

# Chemical activation of carbon nano-onions for high-rate supercapacitor electrodes

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## ABSTRACT

Recent studies have demonstrated that carbon nano-onion (CNO) is a promising candidate for high-power supercapacitors due to the nonporous outer shell, which is easily accessible to electrolyte ions. However, the nonporous ion-accessible outer shells also limit the energy density of the CNOs, which requires large specific surface area. Introducing porosity to the outer shells of CNOs can effectively improve the specific surface area by exposing the inner shells to electrolytes. In this study, the electrochemical performance of supercapacitor electrodes based on CNOs is improved through the controlled introduction of porosity on the outer shells of CNOs by chemical activation. The capacitance of the activated CNOs is five times larger than the pristine ones with a measured power density of 153 kW/kg and an energy density of 8.5 Wh/kg in a 2 mol/l potassium nitrate electrolyte. The capacitance retention ratio of activated CNOs decreases slightly as the current density increases from 0.75 to 25 A/g. About 71% of initial capacitance (at 0.75 A/g) is preserved for activated CNOs at current densities up to 25 A/g.

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# 1. Introduction

As an important energy storage device, supercapacitors, also called electrochemical capacitors or ultracapacitors, fill the gap between conventional dielectric capacitors and batteries in terms of specific energy and power [1–4]. Due to the bene-fits of high power density and long cycle life [5], supercapacitors have been used in a broad range of applications [5–11], such as electric vehicles, digital communication instruments, emergency doors on jet planes, and pulsed lasers. Supercapacitors store energy directly through the electrostatic charge accumulated at the electrode/electrolyte interfaces. During the charging process, cations and anions in the electrolytes

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are attracted to the cathode and anode, respectively and form electrical double layers in the pores of the electrodes [10,11]. Carbon materials, including carbon nanotubes (CNTs) [6–9], activated carbon [12], graphene [13,14], carbon aerogels [15], carbon nanofibers (CNFs) [16], and templated porous carbon [17], have been extensively studied for supercapacitor electrodes because of their large specific surface area (SSA), high conductivity, and chemical stability [5]. For carbon materials, their SSA and porosity are essential to their electrochemical performance in supercapacitors [18]. A large SSA provides a high capacitance, promising a high energy density. Suitable micro- and mesopore architecture can improve the electrochemical performance of the materials [19]. Carbon materials

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with abundant micropores can enhance the capacitance of the materials. Especially when micropores have pore sizes less than that of the solvated electrolyte ion size, the distortion of solvation shell makes the ion center closer to the electrode surface, and hence significantly improve the capacitance [20,21]. The mesopores provide low-resistant ionic pathway, improving the accessibility of micropores to electrolytes. A pore network with large pores (>3 nm) ensures a high charging rate, contributing to a high power density [11]. Therefore, carbon electrodes with high SSAs and proper pore distributions are highly desired to construct supercapacitors with high energy and power densities [22].

As an important member in the fullerene family, carbon nano-onions (CNOs), also known as onion-like carbons, which consist of multiple concentric graphitic shells to form encapsulated structures, have been envisioned to be a promising supercapacitor electrode material with high power density due to nonporous outer shells which are easily accessible to electrolyte ions [23-25]. Despite their attributes, CNOs have not received sufficient attention as an electrode material for supercapacitors [24-26]. In those studies [24-26], CNOs were synthesized by annealing nanodiamond powder at high temperatures (>1200 °C). The CNOs obtained from this method show an SSA of  $\sim$ 500 m<sup>2</sup>/g, significantly smaller than that of activated carbon (1000-3000 m<sup>2</sup>/g). There is an opportunity that the capacitance of CNOs could be improved by making inner shells accessible to electrolytes, which increases the SSA of the CNOs while keeps the easy ion transportation. A direct approach to exposing the inner shells of CNOs to electrolytes is to introduce porosity on the outer shells. The micropores increase the capacitance, while the mesopores improve the accessibility of micropores to electrolytes.

Chemical activation [27,28] has been widely employed for various carbon materials (e.g., CNFs [18], CNTs [22], and graphene [29]) to significantly improve corresponding electrochemical performance. Merino et al. [18] reported that the capacitance of CNFs increased from 1 to 60 F/g after chemical activation using potassium hydroxide (KOH). The increase in capacitance was ascribed to the increase in SSA and porosity (micropores and mesopores) of CNFs after KOH activation. Yang et al. [22] have demonstrated that KOH-activated CNT electrodes doubled capacitances to approximately 50 F/g. The increased SSA after KOH activation contributed to the increase in capacitance. Recently, Zhu et al. [29] reported that KOH-activated graphene has achieved an energy density of 70 Wh/kg in an organic electrolyte, which is ascribed to the increases in SSA (up to 3100 m<sup>2</sup>/g) and porosity of graphene. However, the resulting porous structures showed increased resistance which compromised the final performance [22]. Therefore, to maximize supercapacitor performance, chemical activation must be optimized to balance the pore size distribution to achieve high SSAs (to increase energy density) without compromising high conductivity (to keep power density) [22].

In this research, KOH activation was used to introduce porosity on the outer shells of CNOs for improved electrochemical performance. CNOs were synthesized by a combustion process in open air using laser resonant excitation of ethylene molecules (see Fig. S1 in Supplementary Information) [30]. Highly concentric CNOs (see Fig. S1c in Supplementary Information) synthesized at a laser wavelength of 10.532 µm were used as the pristine CNOs for KOH activation. The KOH induced changes in structure, SSA, and pore size distribution of CNOs have been investigated. The electrochemical performance of the activated CNOs in aqueous electrolyte has been studied with cyclic voltammetry, galvanostatic charge/discharge, and ac impedance spectroscopy. The capacitance of CNOs activated by 6 mol/l KOH solution is 122 F/g (about five times larger than the pristine CNOs) with a measured power density of 153 kW/kg and an energy density of 8.5 Wh/kg.

# 2. Experimental

## 2.1. Activation of CNOs

A standard procedure was used to activate CNOs synthesized by laser resonant excitation of ethylene molecules [30]. CNOs of 40 mg were dispersed in 20 ml KOH solutions with different concentrations from 4 to 7 mol/l. After ultrasonication for 1 h. the CNOs were impregnated in the KOH solutions for another 23 h under ambient conditions. The extra KOH was then removed by vacuum filtration. The pH values of KOH solution before and after filtration were measured to estimate how much KOH was used for activation (see Table S1 in Supplementary Information). The remaining mixtures were directly put into oven for drying at 80 °C for 24 h. The activation process was continued by heating at 800 °C for 1 h in a horizontal tube furnace with a nitrogen flow of 100 sccm and a temperature ramp rate of 10 °C/min. After cooling down to the room temperature, the CNO samples were repeatedly washed with deionized water until a pH value of 7 was reached. Finally, the activated CNOs were dried for 12 h in air at 80 °C. Activated CNOs prepared using n mol/l KOH solutions are identified below with the symbol "ACNO-nM".

## 2.2. Characterization of CNOs

The CNOs were characterized by a field-emission TEM (FEI Tecnai G2 F30, 300 kV) and a Renishaw inVia dispersive micro-Raman spectrometer with a 514 nm excitation source. The Brunauer–Emmett–Teller (BET) surface area and pore volume were measured by  $N_2$  adsorption using an adsorption apparatus (Micromeritics ASAP 2020, USA). A degassing process was used to remove the impurities adsorbed onto the samples. The degassing vacuum was 0.3 mmHg for 30 min. The degassing temperature was 250 °C. The pore size distributions were calculated by applying the density functional theory (DFT) to the  $N_2$  isotherms using the microactive interactive data analysis software. Static water contact angle measurement was carried out using a contact angle goniometer (Powereach JC2000D, China).

#### 2.3. Electrochemical measurements

CNO electrodes were fabricated by electrophoretic deposition (EPD) into Ni foams (95% porosity, 500 g/m surface area density, MarkeTech International) [24]. CNOs were dispersed in ethanol containing 0.03-0.05 wt.% of Al(NO)<sub>3</sub> for stabilizing the CNOs. A DC voltage of 80 V/cm was then applied between a Ni foam and a gold electrode to deposit the CNOs. After the

EPD process, CNO electrodes were dried at 80 °C in a furnace for 2 h. All electrochemical measurements, including cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD), were carried out in a 2 mol/l KNO<sub>3</sub> electrolyte using a threeelectrode configuration on a CHI 760D (Shanghai Chenhua, China) electrochemical workstation. The  $1 \times 1.5$  cm<sup>2</sup> CNO/Ni foam electrodes, a platinum gauze electrode, and an Ag/AgCl electrode were used as the work, counter, and reference electrodes, respectively. The impedance behavior of the CNO electrodes was tested in a frequency range of 10 mHz–100 kHz with an ac potential amplitude of 5 mV.

## 3. Results and discussion

Fig. 1a shows a schematic of a CNO before and after chemical activation. The pristine CNOs used for KOH activation have sizes ranging from 5 to 50 nm (see Fig. S1d in Supplementary Information). Fig. 1b–e shows the transmission electron microscopic (TEM) images of CNOs before and after KOH activation. The pristine CNOs show concentric structures containing long-range ordered graphitic striations on each shell. The structure of the CNOs changed significantly after KOH activation. Defects are observed in the outer shell of ACNO-4M, though the concentric structure is still maintained (Fig. 1c). As the KOH concentration increases to 6 mol/l, the surfaces of outer shells become increasingly rough, indicating the creation of pores. When the KOH concentration further increases to 7 mol/l, the concentric structures of the CNOs are destroyed.

The electrochemical performance of a carbon material is generally determined by its electrolyte-accessible SSA and the pore structure [18]. The SSA and pore size distribution of the CNOs before and after activation were examined using BET method. Fig. 2a shows the BET SSA and pore volume of the CNOs as a function of the KOH concentration. When other process parameters (e.g., the amount of CNOs used for activation, the volume of KOH solution) are kept constant, the amount of KOH used for CNO activation can be controlled by the KOH concentration (see Fig. S2 in Supplementary Information). The KOH loading on CNOs was almost linearly dependent on the concentration of the KOH solution (Fig. S2 in Supplementary Information). By increasing the KOH concentration or KOH loading on CNOs, the SSA increases dramatically, reaching a value of 804 m<sup>2</sup>/g for ACNO-6M, before the CNO cage structure collapses at 7 mol/l (Fig. 1e). Meanwhile, as the KOH concentration increases, the pore volume of the CNOs increases from 0.80 for pristine CNOs to 1.27 cm<sup>3</sup>/g for ACNO-6M. Fig. 2b shows the DFT pore size distribution of the CNOs at different KOH concentrations. The KOH activation process introduces microporoes and mesoporoses on the CNOs. The pristine CNOs show a dominant pore size distribution from 3 to 100 nm and have fewer small pores less than 2 nm. After KOH activation, CNOs demonstrate more porosity than pristine CNOs. The mesopores larger than 3 nm are largely increased, which provide lowresistant ionic pathway, improving the accessibility of micropores to electrolytes. Moreover, micropores less than 2 nm are introduced on the surface of the CNOs by KOH activation, as shown in Fig. 2b. The micropore SSA arrives the maximum value of 200 m<sup>2</sup>/g, when 6 mol/l KOH was used to activate the CNOs (see Table S2 in Supplementary Information). Those micropores introduced by KOH activation can enhance the capacitance of the CNOs [19]. In addition, the chemical activation turned the hydrophobic surfaces of the pristine CNOs to hydrophilic in the KNO3 electrolyte (see Fig. S4 in Supplementary Information), thus further improving electrolyte access to the CNO electrodes [31].

The electrochemical properties of ACNO-nMs were studied by CV and GCD curves measured in a KNO<sub>3</sub> electrolyte solution of 2 mol/l. Fig. 3a shows the CV behaviors of the CNO electrodes at a potential scan rate of 50 mV/s. The pristine CNOs demonstrate a narrow rectangular curve, which corresponds to a low capacitance due to their small SSAs, low pore volumes, and hydrophobic surfaces (see Fig. S4 in Supplementary



Fig. 1 – (a) A schematic showing the chemical activation of CNOs in KOH. TEM images of pristine CNO (b), ACNO-4M (c), ACNO-6M (d), and ACNO-7M (e). "ACNO-nM" denotes the activated CNO prepared using n mol/l KOH solution.



Fig. 2 – (a) The BET SSAs and the pore volumes of CNOs as functions of the KOH concentration. (b) The DFT pore size distribution of CNOs activated with different KOH concentrations.



Fig. 3 – Electrochemical performance of CNOs using a threeelectrode cell in 2 mol/l KNO<sub>3</sub> electrolyte: (a) CV curves at a potential scan rate of 50 mV/s; (b) GCD curves at a current density of 3 A/g; (c) the capacitance as a function of the KOH concentration.

Information). After activation, the CNO electrodes continue to exhibit simple capacitive behaviors manifested by nominally rectangular CV curves. The specific capacitance of the CNO electrodes from CV was calculated by the following equation:

$$C = \frac{\int \frac{dw}{m}}{v\Delta V} \tag{1}$$

where i is the response current, *m* is the mass of CNOs,  $\Delta V$  is the potential range of CV, *v* is the potential scan rate, respectively. The capacitance increases continuously with the increase in the KOH concentration (Fig. 3a). The largest capacitance of 111 F/g was obtained for ACNO-6M at the scan rate of 50 mV/s. Fig. 3b shows the GCD curves of the CNO electrodes at a constant current density of 3 A/g. All of the discharge curves are nearly linear in the potential range, indicating a purely capacitive nature [32]. The specific capacitance from GCD was calculated using the following formula:

$$C = \frac{1}{m(dV/dt)}$$
(2)

where i is the constant current and *m* is the mass for the CNO electrodes, and *dV/dt* is the slope of the discharge curve. The capacitances evaluated from the GCD curves are shown in Fig. 3c. The largest capacitance of 115 F/g was obtained for ACNO-6M, which is almost five times larger than that of the pristine CNOs (24 F/g). The significant improvement of CNO capacitance is ascribed to the increased SSA, optimized porosity, and hydrophilic surface after KOH activation [6]. Since the CNO cage structures collapsed when treated in the 7 mol/l KOH solution, the capacitance of the CNOs did not show any improvement.

The capacitance retention ratio was investigated at different potential scan rates and different charge/discharge current densities. Fig. 4a shows CV curves for ACNO-6M recorded at scan rates from 10 to 5000 mV/s. At a low potential scan rate of 10 mV/s, the CV curve exhibits a rectangular shape, indicating a typical electric double-layer capacitive behavior. With increased potential scan rates up to 5000 mV/s, ACNO-6M CV curves remain highly rectangular, indicating facile charging and discharging events for ACNO-6M. The inset in Fig. 4a shows the log of peak current versus log of scan rate for the ACNO-6M. The slope is ~0.9, which is closer to 1, indicating an idea capacitive behavior of the electrode [33]. As shown in the inset of Fig. 4a, the capacity starts to be limited at 5 V/s. Fig. 4b shows



Fig. 4 – Electrochemical performance of ACNO-6M using a three-electrode cell in 2 mol/l KNO<sub>3</sub> electrolyte: (a) CV curves at scan rates from 10 to 5000 mV/s (The inset shows the log of peak current versus log of scan rate); (b) the capacitance as a function of the scan rate; (c) capacitances and (d) capacitance retention ratios of ACNO-6M and pristine CNOs as functions of the current density.

the capacitance of the activated CNOs as a function of the potential scan rate. ACNO-6M demonstrates the highest capacitance at all scan rates. At 10 mV/s, the capacitance of ACNO-6M is 122 F/g, which is almost five times larger than the pristine CNOs (25 F/g). When the scan rate increases to 5000 mV/s, ACNO-6M still shows a capacitance of 76 F/g corresponding to a 62% remaining capacitance, not much smaller than the retention ratio of 82% for pristine CNOs. The rate capability of ACNO-6M was further studied at different charge/discharge current densities (Fig. 4c and d). The capacitance of ACNO-6M decreases from 126.3 to 89.6 F/g as the current density increases from 0.75 to 25 A/g, corresponding to about 71% capacitance retention. In contrast, the pristine CNO has a capacitance retention of 77% but a much smaller capacitance of 25.8 F/g at 0.75 A/g. These results demonstrate that the chemically formed porosity promote charges/discharges at the electrode surfaces. The mesopores increase the ion accessible surfaces and the micropores contribute to the increase in capacitance of the activated CNOs [19].

The capacitance of ACNO-6M at different operating frequency was studied by the electrochemical impedance spectroscopy. Fig. 5a shows the Nyquist plots of ACNO-6M. At a low frequency, the imaginary part of the impedance increases sharply, exhibiting a nearly vertical line as a characteristic of capacitive behavior. For a given capacitive material, a high knee frequency, which is associated with a small relaxation time constant, is desired. The knee frequency of ACNO-6M is obtained from the admittance plot (Fig. 5b) with a value of 825 Hz, which is higher than the activated graphene sheets (382 Hz) [29]. Fig. 5c and d shows the frequency response of the real and imaginary parts of the capacitance. The relaxation time constant ( $\tau_0 = 1/f_0$ ), which defines the limit between the resistive and the capacitive behaviors, can be obtained from the peak frequency in Fig. 5d. [34–36] ACNO-6M shows a relaxation time constant of 82.5 ms.

The energy and power densities of ACNO-6M and pristine CNO were shown in Fig. 6(a). The energy and power densities of the CNO electrodes were estimated by the following equations:

$$E = \frac{C(\Delta U)^2}{2m}$$
(3)

$$\mathsf{P} = \frac{(\Delta U)^2}{4 \times mR} \tag{4}$$

where  $\Delta U$  is the discharge potential after the iR drop, and R is the internal resistance which can be obtained from the GCD curves. The maximum energy density of 8.5 Wh/kg was obtained at a power density of 153 kW/kg for ACNO-6M. This energy density is almost six times larger than that of the pristine CNOs (1.5 Wh/kg). ACNO-6M has a lower maximum power density than that of the pristine CNOs, due to the increased internal resistance in CNOs after KOH activation. Nevertheless, at a current density of 5 A/g, ACNO-6M still maintains a power density of 289 kW/kg. A total of 4000 complete charge/discharge cycles were carried out at a constant current density of 5 A/g to investigate the lifetime and durability of ACNO-6M, as shown in Fig. 6b. After 4000 cycles, approximately 89% of the initial capacitance is preserved. The KOH activation



Fig. 5 – Electrochemical impedance spectra of capacitive behavior of ACNO-6M in a 2 mol/l KNO<sub>3</sub> electrolyte: (a) Nyquist plots, (b) admittance plot, and (c and d) the frequency response of the real and imaginary parts of the capacitance.



Fig. 6 – (a) Ragone plots of the ACNO-6M and pristine CNOs. (b) Retention ratio of ACNO-6M in 4000 charge–discharge cycles at a constant current density of 5 A/g.

process introduces oxygen functional groups on the surface of the CNOs (see Fig. S4 in Supporting Information), which can result into the deterioration of capacitance [37].

# 4. Conclusions

In summary, we have demonstrated that the chemical activation is effective in creating porosity in outer shells of CNOs to improve the energy density and preserve the power density in CNO electrodes. After activating CNOs using a 6 mol/l KOH solution, a maximum specific capacitance of 122 F/g, power density of 153 kW/kg, and energy density of 8.5 Wh/kg were achieved. The same parameters for pristine CNOs are 25.8 F/ g, 123 kW/kg, and 1.5 Wh/kg, respectively. The enhanced electrochemical performance of CNOs is the result of the introduction of porosity (increased SSA) and the improved surface hydrophilicity due to the KOH activation. The activated CNOs display high charge/discharge rates at scan rates up to 5000 mV/s. A high capacitance retention ratio of 71% is preserved as the current density increased from 0.75 to 25 A/g. Additionally, the activated CNOs have a high knee frequency (825 Hz) and a smaller relaxation time constant (82.5 ms).

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon. 2012.08 009.

## REFERENCES

- Miller JR, Simon P. Electrochemical capacitors for energy management. Science 2008;321(5889):651–2.
- [2] Zhao L, Fan LZ, Zhou MQ, Guan H, Qiao SY, Antonietti M, et al. Nitrogen-containing hydrothermal carbons with superior performance in supercapacitor. Adv Mater 2010;22(45):5202–6.
- [3] Inagakia M, Konnoa H, Tanaike O. Carbon materials for electrochemical capacitors. J Power Sources 2010;195(24):7880–903.
- [4] Simon P, Gogotsi Y. Materials for electrochemical capacitors. Nat Mater 2008;7(11):845–54.
- [5] Zhang LL, Zhao XS. Carbon-based materials as supercapacitor electrodes. Chem Soc Rev 2009;38(9):2520–31.
- [6] An KH, Kim WS, Park YS, Choi YC, Lee SM, Chung DC, et al. Supercapacitors using single-walled carbon nanotube electrodes. Adv Mater 2001;13(7):497–500.
- [7] Izadi-Najafabadi A, Yamada T, Futaba DN, Yudasaka M, Takagi H, Hatori H, et al. High-power supercapacitor electrodes from single-walled carbon nanohorn/nanotube composite. ACS Nano 2011;5(2):811–9.
- [8] Kaempgen M, Chan CK, Ma J, Cui Y, Gruner G. Printable thin film supercapacitors using single-walled carbon nanotubes. Nano Lett 2009;9(5):1872–6.
- [9] Li P, Lim X, Zhu Y, Yu T, Ong CK, Shen Z, et al. Tailoring wettability change on aligned and patterned carbon nanotube films for selective assembly. J Phys Chem B 2007;111(7):1672–8.
- [10] Burke A. Ultracapacitors: why, how, and where is the technology. J Power Sources 2000;91(1):37–50.
- [11] Xing W, Qiao SZ, Ding RG, Li F, Lu GQ, Yan ZF, et al. Superior electric double layer capacitors using ordered mesoporous carbons. Carbon 2006;44(2):216–24.
- [12] Raymundo-Piñero E, Leroux F, Béguin F. A high-performance carbon for supercapacitors obtained by carbonization of a seaweed biopolymer. Adv Mater 2006;18(14):1877–82.
- [13] Wong SL, Huang H, Wang Y, Cao L, Qi DC, Santoso I, et al. Quasi-free-standing epitaxial graphene on SiC(0001) by fluorine intercalation from a molecular source. ACS Nano 2011;5(9):7662–8.
- [14] Yang XW, Zhu JW, Qiu L, Li D. Bioinspired effective prevention of restacking in multilayered graphene films: towards the next generation of high-performance supercapacitors. Adv Mater 2011;23(25):2833–8.
- [15] Fischer U, Saliger R, Bock V, Petricevic R, Fricke J. Carbon aerogels as electrode material in supercapacitors. J Porous Mater 1997;4(4):281–5.
- [16] Yoon SH, Lim S, Song Y, Ota Y, Qiao W, Tanaka A, et al. KOH activation of carbon nanofibers. Carbon 2004;42(8–9):1723–9.
- [17] Ryoo R, Joo SH, Jun S. Synthesis of highly ordered carbon molecular sieves via template-mediated structural transformation. J Phys Chem B 1999;103(37):7743–6.
- [18] Merino C, Soto P, Vilaplana-Ortego E, Gomez de Salazar JM, Pico F, Rojo JM. Carbon nanofibres and activated carbon nanofibres as electrodes in supercapacitors. Carbon 2005;43(3):551–7.

- [19] Chena H, Wang F, Tong S, Guo S, Pan X. Porous carbon with tailored pore size for electric double layer capacitors application. Appl Surf Sci 2012;58(16):6097–102.
- [20] Chmiola J, Yushin G, Gogotsi Y, Portet C, Simon P, Taberna PL. Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer. Science 2006;313(5794):1760–3.
- [21] Largeot C, Portet C, Chmiola J, Taberna PL, Gogotsi Y, Simon P. Relation between the ion size and pore size for an electric double-layer capacitor. J Am Chem Soc 2008;130(9):2730–1.
- [22] Xu B, Wu F, Su YF, Cao GP, Chen S, Zhou ZM, et al. Competitive effect of KOH activation on the electrochemical performances of carbon nanotubes for EDLC: balance between porosity and conductivity. Electrochim Acta 2008;53(26):7730–5.
- [23] Xu BS. Prospects and research progress in nano onion-like fullerenes. New Carbon Mater 2008;23(4):289–301.
- [24] Kovalenko I, Bucknall DG, Yushin G. Detonation nanodiamond and onion-like-carbon-embedded polyaniline for supercapacitors. Adv Funct Mater 2010;20(22):3979–86.
- [25] Pech D, Brunet M, Durou H, Huang PH, Mochalin V, Gogotsi Y, et al. Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon. Nat Nanotechnol 2010;5(9):651–4.
- [26] Portet C, Yushin G, Gogotsi Y. Electrochemical performance of carbon onions, nanodiamonds, carbon black and multiwalled nanotubes in electrical double layer capacitors. Carbon 2007;45(13):2511–8.
- [27] Wang KX, Wang YG, Wang YR, Hosono E, Zhou HS. Mesoporous carbon nanofibers for supercapacitor application. J Phys Chem C 2009;113(3):1093–7.
- [28] Lillo-Rodenas MA, Cazorla-Amoros D, Linares-Solano A. Understanding chemical reactions between carbons and NaOH and KOH an insight into the chemical activation mechanism. Carbon 2003;41(3):267–75.
- [29] Zhu YW, Murali S, Stoller MD, Ganesh KJ, Cai WW, Ferreira PJ, et al. Carbon-based supercapacitors produced by activation of graphene. Science 2011;332(6037):1537–41.
- [30] Gao Y, Zhou YS, Park JB, Wang H, He XN, Luo HF, et al. Resonant excitation of precursor molecules in improving the particle crystallinity, growth rate and optical limiting performance of carbon nano-onions. Nanotechnology 2011;22(16):165604.
- [31] Pusawale SN, Deshmukh PR, Lokhande CD. Chemical synthesis of nanocrystalline SnO<sub>2</sub> thin films for supercapacitor application. Appl Surf Sci 2011;257(22):9498–502.
- [32] Wang Y, Shi ZQ, Huang Y, Ma YF, Wang CY, Chen MM, et al. Supercapacitor devices based on graphene materials. J Phys Chem C 2009;113(30):13103–7.
- [33] McDonough JK, Frolov AI, Presser V, Niu J, Miller CH, Ubieto T, et al. Influence of the structure of carbon onions on their electrochemical performance in supercapacitor electrodes. Carbon 2012;50(9):3298–309.
- [34] Wang KP, Teng H. The performance of electric double layer capacitors using particulate porous carbons derived from PAN fiber and phenol-formaldehyde resin. Carbon 2006;44(15):3218–25.
- [35] Korenblit Y, Rose M, Kockrick E, Borchardt L, Kvit A, Kaskel S, et al. High-rate electrochemical capacitors based on ordered mesoporous silicon carbide-derived carbon. ACS Nano 2010;4(3):1337–44.
- [36] Taberna PL, Simon P, Fauvarque JF. Electrochemical characteristics and impedance spectroscopy studies of carbon–carbon supercapacitors. J Electrochem Soc 2003;150(3):A292–300.
- [37] Hsieh CT, Teng H. Influence of oxygentreatment on electricdouble-layercapacitance of activatedcarbonfabrics. Carbon 2002;40(5):667–74.