Hierarchical porous carbon materials from nanosized metal-organic complex for high-performance symmetrical supercapacitor

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A B S T R A C T

The accessible surface area, conductivity, and pore size determine the capacitive properties of carbon-based materials. In this work, hierarchical nanoporous carbon (NPC) materials with a large specific surface area, high conductivity, and suitable pore size are prepared from nanoscaled Al-based metal-organic complex (Al-MOC) by annealing. The annealing temperature has a profound influence on the morphology of the NPC materials which in turn impact the electrochemical performance. Compared to annealing at a low temperature, an interconnected structure is formed at an annealing temperature exceeding 950 °C to produce a larger accessible surface area. Owing to the interconnected structure and high conductivity, sample NPC-950 with the two-electrode configuration has the highest specific capacitance and the best stability. The specific capacitances are 298 Fg⁻¹ at a scanning rate of 1 mVs⁻¹ in symmetrical supercapacitor device. These values are the largest values reported from ultrapure carbon-based EDLCs in an aqueous electrolyte so far. Furthermore, 96.73% of the capacity is retained after 5000 cycles in 1 M H₂SO₄ electrolyte. In an organic electrolyte, the supercapacitor cells composed of NPC produce an energy density of 43 Wh kg⁻¹. The NPC materials with large specific capacity and excellent stability produced by the simple and cost effective technique have large potential in supercapacitors.

1. Introduction

Cost effective and eco-friendly renewable energy storage systems have attracted much attention because of the trend to reduce the use of fossil fuel. Although double layer supercapacitors (EDLCs) are popular energy storage devices due to their unique properties such as the high charge/discharge rate, large power density, and long cycle life [1–6], the low energy density has hampered wider application. Currently, commercial EDLCs have an energy density of 4–5 Wh/kg that is much smaller than that of batteries (20–150 Wh/kg) [7–9] and in order for EDLCs to be more competitive, novel electrode materials with higher conductivity, larger accessible surface area, and desirable pore size are imperative. Electrode materials for EDLCs are commonly based on carbon to take advantage of the high conductivity and stability [10–16]. However, owing to the small accessible surface area, the specific capacitance of carbon materials in practice is less than the theoretical capacitance of 550 Fg⁻¹ [17–22].

In order to increase the accessible surface area on the electrode, many types of porous carbon materials such as activated carbon (AC) [23–26], porous carbon spheres (PCS) [27–29], graphene [20,30–32], carbon nanofibers [33] and carbonized metal-organic framework (CMOF) [34,35], have been proposed. In particular, CMOF supplies the desirable building blocks to produce porous carbon materials due to the large specific surface area and open pore structure and the composition and morphology can be tailored for EDLC electrodes [36–40]. However, in spite of recent advance, the specific capacity is still not satisfactory because of the size is on the micrometer and sub-micrometer scales [34,41].

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Recently, carbon materials with a smaller size have been demonstrated to have a larger capacitance under the same conditions [42], as a smaller size reduces the mass transport distance and charge transfer resistance and improves the accessible surface area consequently enhancing the specific capacitance [43–48]. In CMOF with a large size, the electrolyte and ions cannot be transported to the bulk freely during high-rate charging and discharging. Furthermore, since only a portion of the surface area is utilized, the specific capacitance is relatively small [49,50]. Hence, reducing the CMOF size is an effective means to improve the electrolyte transport and specific capacitance. On the other hand, the morphology and pore size of the carbon materials also have a large impact on the electrochemical characteristics [21,51,52]. From the perspective of the pore size, the combination of mesopores and micropores can improve the capacitance as the electrolyte solution traverse through the mesopores while electrolyte ions are stored in the micropores during charging/discharging [21]. Nonetheless, how to tailor the porous structure while maximizing the accessible surface area by optimizing the surface morphology of carbon materials is quite challenging.

Herein, highly porous and interconnected carbon materials are designed and fabricated by carbonization of nano-scale Al-based metal-organic complex (Al-MOC) and the morphology is optimized by the carbonization temperature. In this hierarchical porous structure, each building block consists of nano-scale carbonized Al-MOC (ca.20–50 nm). Due to the interconnect structure derived from temperature-related self-assembly process, the NPC sample has a large accessible surface area, short diffusion distance, high conductivity, and improved electron transport pathways. Two types of micropores and mesopores are found in the framework, large pores between adjacent carbonized Al-MOC and small pores in the carbonized Al-MOC unit. As a result, the unique structure with high conductivity boasts a large specific surface area of 1593 m²g⁻¹. The capacitive performance of the nanoporous carbon (NPC) made from carbonized Al-MOC is excellent. Without chemical activation, the NPC carbonized at 950 °C shows specific capacitances of 298 and 249 Fg⁻¹ at a scanning rate of 1 mVs⁻¹ and current density of 1 Ag⁻¹ in a symmetrical supercapacitor (1 M H₂SO₄) respectively. About 97% of the initial capacitance is retained after 5000 cycles of rapid charging/discharging at 10 Ag⁻¹. A large energy density of 43 Wh kg⁻¹ is observed from an organic electrolyte suggesting large commercial potential of the MOC derived porous carbon in supercapacitors.

2. Experimental section
2.1. Materials

Benzene-1,4-dicarboxylic acid (BDC), Aluminum nitrate non-aquahydrate (Al(NO₃)₃·9H₂O), N,N-Dimethylformamide (DMF), 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄), Acetonitrile (AN), Hydrochloric acid (HCl) were purchased from Sigma-Aldrich Chemical Co. All chemicals were used without further purification.

2.2. Synthesis of Al-based metal-organic complex

1.875 g of Al(NO₃)₃·H₂O and 0.81 g of 1,4-Benzenedicarboxylic acid (BDC) were dissolved into 40 mL N,N-Dimethylmethanamide (DMF), then the mixture was under 30 min ultrasonication to make a homogeneous solution. Subsequently, the solution was heated to 150 °C in an oil bath for 48 h under stirring with reflux, and the color of solution should become white with the time pass. After cooling to room temperature, the solution was centrifuged under 8000 rpm, and white crystals were collected. The as-prepared material was washed 3 times by DMF to remove the probable impurities. Then the material was dried at 60 °C under vacuum after exchanged DMF via dichloromethane for 24 h.

2.3. Carbonization of Al-based metal-organic complex

In each experiment, 2 g of the Al-based metal-organic complex was put in a quartz boat, and heated to 650, 750, 850, 950 or 1050 °C respectively for 3 h in Ar atmosphere. Black powder like samples were collected after the furnace cooling to room temperature. To compare with the direct sintered samples, NPC-850 sample was reheated to 950 °C with the same procedure, and the sample was named NPC-850 (950).

2.4. Removal of Al from carbonized Al-based metal-organic complex

In a typical synthesis, 1 g of carbonized Al-based metal-organic complex was mixed with 10 mL 17% HCl in a 25 mL flask and reflux in 120 °C for 4 h. The sample was filtered via 0.2 μm porous film, and washed 5 times with DI water. Then the final products were dried at 75 °C under 10 mmHg vacuum and named NPC-650, NPC-750, NPC-850, NPC-950 and NPC-1050, respectively.

2.5. Electrochemical measurements

The working electrodes were prepared by mixing NPC (80 wt%), raw carbon nanotubes (Sigma-Aldrich Chemical Co., 10 wt%), and polyvinylidenedifluoride (PVDF, Solvay, 10 wt%) and pressing under a pressure of 10 MPa to form pieces with diameter of 1 cm. The mass of the active material was 3 mg and 1 M H₂SO₄ aqueous (with 0.1% w/w SDS) solution was used as electrolyte [53]. The electrochemical performance was evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) measurements with an EC-LAB VMP3 (BioLogic Science Instruments). The CV curves were performed under a potential window from 0 V to 1 V at different scan rates in the range from 1 to 200 mVs⁻¹. Galvanostatic charge/discharge (GCD) measurements were investigated in potential window from 0 to 0.9 V at different current densities from 1 to 10 A g⁻¹. EIS was taken in the frequency range from 100 kHz to 1 mHz with amplitude of 10 mV.

Specific capacitance values from CV curves are calculated via the following equation:

\[ C = \frac{1}{m \times \Delta v \times s} \left( \int_{0}^{t_f} iv \, dt + \int_{t_f}^{t_i} idv \right) \]

Which \( C \) is the specific capacitance (F g⁻¹), \( m \) is the mass loading (mg) of active material in single electrode, \( \Delta v \) is the voltage window(V) for CV test, \( s \) is the scan rate (mV s⁻¹) for each CV cycle, the integral part is the area of CV curve at each scan rate.

Specific capacitance values from GCD curve are calculated via the following equation:

\[ C = \frac{2I \Delta t}{mU} \]

Which \( C \) is the specific capacitance (F g⁻¹), \( I \) is the discharging current (mA) during the GCD measurement, \( \Delta t \) is the time (s) of discharging during GCD measurement, \( m \) is the mass loading (mg) of active material in single electrode, \( U \) is the voltage difference(V) in the discharging time.

Energy density was calculated via the following equation:
\[ E = \frac{CV^2}{8 \times 3.6} \]

Which \( E \) is the energy density (\( \text{Wh kg}^{-1} \)), \( C \) is the capacitance \( \text{of material (F g}^{-1} \)), \( V \) is the voltage window in measurement.

Power density was calculated via the following equation:
\[ P = \frac{E}{t} \]

Which \( P \) is the power density \( \text{(W kg}^{-1}) \), \( E \) is the energy density from the above equation, \( t \) is the discharge time (h).

### 2.6. Preparation of flexible supercapacitor device with NPC-950

10 mg of NPC-950 sample was mixed with 1.6 mg of PVDF and 2.3 mL of Methylpyrrolidone (NMP). The mixture slurry was prepared after ground in a mortar. 16 μm thick aluminium foil was first cleaned with acetone, then coated with the mixture with the thickness of 30 μm. The aluminium foil with material coated was dried at 120 °C in vacuum for 24 h, then the foil was cut for electrode with the size of 2 cm². A sandwich-like supercapacitor device with two pieces of electrodes and one separator was assembled inside an Ar saturated glove box, then sealed with plastic package after filled with BMIMBF4/AN electrolyte. Then the device is ready for the further test.

### 2.7. Characterizations

Transmission electron microscopy (TEM) was performed on FEI Tecnai F30 transmission electron microscope operating at an acceleration voltage of 200 kV. X-ray diffraction (XRD) was recorded by a Philips diffractometer using Cu Kα radiation. The thermogravimetric analysis (TGA) was conducted on Q600 SDT TA at a heating rate of 10 °C min⁻¹ from room temperature to 900 °C under flowing air. The \( \text{N}_2 \) adsorption/desorption isotherms were obtained at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2010 M instrument. Brunauer-Emmett-Teller (BET) and Barret-Jonner-Halenda (BJH) methods were used to calculate the specific surface area and the pore size distribution. Raman scattering was scanned with a Renishawmicro Raman spectrometer \((\lambda = 785 \text{ nm})\). The X-ray photoelectron spectra (XPS) were obtained using Al Kα (hv = 1486.6 eV) radiation with a Prevac system equipped with a Scienta SES 2002 electron energy analyzer operating at constant transmission energy \((\text{Ep} = 50 \text{ eV})\).

The accessible surface area of NPC-950 is determined by methylene blue (MB) adsorption method. MB adsorption is a standard method for measuring the specific surface area of graphitic materials, with 1 mg of adsorbed MB molecules covering 2.34 m² of surface area \([54]\). The surface areas were calculated by adding a carefully weighted NPC-950 sample into a standard concentration of MB in DI water for a total of 24 h to reach adsorption equilibrium. The MB concentration was determined by analysing the supernatant through UV–vis spectroscopy at a wavelength of 665 nm and compared with the initial standard concentration of MB before interacting with NPC-950 sample.

### 3. Results and discussion

The interconnected hierarchical nanoporous carbon materials are prepared by direct carbonization of Al-based metal-organic complex (Al-MOC) as shown in Fig. 1. Benzene-1,4-dicarboxylic acid (BDC) as the organic ligand and Al(NO₃)₃ • 9H₂O as the metal salt are used to form the Al-MOC nanostructure with a length of 20–50 nm as illustrated in Fig. 2a. Comparing the morphology of Al-MOC before and after carbonization, the NPC size is significantly smaller. The porous structure shown in Fig. 2b–f is produced by removing Al from the carbonized Al-MOC. Eliminating the metal skeleton does not destroy the bulk structure but can expose more micropores blocked by metal oxide in the NPC nanoparticles. The samples are labeled by the annealing temperature as NPC-650, NPC-750, NPC-850, NPC-950, and NPC-1050. The NPCs produced at lower carbonization temperature (NPC-650, NPC-750, and NPC-850) remain as separate nanoparticles, whereas the particles in NPC-950 and NPC-1050 agglomerate into an interconnected structure due to high-temperature sintering of the mesopores in NPC-950 as indicated by the white arrow in the inset in Fig. 2e. The self-assembly process depends on the temperature and a higher temperature is more desirable. As a result of sintering, extra mesopores appear from the micro- and micropores existing in the bulk NPC materials. In this way, the electrolyte can permeate freely and the paths of the electrolyte ions are shortened during charging-discharging. The temperature-dependent self-assembly is thus a convenient method to modulate nanoporous carbon materials. We suppose the mechanism of the temperature-derived aggregation of NPC can be explained as: when the Al-MOC was heated to high temperature, the coordinative bonding between metal ions or clusters and organic linkers will break from the initial structure and connect with the other part of MOC structure aside. The broken and regroup of the coordinative bond need a specific high energy to break the bandgap. So the aggregation phenomenon can only occur at high temperature but not at lower temperature. Heteroatoms (O, N, etc.) in the Al-MOC and other MOF-like structures play an important role in the bond-rebuild process. The preparation of NPC-850 (950) sample can somehow verify this viewpoint. After pre-carbonized at 850 °C, almost all of the heteroatom has been removed, leaving only pure carbon \((\text{Table} \ 1)\). At this time, the nano-sized carbon particles still separated from each other. Then the pre-carbonized sample was heated to 950 °C, the separated NPC structure maintained, and no aggregation occurred \((\text{Fig. S1})\).

The XRD patterns of the NPC samples are displayed in Fig. 3a. The two broad peaks at 2θ = 23° and 44° are assigned to carbon \((\text{002})\) and \((\text{101})\) diffraction suggesting complete conversion to carbon leaving no aluminum oxide \([55,56]\). The ratio of the height of the \((\text{002})\) peak to background may be used to evaluate the degree of graphitization \([57]\). NPC-650 exhibits the lowest degree of graphitization. The Raman scattering spectrum \((\text{Fig. 3d})\) shows two peaks at 1320 and 1590 cm⁻¹ corresponding to the D and G bands. The D band is ascribed to disordered carbon, whereas the G band indicates graphitic sp² carbon \([58]\). The ratios \(\text{I}_D/\text{I}_G\) of NPC-650, NPC-750, NPC-850, NPC-950, and NPC-1050 are 2.49, 2.41, 2.38, 2.32, and 2.23 respectively, revealing increased formation of graphitic sp² carbon with carbonization temperature. The results are consistent with XRD disclosing that a higher temperature facilitates a larger degree of graphitization, which can decrease the resistance during electrochemical measurements. The TGA data \((\text{Fig. S2})\) show that aluminum oxide is removed from all the NPC samples.

As shown in Fig. 3c–d and Fig. S4, the surface composition of the Al-MOC and NPC samples is determined by X-ray photoelectron spectroscopy (XPS). The surface of Al-MOC contains carbon, oxygen and aluminum \((\text{Fig. S4})\) and after carbonization and removal of aluminum oxide, the aluminum signal diminishes significantly \((\text{Fig. 3c})\). The surface elemental concentrations are as follows: carbon \(\text{C}, \text{oxygen} \text{O}, \text{and aluminum} \text{Al} \) \([59]\). Which \( P \) is the power density \((\text{W kg}^{-1})\), \( E \) is the energy density from the above equation, \( t \) is the discharge time (h).
constituted mostly by 1,4-Benzenedicarboxylic acid molecules and the other one at 288.7 eV is ascribed to two carboxylic groups complementing the molecules [60]. After carbonization, the C 1s peak shifts to 284.3 eV due to sp²-hybridized carbon atoms in the graphite-like nanometric materials [61]. The C 1s peak with a sharp maximum on the low-binding energy side and long tail on the high-binding energy side are typical of pure carbon materials obtained by carbonization of organic species [62]. Table 1 shows the elemental composition calculated from the peak areas with the proper sensitivity factors.

The porosity of Al-MOC and NPC is determined by the N₂ adsorption/desorption technique at 77 K. The isotherms in Fig. 4...
suggest different pore sizes ranging from micro- to macro-pores [63]. The steep increase in the adsorbed N2 volume at low pressure reveals the existence of micropores, whereas the small slope at medium pressure and hysteresis loop show the existence of a significant amount of mesopores. The vertical tails at a relative pressure near 1.0 indicate that macropores are present as well [64,65]. The trend of the specific surface area value is related to the carbonization temperature of NPC samples. Lower carbonization temperature (650 °C) can somehow maintain and stabilize the porous structure so that the NPC-650 sample has a similar SSA like the complex. However, the increase of carbonization temperature would provide higher energy for breaking more coordinative bonds in the complex and eliminate the porous structure, leading to a lower SSA value. When continue increasing the carbonization temperature, the separated nanomaterial would conjugate with each other to form a hierarchical nanoporous structure. The trend of SSA change also corresponds with the morphology study of all NPC samples. Owing to sintering of the NPC materials at over 950 °C, adjacent carbonized Al-MOCs merge and extra mesopores form among the NPC particles consequently increasing the BET area from 809 to 1593 m²/g (from NPC-750 to NPC-950). Methylene blue (MB) adsorption method was used for investigating the accessible surface area simultaneously. 1 g of the NPC material can adsorb 415 mg of the MB dye, which means the accessible surface

| Properties of NPCs: Atomic concentrations based on XPS spectrum and specific surface area, pore size, and pore volume data based on nitrogen adsorption/desorption isotherms (Fig. 4). |
|---------------------------------|----------------|----------------|----------------|----------------|----------------|
| % C 1s                          | Complex        | NPC-650        | NPC-750        | NPC-850        | NPC-950        | NPC-1050       |
| % O 1s                          | 57.6           | 94.7           | 96.6           | 97.4           | 96.7           | 96.6           |
| % Al 2p                         | 35.2           | 4.7            | 3.0            | 1.5            | 3.1            | 3.0            |
| Surface area                    | 6.9            | 6.9            | 6.9            | 6.9            | 6.9            | 6.9            |
| Multipoint BET (m²/g)           | 1525           | 1580           | 809            | 1251           | 1593           | 1580           |
| Pore size                       | 1.93           | 2.46           | 1.51           | 1.36           | 2.49           | 3.08           |
| Average pore diameter (nm)      | 1.942          | 0.972          | 3.087          | 4.251          | 2.001          | 1.215          |
| BJH method (cm³/g)              | 1.752          | 0.895          | 2.562          | 3.001          | 0.924          | 1.147          |
| DFT method (cm³/g)              |                |                |                |                |                |                |

Fig. 3. (a) XRD and (b) Raman scattering spectra of NPC-650, NPC-750, NPC-850, NPC-950, and NPC-1050; X-ray photoelectron spectra (XPS): (c) Survey and (d) C 1s of NPC produced at different carbonization temperature.
increased from 20 to 200 mVs⁻¹ (Fig. 5b). This benefit slightly decreasing capacitance when the scanning rates are no significant diffusion limitation can be derived based on the slightly decreasing capacitance when the scanning rates are increased from 20 to 200 mVs⁻¹ (Fig. 5b). This benefit from the mesoporous structure because the mesopores may be accessed freely and quickly by electrolyte ions. Hence, the pore size is a crucial factor of the capacitance. Galvanostatic charging/discharging measurements are performed in the potential window from 0 to 0.9 V at different current densities between 1 and 10 A g⁻¹ (Fig. 5c). The discharging time increases from NPC-650 to NPC-950 and then decreases for NPC-1050. The highest specific capacitance is observed from NPC-950 consistent with CV. NPC-950 and NPC-1050 show an almost symmetrical triangular shape implying excellent coulombic efficiency and electrochemical reversibility for NPC materials prepared at a high carbonization temperature. As an example, the galvanostatic charging/discharging curves of NPC-950 at different current densities (1–10 A g⁻¹) are displayed in Fig. S5. The specific capacitances at current densities of 1, 2, 5, and 10 A g⁻¹ are 249, 225, 197, and 157 F g⁻¹ respectively (Fig. 5d) and NPC-950 exhibits the best electrochemical behavior. To the best of our knowledge about pure carbon materials without any activation and heteroatom doping, the largest reported value is 249 F g⁻¹ at a current density of 1 A g⁻¹ in 1 M H₂SO₄ aqueous solution (two-electrode system). Table S1 compares the results of two-electrode systems in aqueous electrolytes with our work. Based on this high capacitance value, the energy density of NPC-950 is 7.1 Wh kg⁻¹, while the power density is 211 W kg⁻¹. In order to prove that aggregation of NPC nanoparticles increases the capacitance and elucidate the mechanism, the supercapacitor properties of NPC-850 (950) are determined (Fig. S6). The specific capacitance of NPC-850 (950) is almost the same as that of NPC-950 (157 F g⁻¹ at 1 A g⁻¹) and significantly less than that of NPC-950. Comparing the TEM images of NPC-950 and NPC-850 (950) (Fig. S1), aggregation of NPC nanoparticles is observed from NPC-950 and both large and small pores are present. However, with regard to NPC-850 (950), the NPC nanoparticles are still separated from each other and no sintering occurs. Therefore, it can be confirmed that capacitance enhancement arises from aggregation of NPC nanoparticles. The construction of hierarchical porous structures that maintain their overall crystalline order is desirable because the high structural regularity may, in turn, afford markedly improved properties [69]. The
aggregation of nanoparticles can also improve the conductivity and electron mobility, and this phenomenon has been proved by the amount of research. For example, compared with single crystalline TiO$_2$, the mesoporous TiO$_2$ has significant advantages on electrochemical properties [70]. Based on the reported research papers and our experiment results, we believe the interconnected structure has a positive effect on electrochemical capacitor behavior.

The Nyquist plots acquired in the frequency range from 100 kHz to 1 mHz are shown in Fig. 5e featuring a vertical curve indicating a nearly ideal capacitive behavior of the cell. The equivalent circuits of the Nyquist plot is shown in Fig. S7. The magnified data of NPC-950 in the high-frequency range (Fig. 5e, inset) shows a transition between the resistance capacitance semicircle and migration of electrolyte is observed at a frequency of 364 Hz corresponding to a resistance of 0.98 $\Omega$. Diffusion of electrolyte ions stops at 5 Hz and then the full capacitance is reached [71]. The electrochemical stability of NPC-950 sample is studied (Figs. 5f) and 96.73% of the capacitance is retained after 5000 cycles at 10 A/g. The Nyquist plots before and after 5000 charging/discharging cycles (Fig. 5f inset) indicate excellent electrochemical stability.

The electrochemical properties of NPC-950 in the organic electrolyte, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM BF$_4$) in acetonitrile (AN) are presented in Fig. 6. The voltage window is extended to 2.5 V on account of the unique properties of organic electrolytes. High capacitances of 233 F g$^{-1}$ at 1 mVs$^{-1}$ and 198 F g$^{-1}$ at 1 Ag$^{-1}$ are obtained by cyclic voltammetry and galvanostatic charging/discharging. The resistance obtained from the Nyquist plot in Fig. 6c is 3.36 $\Omega$ and smaller than 6–15 $\Omega$ achieved from other supercapacitors in the same electrolyte [72,73]. Long cycle stability is also observed at a current density of 10 Ag$^{-1}$ (Fig. 6d) and 78.89% of the capacitance is retained after 10,000 charging/discharging cycles. In the Bode plots, the characteristic frequency $f_0$ at the phase angle of $-45^\circ$ of NPC-950 is 1.03 Hz corresponding to a time constant $\tau_0$ = 1/$f_0$ of 0.97 s (Fig. 6e), which is less than that of conventional activated-carbon supercapacitors (~10 s) indicating faster charging/discharging [74,75]. The Ragone plot (Fig. 6f) shows that the energy density of NPC-950 in the organic electrolyte is 43 Wh kg$^{-1}$ which is again larger than that of many commercial carbon-based supercapacitors with energy densities between 4 and 5 Wh kg$^{-1}$ [76]. To evaluate the practical application of the materials, a flexible sandwiched supercapacitor device composed of NPC-950 and a commercial separator is fabricated. After the prototype containing the BMIM BF$_4$/AN electrolyte is charged for 20 s with a 9 V battery, it can light a yellow LED for about 10 min (movie S1). The good results arise from the large contact surface area between the electrolyte and electrode, large pores facilitating fast penetration of electrolyte ions, and porous structure enabling efficient storage of electrolyte ions and shortening the pathway during charging-discharging. The high-temperature treatment increases the electrical conductivity due to a larger degree of graphitization. Fig. 6S presents the relationship between the specific capacitance, carbonization temperature, and specific surface area. The carbonization temperature has profound effects on the morphology, porosity, graphitization degree of the carbonized Al-MOC, and consequently electrochemical performance of the supercapacitor. The specific capacitance is proportional to the specific surface area and NPC-950 has the highest specific capacitance as a result of the largest surface area and interconnected structure in which extra pores are created between adjacent Al-MOC after annealing. The hierarchical pores and interconnected structure provide short diffusion paths and low resistance for ion passage resulting in high capacitance.

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2018.03.043.
Fig. 6. Supercapacitor performance of NPC-950 in an organic electrolyte: (a) Cyclic voltammetry, (b) Galvanostatic charging/discharging curves, (c) Nyquist plot, (d) Electrochemical stability, (e) Bode plots, (f) Ragone plots in comparison with commercial ECs and lithium-ion batteries [14,52]. Inset: LED powered by the NPC-950 based supercapacitor device.

4. Conclusion

The hierarchical NPC prepared by annealing of nano-scale Al-based Al-MOC has an interconnected porous structure, large specific surface area (1593 m² g⁻¹), high conductivity suitable pore size distribution, and excellent capacitive characteristics boding well for energy storage. Without chemical activation, NPC-950 delivers in the symmetrical supercapacitors, for instance, high specific capacitances of 298 and 249 F g⁻¹ at a scanning rate of 1 mV s⁻¹ and current density of 1 A g⁻¹ and retained values of 197 and 157 F g⁻¹ even at large current densities of 5 and 10 A g⁻¹ respectively. Long-term stability is observed for both aqueous and organic electrolytes and the large energy density of 43 Wh kg⁻¹ suggest large potential in next-generation supercapacitors.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2018.03.043.

References


Supporting Information for

Hierarchical Porous Carbon Materials from Nanosized Metal-organic Complex for High-Performance Symmetrical Supercapacitor

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Fig. S1 TEM image of reheated NPC-850(950).
Fig. S2. Thermogravimetric analysis (TGA) curves of NPC-650, NPC-750, NPC-850, NPC-950 and NPC-1050.
Fig. S3 (a) XRD spectrum of Al-based metal-organic complex. Certain amount of aluminum oxide is still contained in the carbonized Al-based metal-organic complex. Because of the as-synthesized Al2O3 is amorphous, no diffraction peak for its crystal plane can be observed. (b) TGA curve of Al-based metal-organic complex, about 51.66 wt% of aluminum oxide remaining in the carbonized Al-based metal-organic complex.
**Figure S4** XPS spectrum of Al-MOC. The precursor contains relatively high amount of aluminum atoms (approx. 6.9 at.%). Correspondingly a high concentration of oxygen atoms (35.2 at.%) is observed. Carbon atomic concentration is 57.6 %. The maximum of XPS Al 2p spectrum acquired for the precursor sample is located at 74.4 eV and corresponds with Al$^{3+}$ ions presumably from aluminum oxide or hydroxide.
Figure S5: Galvanostatic charge/discharge curves of NPC-950.
Fig. S6  Cyclic voltammetry curves (a) and Galvanostatic charge/discharge curves (b) of NPC-850(950) sample.
**Figure S7:** The equivalent circuits of Nyquist Plot, which comprises the uncompensated resistance of the electrolyte ($R_s$), in series with the capacitance of the dielectric layer ($C_{dl}$), the charge-transfer resistance ($R_{ct}$) and the Warburg impedance ($Z_w$)
Figure S8  The relationship between the specific capacitance, carbonization temperature, and specific surface area of NPC samples.
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<th>Materials Reported</th>
<th>Electrolyte (voltage)</th>
<th>Voltage window</th>
<th>$C_{GCD}$/$F$ g$^{-1}$ (Current density)</th>
<th>Ref.</th>
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<td>holey graphene frameworks</td>
<td>6M KOH</td>
<td>0–1V</td>
<td>310 (1 A g$^{-1}$)</td>
<td>[1]</td>
</tr>
<tr>
<td>laser-scribed graphene</td>
<td>1M H$_2$SO$_4$</td>
<td>0–1V</td>
<td>222 (1 A g$^{-1}$)</td>
<td>[2]</td>
</tr>
<tr>
<td>self-assembled Graphene Hydrogel</td>
<td>5M KOH</td>
<td>0–1V</td>
<td>175 (1 A g$^{-1}$)</td>
<td>[3]</td>
</tr>
<tr>
<td>porous activated rGO</td>
<td>1M KOH</td>
<td>0–1V</td>
<td>~140 (10 A g$^{-1}$)</td>
<td>[4]</td>
</tr>
<tr>
<td>GO</td>
<td>6M KOH</td>
<td>0–1V</td>
<td>189 (0.5 A g$^{-1}$)</td>
<td>[5]</td>
</tr>
<tr>
<td>graphene</td>
<td>6M KOH</td>
<td>0–1V</td>
<td>120 (1 A g$^{-1}$)</td>
<td>[6]</td>
</tr>
<tr>
<td>carbon nanocage</td>
<td>1M H$_2$SO$_4$</td>
<td>0–0.9V</td>
<td>216 (1 A g$^{-1}$)</td>
<td>[7]</td>
</tr>
<tr>
<td>mesoporous carbon@rGO</td>
<td>6M KOH</td>
<td>0–1V</td>
<td>41.5 (1 A g$^{-1}$)</td>
<td>[8]</td>
</tr>
<tr>
<td>exfoliated graphene paper</td>
<td>PVA/H$_2$SO$_4$</td>
<td>0–1V</td>
<td>56.6 (1 mA cm$^{-2}$)</td>
<td>[9]</td>
</tr>
<tr>
<td>graphene hydrogels</td>
<td>1 M H$_2$SO$_4$</td>
<td>0–1V</td>
<td>211 (1 A g$^{-1}$)</td>
<td>[10]</td>
</tr>
<tr>
<td>carbon sphere@GO</td>
<td>6M KOH</td>
<td>0–1V</td>
<td>198 (175mA g$^{-1}$)</td>
<td>[11]</td>
</tr>
<tr>
<td>graphene</td>
<td>1M Na$_2$SO$_4$</td>
<td>0–1.7V</td>
<td>58.6 (2mA cm$^{-2}$)</td>
<td>[12]</td>
</tr>
<tr>
<td>MWCNT@graphene</td>
<td>6M KOH</td>
<td>0–1V</td>
<td>286 (1.78mA cm$^{-2}$)</td>
<td>[13]</td>
</tr>
<tr>
<td>porous graphene-like carbon</td>
<td>1 M Na$_2$SO$_4$</td>
<td>0–1.8V</td>
<td>58 (1 A g$^{-1}$)</td>
<td>[14]</td>
</tr>
<tr>
<td>porous graphene @ carbon cloth</td>
<td>PVA/H$_2$SO$_4$</td>
<td>0–1V</td>
<td>79.19 (0.5 A g$^{-1}$)</td>
<td>[15]</td>
</tr>
<tr>
<td>Graphene Nanoribbon</td>
<td>6M KOH</td>
<td>0–0.8V</td>
<td>106.2 (100 mA cm$^{-2}$)</td>
<td>[16]</td>
</tr>
<tr>
<td>Porous Graphene</td>
<td>1 M H$_2$SO$_4$</td>
<td>0–1V</td>
<td>71.0 mA cm$^{-2}$</td>
<td>[17]</td>
</tr>
<tr>
<td>carbon nanofiber@ultrathin graphite</td>
<td>PVA/H$_2$SO$_4$</td>
<td>0–1V</td>
<td>~120 (1 A g$^{-1}$)</td>
<td>[18]</td>
</tr>
<tr>
<td>porous graphene ribbons</td>
<td>PVA/H$_3$PO$_4$</td>
<td>0–0.8V</td>
<td>208.7 (0.1A g$^{-1}$)</td>
<td>[19]</td>
</tr>
<tr>
<td>Porous Graphene</td>
<td>1 M H$_2$SO$_4$</td>
<td>0–1V</td>
<td>243 (1 A g$^{-1}$)</td>
<td>[20]</td>
</tr>
<tr>
<td>interconnected microporous carbon</td>
<td>1 M H$_2$SO$_4$</td>
<td>0–1V</td>
<td>239 (1 A g$^{-1}$)</td>
<td>[21]</td>
</tr>
<tr>
<td>NPC</td>
<td>1 M H$_2$SO$_4$</td>
<td>0–0.9V</td>
<td>249 (1 A g$^{-1}$)</td>
<td>This work</td>
</tr>
</tbody>
</table>
Table S1  Performance of various carbon based material for supercapacitor via two-electrode system test.

Reference


