact angle measurement system (OCA 30, Data-Physics Instruments GmbH).

Fabrication of supercapacitors

The symmetric supercapacitor of coin-cell type was fabricated to evaluate the supercapacitive performance of the products. Briefly, 95 wt% product and 5 wt% polytetrafluoroethylene (PTFE, 60 wt% dispersion in water) were homogeneously mixed into a paste using an agate mortar and pestle. Then the mixture was rolled onto the stainless steel wire meshes (316L, 400 meshes) with a diameter of 1.4 cm. The electrodes/collectors were dried at 180°C for 6 h under high vacuum to completely remove the water. The dried electrodes/collectors were vacuum transferred into a glove box filled with Ar to construct symmetrical

supercapacitors (CR2032) with the porous cellulose membrane as separator. The active material on each electrode was 1.0 mg, with the mass loading of 0.65 mg cm^{-2} . The mass was measured by Sartorius Ultra-microbalance ($0.1 \mu\text{g}$ resolution).

Electrochemical characterizations and calculations

All the supercapacitive performances were performed with a VMP3 Electrochemical Workstation (Bio-logic). The electrochemical impedance spectroscopy (EIS) was performed at open circuit potential with a sinusoidal signal over a frequency range from 100 kHz to 10 mHz at an amplitude of 10 mV. The cycling test was evaluated by galvanostatic charge–discharge (GCD) measurement.

Specific capacitance of the electrode material (C_s , F g^{-1}) was calculated from the chronopotentiometry (CP) discharge curve:

$$C_s = \frac{2 \times I_{\text{cons}} \times \Delta t}{m \times \Delta V}, \quad (1)$$

where I_{cons} is the constant current in discharging, m is the mass of active material on one electrode, Δt is the discharge time, and ΔV is the voltage change during discharge (excluding the limited voltage (IR) drop).

Energy density (E , W h kg^{-1}) of the cell was calculated by:

$$E = \frac{C_s \times \Delta V^2}{2 \times 4 \times 3.6}. \quad (2)$$

Average-power density (P , W kg^{-1}) of the cell was obtained by:

$$P = \frac{E \times 3600}{\Delta t}. \quad (3)$$

Maximum-power density (P_{max} , W kg^{-1}) of the cell was obtained by:

$$P_{\text{max}} = \frac{\Delta V^2}{8 \times R_{\text{ESR}} \times m}, \quad (4)$$

$$R_{\text{ESR}} = \frac{V_{\text{drop}}}{2 \times I_{\text{cons}}}, \quad (5)$$

where V_{drop} is the IR drop between the first two points in the discharge curve, R_{ESR} is the equivalent series resistance.

RESULTS AND DISCUSSION

The a-hCNCs treated at 800, 900, and 1000°C for 1 or 2 h were designated as a-hCNC800-1h, a-hCNC900-1h, a-hCNC1000-1h and a-hCNC1000-2h, respectively. Fig. 1 shows the change of pore size distribution of hCNC before and after activation. The N_2 sorption isotherms for all the products are similar with each other, indicating the slight change in the pore structure. The steep uptake at

$P/P_0 < 0.01$ indicates the existence of abundant micropores, while the hysteresis loop at $0.42 < P/P_0 < 1$ with no limiting adsorption at high P/P_0 corresponds to meso- and macropores (Fig. 1a) [30,31]. Both the SSA and the pore volume increase from $1890 \text{ m}^2 \text{ g}^{-1}$ and $4.66 \text{ cm}^3 \text{ g}^{-1}$ for hCNC to $2119 \text{ m}^2 \text{ g}^{-1}$ and $4.75 \text{ cm}^3 \text{ g}^{-1}$ for a-hCNC800-1h, $2399 \text{ m}^2 \text{ g}^{-1}$ and $5.26 \text{ cm}^3 \text{ g}^{-1}$ for a-hCNC900-1h, and $2776 \text{ m}^2 \text{ g}^{-1}$ and $6.52 \text{ cm}^3 \text{ g}^{-1}$ for a-hCNC1000-1h, then slightly decrease to $2497 \text{ m}^2 \text{ g}^{-1}$ and $5.03 \text{ cm}^3 \text{ g}^{-1}$ for a-hCNC1000-2h (Table S1). Meanwhile, the micropore size gradually increases as reflected in the corresponding positive extending of the micropore size distribution curves (inset in Fig. 1b), which is indeed what we expected as schemed in Fig. 1c [32,33]. This result also indicates that the etching predominantly occurs on the micropore edge, where the carbon atoms are more active than those in the basal plane [34], as supported by our theoretical calculations (Fig. S2). The well-maintained nanocage structure coupled with the enlarged micropore size should be responsible for the general increase of SSA and pore volume for the treated samples except for the over-treated a-hCNC1000-2h with somewhat collapse of the nanocage structure [27]. SEM and TEM observations also confirm the similar structure and morphology of the 1h-treated samples to hCNC, as shown in Fig. 2 (Fig. S3). The enlarged micropore size is favorable for the ion transfer through the cages as schemed in Fig. 1d. Actually, we calculated the EMIM⁺ adsorption energy in the micropores with different sizes of $4 \text{ \AA} \times 4 \text{ \AA}$, $6 \text{ \AA} \times 6 \text{ \AA}$, $6 \text{ \AA} \times 10 \text{ \AA}$, $10 \text{ \AA} \times 10 \text{ \AA}$, $14 \text{ \AA} \times 14 \text{ \AA}$ and infinite (the edge model) by the using the density functional theory method. With increasing micropore size, the carbon and hydrogen numbers that can interact with EMIM⁺ through van der Waals force decrease gradually, and converge to the case of edge. Therefore, pore widening can effectively promote the ion diffusion through the micropores (Fig. 1e).

After activation, the conductivity firstly increased from 663 S m^{-1} for hCNC to 734 S m^{-1} for a-hCNC800-1h and 794 S m^{-1} for a-hCNC900-1h, and then decreased to 573 S m^{-1} for a-hCNC1000-1h and 212 S m^{-1} for a-hCNC1000-2h (Fig. S3d). Such a change could be attributed to the initial removal of the poorly crystallized carbon by CO_2 etching followed by the regeneration of new defects of the destroyed conjugated structure of sp^2 carbon due to the excessive activation with increasing activation temperature and time (Fig. S2) [35–38]. The increased micropore size, SSA and pore volume, as well as the well maintained or even enhanced conductivity after activation are expected to elevate the supercapacitive

Figure 1 Pore structure evolution of hCNC before and after activation at 800, 900, and 1000°C. (a) N_2 sorption isotherms. (b) Pore size distributions. Inset is the local enlargement of the micropore distributions. (c) Schematic of micropore size enlargement by Boudouard reaction. (d) Schematic EMIM⁺ transfer across the micropore channels of hCNC and a-hCNC with the latter case the easier due to the enlarged size. (e) Adsorption energy of EMIM⁺ diffusion through the micropores with different sizes. Inset is the schematic ion diffusion through the micropore.

performances of hCNC in EMIMBF₄.

The supercapacitive performances were evaluated by the two-electrode coin-type supercapacitors. Fig. 3 shows the electrochemical performances for the hCNC-, a-hCNC800-1h-, a-hCNC900-1h- and a-hCNC1000-1h-based supercapacitors, denoted as hCNC-SC, a-

hCNC800-1h-SC, a-hCNC900-1h-SC and a-hCNC1000-1h-SC, respectively. The typical cyclic voltammetry (CV) curves for the hCNC-SC and a-hCNC900-1h-SC show good rectangle-like shapes at the scan rate of 200 mV s^{-1} , indicating the ideal capacitive behavior. With increasing scan rate up to 1000 mV s^{-1} , the CV curves for the a-

Figure 2 Morphological and structural characterizations of the products. (a–d) SEM images. (e–h) TEM images. (a, e) hCNC, (b, f) a-hCNC800-1h, (c, g) a-hCNC900-1h, (d, h) a-hCNC1000-1h. Insets in (e–h) are the corresponding high-resolution TEM images. Arrows indicate the broken fringes.

hCNC900-1h-SC is more close to rectangle than that for the hCNC-SC, demonstrating the better capacitive behavior with higher rate capability and smaller R_{ESR} (Fig. 3a) [25–28]. The weak humps in the CV curves of 200 mV s^{-1} indicate the slight contribution of pseudocapacitance, which should be caused by the small amount of oxygen-containing groups in the products [26,39]. The a-hCNC800-1h-SC and a-hCNC1000-1h-SC also exhibit better capacitive behavior than the hCNC-SC, but slightly inferior to the a-hCNC900-1h-SC (Fig. S4). GCD curves show high symmetry and nearly linear slopes at the current density of 1 A g^{-1} for all the supercapacitors, but the discharge times for the a-hCNC-based supercapacitors are longer than that for the hCNC-SC, in agreement with the CV characterization results (Fig. 3a, b). At each current density, the IR drops for all the a-hCNC-based supercapacitors are smaller than that for the hCNC-SC, which also indicates the enhanced performance for the a-hCNC, with a-hCNC900-1h the best (Fig. 3b and Figs S5, S6). At the current density of 1 A g^{-1} , the specific capacitance obtained from the discharge curve is 236, 265, 278 and 270 F g^{-1} for hCNC, a-hCNC800-1h, a-hCNC900-1h and a-hCNC1000-1h, respectively, locating at the top-level for carbon-based materials, especially in ionic liquid electrolyte (Table S2) [28,40–43]. With increasing current density up to 200 A g^{-1} , a-hCNC900-1h still maintains ca. 62.2% of its initial capacitance (173 F g^{-1}), superior to the corresponding 37.4%, 53.2% and 52.6% for hCNC, a-hCNC800-1h and a-hCNC1000-1h, respectively (Fig. 3c). The inferior supercapacitive performance for a-hCNC1000-1h to a-hCNC900-1h could be attributed to the decreased conductivity for the former [28,44,45].

Ragone plots further demonstrate the best performance of the a-hCNC900-1h-SC among the four supercapacitors, which delivers an ultrahigh energy density of $153.8 \text{ W h kg}^{-1}$ at the average-power density of 1.8 kW kg^{-1} based on the weight of a-hCNC900-1h. Even at an ultrahigh power density of 480.1 kW kg^{-1} , the energy density still reaches 54.0 W h kg^{-1} , indicating the simultaneous high energy density and high power output (Fig. 3d). Actually, the energy storage capabilities of all the four samples locate at the top-level for carbon-based materials (Fig. 3d, e and Table S2) [28,40–43,46–50]. Such a high energy density is attributed to the large specific capacitance of a-hCNC900-1h and the high operating voltage up to 4 V in EMIMBF₄. In addition, the a-hCNC900-1h-SC displays an excellent stability, showing ca. 93.8% capacitance retention after 20,000 cycles at the high current density of 100 A g^{-1} , with the Coulombic efficiency of ca. 100% through the testing cycles. The slight increase of capacitance at the beginning of cycling test could be attributed to the electrochemical activation (Fig. S7) [43]. Moreover, the cage structure of a-hCNC900-1h is well maintained after cycling for 20,000 cycles (Fig. S8). These results indicate the high stability of the electrode material. Its theoretical maximum-power density, which is obtained to be 634 kW kg^{-1} at the current density of 20 A g^{-1} , also locates at the top-level for carbon-based supercapacitors in nonaqueous electrolytes (Fig. S9 and Table S2). With increasing mass loading to higher values of 3.25 and 5.19 mg cm^{-2} , the performance for a-hCNC900-1h decreases accordingly due to the increased ion transfer resistance, but still maintains at the high level (Fig. S10). The influences of defects and functional groups on the capacitive performance are very

Figure 3 Supercapacitor performance of the products in EMIMBF₄. (a) CV curves of the a-hCNC900-1h-SC and hCNC-SC at the scan rates of 200 and 1000 mV s⁻¹, respectively. (b) GCD curves at current densities of 1 and 200 A g⁻¹, respectively. (c) Specific capacitances at different charge-discharge current densities. (d) Ragone plots of the average-power density *versus* energy density of supercapacitors. (e) Ragone plots of average-power density *versus* energy density of the supercapacitor based on a-hCNC900-1h (in red). The other data are taken from the literatures for the typical high-performance carbon-based supercapacitors for comparison [29,42–44,47–51]. Inset shows three parallel LEDs lighted by an a-hCNC900-1h-SC.

limited as evaluated by Raman spectra, XPS, and FTIR spectroscopy (Fig. S11). All these results indicate the effectiveness to elevate the supercapacitive performance of hCNC in EMIMBF₄ by properly enlarging the micropore size. Inset in Fig. 3e demonstrates the lighting of three parallel light-emitting diodes (LEDs) powered by an a-hCNC900-1h-SC.

EIS was performed to further understand the correlation of the supercapacitive performance with the structural evolution, as shown in Fig. 4. The nearly vertical Nyquist plots in low-frequency range demonstrate the ideal capacitive behavior for all the supercapacitors, in which the a-hCNC900-1h-SC is the best (Fig. 4a) [28,51]. The enlarged high-frequency region presents a transition

Figure 4 Frequency responses of the supercapacitors. (a) Nyquist plots. Inset magnifies the high-frequency range. (b) Bode plots of phase angle versus frequency.

from the vertical curve to the 45° Warburg region followed by a semicircle (inset in Fig. 4a). By extrapolating the vertical portion of the plot to the real axis, the R_{ESR} values of 5.49, 4.04, 3.22 and 4.81 Ω were obtained for the hCNC-SC, a-hCNC800-1h-SC, a-hCNC900-1h-SC and a-hCNC1000-1h-SC, respectively, in agreement with the CV and GCD results (Fig. 3a, b and Figs S4, S5). As known, R_{ESR} is mainly composed of the intrinsic Ohmic resistance (R_s , the first intercept along the real axis), the interfacial charge (ion and electron) transfer resistance (R_{ct} , the diameter of the semicircle), and the Warburg diffusion resistance (R_w , the projected length of Warburg region on the real axis), in which R_s mainly relies on the electrode conductivity, while R_{ct} and R_w are associated with the charge transfer at the electrode/electrolyte interface and the ion diffusion within pores [28]. R_s are 1.98, 1.93, 1.69 and 2.17 Ω for the hCNC-SC, a-hCNC800-1h-SC, a-hCNC900-1h-SC and a-hCNC1000-1h-SC, respectively, consistent with the conductivity evolution (inset in Fig. 4a and Fig. S3d). Due to the similar wettability for all the products in EMIMBF₄, the R_{ct} and R_w in this study should be mainly determined by the pore structure and conductivity of the products (Fig. S1) [28]. With increasing the activation temperature, R_{ct} and R_w decrease from 2.20 and 1.31 Ω for the hCNC-SC to 0.85 and 1.26 Ω for the a-hCNC800-1h-SC, and then 0.42 and 1.11 Ω for the a-hCNC900-1h-SC. This change could be ascribed to the increase of micropore size and conductivity of the electrode materials, which favors the charge transfer. Further increasing to 1000°C leads to the rebound of R_{ct} and R_w to 1.50 and 1.14 Ω for the a-hCNC1000-1h-SC due to the decrease of conductivity. In the Bode plots, the characteristic frequencies (f_0) at the phase angle of -45° for the hCNC-SC, a-hCNC800-1h-SC, a-hCNC900-1h-SC and a-hCNC1000-1h-SC are 0.35,

0.61, 0.77 and 0.48 Hz, corresponding to the time constants ($\tau_0=1/f_0$) of 2.86, 1.64, 1.30 and 2.08 s, respectively (Fig. 4b). The decreasing τ_0 from hCNC-SC to a-hCNC800-1h-SC and then a-hCNC900-1h-SC also indicates the increasing micropore size [52]. The slight rebound of τ_0 for a-hCNC1000-1h-SC should be ascribed to the partial collapse of the cage structure (Fig. S3). The shortest τ_0 for the a-hCNC900-1h-SC among the four supercapacitors further demonstrates its fastest charge/discharge rate and power output.

CONCLUSIONS

In summary, Boudouard reaction ($\text{C} + \text{CO}_2 = 2\text{CO}$) was successfully adopted to properly enlarge the size of micropore channels on the shell of hCNC, which is accompanied by the simultaneous increase of the SSA, pore volume and conductivity while remaining the hierarchical framework of hCNC under optimal activation temperature. Such a modification boosts the ion transfer of the large-sized ionic liquid electrolyte of EMIMBF₄ with a high operating voltage (4 V) and endows more charge storage space, which leads to the obvious decrease of equivalent series resistance and thus the dramatic increase of supercapacitive performance thereof. The optimized a-hCNC-900-1h exhibits a top-level capacitance of 278 F g^{-1} at 1 A g^{-1} for the carbon-based materials in ionic liquid electrolytes, along with a superior rate capability and long cycle life. The high energy density was achieved up to 153.8 W h kg^{-1} at the power density of 1.8 kW kg^{-1} , and kept at 54.0 W h kg^{-1} even under an ultrahigh power density of 480.1 kW kg^{-1} , which locates at the top-level for carbon-based electrode materials and suggests the great potential applications. This study clearly demonstrates the strong correlation of the supercapacitive performance with the micropore size, which

provides an effective way to explore advanced electrode materials.

Received 10 November 2020; accepted 8 January 2021;
published online 1 April 2021

- 1 Miller JR, Burke A. Electrochemical capacitors: challenges and opportunities for real-world applications. *Electrochem Soc Interface*, 2008, 17: 53–57
- 2 Simon P, Gogotsi Y, Dunn B. Where do batteries end and supercapacitors begin? *Science*, 2014, 343: 1210–1211
- 3 Chen X, Paul R, Dai L. Carbon-based supercapacitors for efficient energy storage. *Natl Sci Rev*, 2017, 4: 453–489
- 4 Wu Q, Yang L, Wang X, *et al.* From carbon-based nanotubes to nanocages for advanced energy conversion and storage. *Acc Chem Res*, 2017, 50: 435–444
- 5 Yang X, Cheng C, Wang Y, *et al.* Liquid-mediated dense integration of graphene materials for compact capacitive energy storage. *Science*, 2013, 341: 534–537
- 6 Conway BE. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*. New York: Kluwer Academic/Plenum Publishers, 1999
- 7 Hall PJ, Mirzaei M, Fletcher SI, *et al.* Energy storage in electrochemical capacitors: designing functional materials to improve performance. *Energy Environ Sci*, 2010, 3: 1238–1251
- 8 Yan J, Wang Q, Wei T, *et al.* Recent advances in design and fabrication of electrochemical supercapacitors with high energy densities. *Adv Energy Mater*, 2014, 4: 1300816
- 9 Béguin F, Presser V, Balducci A, *et al.* Supercapacitors: Carbons and electrolytes for advanced supercapacitors. *Adv Mater*, 2014, 26: 2283
- 10 Wang X, Mehandzhyski AY, Arstad B, *et al.* Selective charging behavior in an ionic mixture electrolyte-supercapacitor system for higher energy and power. *J Am Chem Soc*, 2017, 139: 18681–18687
- 11 Wang DW, Li F, Liu M, *et al.* 3D aperiodic hierarchical porous graphitic carbon material for high-rate electrochemical capacitive energy storage. *Angew Chem Int Ed*, 2008, 47: 373–376
- 12 Luo J, Jang HD, Huang J. Effect of sheet morphology on the scalability of graphene-based ultracapacitors. *ACS Nano*, 2013, 7: 1464–1471
- 13 Zheng X, Luo J, Lv W, *et al.* Two-dimensional porous carbon: synthesis and ion-transport properties. *Adv Mater*, 2015, 27: 5388–5395
- 14 Wang Q, Yan J, Fan Z. Carbon materials for high volumetric performance supercapacitors: design, progress, challenges and opportunities. *Energy Environ Sci*, 2016, 9: 729–762
- 15 Shao H, Wu YC, Lin Z, *et al.* Nanoporous carbon for electrochemical capacitive energy storage. *Chem Soc Rev*, 2020, 49: 3005–3039
- 16 Ma H, Geng H, Yao B, *et al.* Highly ordered graphene solid: an efficient platform for capacitive sodium-ion storage with ultrahigh volumetric capacity and superior rate capability. *ACS Nano*, 2019, 13: 9161–9170
- 17 Zhai Y, Dou Y, Zhao D, *et al.* Carbon materials for chemical capacitive energy storage. *Adv Mater*, 2011, 23: 4828–4850
- 18 Sevilla M, Mokaya R. Energy storage applications of activated carbons: supercapacitors and hydrogen storage. *Energy Environ Sci*, 2014, 7: 1250–1280
- 19 El-Kady MF, Shao Y, Kaner RB. Graphene for batteries, supercapacitors and beyond. *Nat Rev Mater*, 2016, 1: 16033
- 20 Salunkhe RR, Kaneti YV, Kim J, *et al.* Nanoarchitectures for metal–organic framework-derived nanoporous carbons toward supercapacitor applications. *Acc Chem Res*, 2016, 49: 2796–2806
- 21 Salunkhe RR, Lee YH, Chang KH, *et al.* Nanoarchitected graphene-based supercapacitors for next-generation energy-storage applications. *Chem Eur J*, 2014, 20: 13838–13852
- 22 Jiang XF, Li R, Hu M, *et al.* Zinc-tiered synthesis of 3D graphene for monolithic electrodes. *Adv Mater*, 2019, 31: 1901186
- 23 Wu Q, Yang L, Wang X, *et al.* Carbon-based nanocages: A new platform for advanced energy storage and conversion. *Adv Mater*, 2019, 1904177
- 24 Wu Q, Yang L, Wang X, *et al.* Mesoporous carbon-based nanocages: an advanced platform for energy chemistry. *Sci China Chem*, 2020, 63: 665–681
- 25 Xie K, Qin X, Wang X, *et al.* Carbon nanocages as supercapacitor electrode materials. *Adv Mater*, 2012, 24: 347–352
- 26 Zhao J, Lai H, Lyu Z, *et al.* Hydrophilic hierarchical nitrogen-doped carbon nanocages for ultrahigh supercapacitive performance. *Adv Mater*, 2015, 27: 3541–3545
- 27 Bu Y, Sun T, Cai Y, *et al.* Compressing carbon nanocages by capillarity for optimizing porous structures toward ultrahigh-volumetric-performance supercapacitors. *Adv Mater*, 2017, 29: 1700470
- 28 Zhao J, Jiang Y, Fan H, *et al.* Porous 3D few-layer graphene-like carbon for ultrahigh-power supercapacitors with well-defined structure-performance relationship. *Adv Mater*, 2017, 29: 1604569
- 29 Lyu Z, Xu D, Yang L, *et al.* Hierarchical carbon nanocages confining high-loading sulfur for high-rate lithium–sulfur batteries. *Nano Energy*, 2015, 12: 657–665
- 30 Sing KSW. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure Appl Chem*, 1985, 57: 603–619
- 31 Cychosz KA, Guillet-Nicolas R, García-Martínez J, *et al.* Recent advances in the textural characterization of hierarchically structured nanoporous materials. *Chem Soc Rev*, 2017, 46: 389–414
- 32 Osswald S, Portet C, Gogotsi Y, *et al.* Porosity control in nanoporous carbide-derived carbon by oxidation in air and carbon dioxide. *J Solid State Chem*, 2009, 182: 1733–1741
- 33 Shen L, Sun T, Zhuo O, *et al.* Alcohol-tolerant platinum electrocatalyst for oxygen reduction by encapsulating platinum nanoparticles inside nitrogen-doped carbon nanocages. *ACS Appl Mater Interfaces*, 2016, 8: 16664–16669
- 34 Wang X, Li X, Zhang L, *et al.* N-doping of graphene through electrothermal reactions with ammonia. *Science*, 2009, 324: 768–771
- 35 Tsang SC, Harris PJF, Green MLH. Thinning and opening of carbon nanotubes by oxidation using carbon dioxide. *Nature*, 1993, 362: 520–522
- 36 Babu DJ, Yadav S, Heinlein T, *et al.* Carbon dioxide plasma as a versatile medium for purification and functionalization of vertically aligned carbon nanotubes. *J Phys Chem C*, 2014, 118: 12028–12034
- 37 Zhang LL, Zhao X, Stoller MD, *et al.* Highly conductive and porous activated reduced graphene oxide films for high-power supercapacitors. *Nano Lett*, 2012, 12: 1806–1812
- 38 Zhang J, Jia K, Lin L, *et al.* Large-area synthesis of superclean graphene via selective etching of amorphous carbon with carbon dioxide. *Angew Chem Int Ed*, 2019, 58: 14446–14451
- 39 Han X, Funk MR, Shen F, *et al.* Scalable holey graphene synthesis and dense electrode fabrication toward high-performance ultra-

capacitors. *ACS Nano*, 2014, 8: 8255–8265

- 40 Xu J, Tan Z, Zeng W, *et al.* A hierarchical carbon derived from sponge-templated activation of graphene oxide for high-performance supercapacitor electrodes. *Adv Mater*, 2016, 28: 5222–5228
- 41 Li C, Zhang X, Wang K, *et al.* Scalable self-propagating high-temperature synthesis of graphene for supercapacitors with superior power density and cyclic stability. *Adv Mater*, 2017, 29: 1604690
- 42 Li J, Wang N, Tian J, *et al.* Cross-coupled macro-mesoporous carbon network toward record high energy-power density supercapacitor at 4 V. *Adv Funct Mater*, 2018, 28: 1806153
- 43 Yao L, Wu Q, Zhang P, *et al.* Scalable 2D hierarchical porous carbon nanosheets for flexible supercapacitors with ultrahigh energy density. *Adv Mater*, 2018, 30: 1706054
- 44 Bo Z, Zhu W, Ma W, *et al.* Vertically oriented graphene bridging active-layer/current-collector interface for ultrahigh rate supercapacitors. *Adv Mater*, 2013, 25: 5799–5806
- 45 Pachfule P, Shinde D, Majumder M, *et al.* Fabrication of carbon nanorods and graphene nanoribbons from a metal–organic framework. *Nat Chem*, 2016, 8: 718–724
- 46 Cui C, Qian W, Yu Y, *et al.* Highly electroconductive mesoporous graphene nanofibers and their capacitance performance at 4 V. *J Am Chem Soc*, 2014, 136: 2256–2259
- 47 Hou J, Cao C, Idrees F, *et al.* Hierarchical porous nitrogen-doped carbon nanosheets derived from silk for ultrahigh-capacity battery anodes and supercapacitors. *ACS Nano*, 2015, 9: 2556–2564
- 48 Niu J, Shao R, Liang J, *et al.* Biomass-derived mesopore-dominant porous carbons with large specific surface area and high defect density as high performance electrode materials for Li-ion batteries and supercapacitors. *Nano Energy*, 2017, 36: 322–330
- 49 Nomura K, Nishihara H, Kobayashi N, *et al.* 4.4 V supercapacitors based on super-stable mesoporous carbon sheet made of edge-free graphene walls. *Energy Environ Sci*, 2019, 12: 1542–1549
- 50 Shang T, Xu Y, Li P, *et al.* A bio-derived sheet-like porous carbon with thin-layer pore walls for ultrahigh-power supercapacitors. *Nano Energy*, 2020, 70: 104531
- 51 Shao Y, El-Kady MF, Lin CW, *et al.* 3D freeze-casting of cellular graphene films for ultrahigh-power-density supercapacitors. *Adv Mater*, 2016, 28: 6719–6726
- 52 Chmiola J, Yushin G, Gogotsi Y, *et al.* Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer. *Science*, 2006, 313: 1760–1763

Acknowledgements This work was jointly supported by the National Key Research and Development Program of China (2017YFA0206500 and 2018YFA0209103), the National Natural Science Foundation of China (21832003, 21773111, 21573107 and 21971061), and the Fundamental Research Funds for the Central Universities (020514380126).

Author contributions Hu Z, Wang X, Ma Y and Zhao J conceived the concept and designed the experiments. Zhao J carried out the experiments. Fan H and Li G assisted with experiments and data preparation. Yang L performed the theoretical simulation. Hu Z, Wu Q and Zhao J wrote the manuscript. All authors analyzed and discussed the data and commented on the manuscript.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Jin Zhao is currently a professor at Nanjing University of Posts and Telecommunications. He received his ME degree from Nanjing University of Posts and Telecommunications in 2012 and PhD degree from Nanjing University in 2016. After that, he worked as a research fellow at the National University of Singapore and Nanyang Technological University. His research focuses on the design and preparation of advanced electrode materials for energy storage and conversion.

Xizhang Wang received his PhD in chemistry from Nanjing University in 2001. He was appointed an associate professor of Nanjing University in 2003 and full professor in 2011. He had been a Japan Society for Promotion of Science Fellow in Tokyo University (2003–2005). His scientific interests mainly focus on nanomaterial chemistry, sustainable energy, and heterogeneous catalysis.

Zheng Hu received his BSc (1985) and PhD (1991) degrees in physics from Nanjing University. After two-year's postdoctoral research in the Department of Chemistry, he became an associate professor in 1993, and subsequently acquired the professor position in 1999, and Cheung Kong Scholar professor in 2007. He was awarded the NSFC fund for outstanding young scientists of China (2005). He is engaged in the research field of physical chemistry and materials chemistry addressing the growth mechanism, materials design and energy applications of a range of nano-/meso-structured materials, especially the carbon nanocages, group III nitrides and transition metal oxides.

增大分级结构碳纳米笼的离子传输微孔通道获得超高的能量密度和功率密度

赵进^{1,2}, 范豪¹, 李国昌¹, 吴强¹, 杨立军¹, 马延文², 王喜章^{1*}, 胡征^{1*}

摘要 提升超级电容器能量密度而不牺牲其高功率密度是能源存储领域的不懈追求。离子液体电解液具有大的工作电压窗口, 以其为电解液可提升超级电容器能量密度。但离子液体离子尺寸大、离子电导率低且粘度高, 通常会导致超级电容器功率密度的减小。本文主要通过增大分级结构碳纳米笼(hCNC)电极材料的离子传输微孔通道, 实现了在EMIMBF₄离子液体电解液中超级电容器能量密度和功率密度的协同提升。通过Boudouard反应, 在保持hCNC独特分级结构的前提下调节了贯穿碳纳米笼壁的微孔尺寸, 同时, 在优化的活化温度下hCNC的比表面积、孔体积和导电性均得以提升。这种独特的调节促进了大尺寸离子的传输, 有效降低了等效串联电阻, 从而显著提升了超级电容器的性能。优化的样品在功率密度为1.8 kW kg⁻¹时的能量密度高达153.8 W h kg⁻¹, 在超高功率密度480.1 kW kg⁻¹时能量密度仍能保持54.0 W h kg⁻¹。本研究展示了一种通过精细调控材料微孔及相关性质开发先进电极材料的有效方法。