Porous-Carbon Nanotube Aerogels



# Controlled Air-Etching Synthesis of Porous-Carbon Nanotube Aerogels with Ultrafast Charging at 1000 A g<sup>-1</sup>

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Supercapacitors are energy storage systems capable of fast charging and discharging, thus generating superior power density. Porous carbon with high surface area and tunable pore size represents a promising candidate to construct ultrafast supercapacitors; so far, most porous carbonbased electrodes can only be charged to a moderate current density  $(100-200 \text{ A g}^{-1})$ , also with significant capacitance loss at increasing rate. Here, it is shown that a 3D aerogel consisting of interconnected 1D porouscarbon nanotubes (PCNs) can serve as a freestanding supercapacitor electrode with excellent rate performance. As a result, the PCN aerogel electrodes achieve 1) ultrafast charging at current densities up to 1000 A g<sup>-1</sup> (corresponding to a charge period of 16 ms), which is the highest value among other porous carbon-based supercapacitors, 2) superior cycling stability at high charging rates (88% capacitance retention after 10<sup>5</sup> cycles at 1000 A  $g^{-1}$ ). Mechanism study reveals favorable kinetics including a centralized pore size distribution at 0.8 nm which is a dominant factor to allow high-rate charging, a low and linear IR drop, and a metallic feature of 1D PCNs by theoretical calculation. The results indicate that 1D PCNs with controlled porous structures have potential applications in ultrafast energy conversion and storage.

# 1. Introduction

Supercapacitors are energy storage systems characterized by ultrafast charging and high power density, which can complement other systems such as batteries in practical applications.<sup>[1]</sup> Electrical double layer capacitors (EDLCs) work by physical adsorption of ions from electrolyte on the porous electrode surface; this mechanism intrinsically enables fast charging/discharging processes and allows us to fully

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explore the advantages of supercapacitors.<sup>[2]</sup> Porous carbon materials possess features such as low cost, high porosity, high surface area, high electrical conductivity, and high chemical stability,<sup>[3]</sup> and have stimulated tremendous interest in developing ultrafast and high-rate performance supercapacitors recently. Zhang et al. reported a multiscale porous carbon electrode synthesized by silica sphere template which can be charged at an ultrahigh current density (500 A g<sup>-1</sup>) and maintain 60% of its capacitance at 1 A g<sup>-1</sup>, in a three-electrode configuration.<sup>[4]</sup> Chen et al. fabricated hollow particle-based N-doped carbon nanofibers by electrospinning, and demonstrated that 1D hollow carbon nanostructures are desired for high performance supercapacitors.<sup>[5]</sup> Bu et al. used MgO particles as template to synthesize collapsed carbon nanocages, and obtained a capacitance of 179 F g<sup>-1</sup> at 200 A g<sup>-1</sup> (87% retention) in aqueous electrolyte although the time constant remained large (0.6 s).<sup>[6]</sup>

In other efforts, mesoporous graphene synthesized by a selfpropagating high-temperature method also exhibited good properties with 98 F g<sup>-1</sup> capacitance tested at 500 A g<sup>-1</sup> (57% retention) in organic electrolyte.<sup>[7]</sup> However, there exist several kinetic issues such as the ion-transport resistance and the diffusion distance within the hierarchical 3D porous structure which limit the charging rate and capacitance retention particularly at high rates,<sup>[8]</sup> and it remains unclear how fast the charging/discharging process can reach in optimized porous carbon EDLC electrodes. So far, very high charging rate (1000 A g<sup>-1</sup>) was only tested in a macromolecule redoxmediated electrolyte system, whereas the pseudocapacitance dropped substantially to 37%.<sup>[9]</sup>

Extensive efforts have been devoted to fabricate porous carbon materials and tailor the electrode structure. Sacrificial templates such as mesoporous silica have been adopted to prepare mesoporous carbon with ordered channels of about 2–6 nm, but the performance is limited by the lack of hierarchical structure and micropores.<sup>[10]</sup> Chemical activation involving KOH or NaOH has been used to produce porous carbon with high specific surface area and pore sizes from sub-nanometers to hundreds of nanometers.<sup>[11–14]</sup> Because the pore-formation process is accompanied by wild chemical



reaction between hydroxide and carbon, the escape of carbon oxide gases results in a wide range of pore sizes that are difficult to control precisely. In addition, porous precursors such as metal-organic frameworks have been chosen to make porous carbon by thermal annealing, but the high temperature treatment usually causes structural collapse and may damage the inner pores.<sup>[5,15]</sup> Furthermore, some theoretical/ experimental studies have revealed possible influence of pore size/morphology on the charge storage behavior. For example, Chmiola et al. found that mesopores are not the ideal size for ion storage in supercapacitors, instead, EDLC with micropores less than 1 nm in size would exhibit anomalous increase due to the reduction of distance between the electrolyte ions and pore walls, and enhancement of effectively adsorbed ions.<sup>[16]</sup> Also, Wang et al. concluded that in mesopore channels, the shorter the length and the larger the diameter/length ratio, the smaller the ion-transport time.<sup>[10]</sup> In addition, Kondrat et al. discovered that a monodisperse porous electrode with appropriate size would be desired for the energy storage in nanoporous EDLC.<sup>[17]</sup> Although intrinsic merits of carbonbased materials (including their high conductivity and surface area) are beneficial properties in applications such as supercapacitors, the microstructure must be tailored and optimized in order to reach the maximum performance. And, the underlying factors that influence the high-rate behavior remain unclear.

The above studies indicate that controlling the pore-formation process and obtaining suitable porous configuration are essential in developing high performance porous carbonbased EDLC. Here, we report a 3D bulk aerogel consisting of interconnected 1D porous-carbon nanotubes (PCNs) which could serve as a freestanding supercapacitor electrode with excellent rate performance. In contrast to previously reported pore-formation methods, we combine a nitric acid (HNO<sub>3</sub>) treatment and low-concentration air-etching processes to controllably create uniform micropores and mesopores in the PCN walls. The resulting PCN aerogels have been configured into two-electrode EDLC, which could be charged at current densities up to 1000 A g<sup>-1</sup> while maintaining a specific capacitance of 120 F g<sup>-1</sup> (≈62% retention of maximum capacitance). The ultrafast charging achieved in our PCN electrodes is the highest recorded among all the porous carbon-based EDLC (less than 100-200 A  $g^{-1}$ ), and we also obtain superior capacitance retention at high charging rates. Moreover, we carried out mechanism and theoretical study to reveal favorable kinetics involved in PCN structures, including a low and linear IR drop, about 85% contribution from electrical double layer capacitance, a very small time constant (0.057 s), and a metallic feature of 1D PCNs. In particular, we disclosed that the centralized distribution of micropores at 0.8 nm acts as a dominant factor in the high-rate performance of PCNs.

# 2. Results and Discussion

Our preparation of PCN aerogels involves two steps, 1) formation of 1D hollow tubes and 3D networks and 2) creation of pores, as illustrated in **Figure 1**a (see the Experimental

Section for details). First, silver nanowires (AgNWs) were chosen as sacrificial substrates to form 1D polypyrrole (PPy) nanotube structures. The wrapping of pyrrole and subsequent polymerization into PPy resulted in 3D-interconnected AgNW/PPy networks, as described in literature.<sup>[18]</sup> We further dissolved the AgNWs by HNO3 and obtained a freestanding large-area PPy nanotube aerogel. The HNO<sub>3</sub> treatment not only removes the inner nanowires, but also induced nitrate  $(NO_3^-)$  anion doping into the aerogel, as can be seen from the color change in the sample (from black to brown). The second step is to involve high-temperature annealing under inert atmosphere (and flowing a small amount of air) during which the PPy nanotubes are transformed into PCNs while maintaining the aerogel structure (slightly shrunk and curled over) and about 80% weight loss. The process of pore creation in PCNs was supposed as follows: 1) HNO<sub>3</sub> treatment provides full anion doping throughout the entire PPy nanotube; 2) parts of the C and N atoms were consumed and escaped as gases during the heat process in Ar, leading to the formation of micropore sites; 3) when temperature arose to 1000 °C, low-concentration air flow (oxygen was supposed to be the main reactant) was introduced to further consume the C and N atoms around the micropore sites and produce uniform micro- and mesopores in the PCN walls. This controlled low-concentration air etching during the annealing process and the HNO3 treatment are two critical conditions for creating uniform micropores throughout the PCN walls both in axial direction and radial direction evenly, whereas directly etching graphitic materials by a large amount of O<sub>2</sub> usually produces mesopores, even macropores with irregular distribution, rather than uniform micropores.<sup>[20-23]</sup> From a microscopic view, the pore formation process is initiated by the reaction between the N and C atoms with both the anion dopants and air, which would release NO<sub>x</sub> and CO<sub>y</sub> gases to leave sub-nanometer pores.<sup>[19–21,24]</sup> And, the pores will become bigger gradually and evenly (coalescence of micropores into mesopores) under continued air attacking, resulting in a hierarchical porous structure (Figure 1b).

The resulting PCN aerogels were characterized by scanning electron microscopy (SEM), which shows a 3D-interconnected network structure consisting of overlapped 1D skeletons (Figure 2a). The introduction of pyrrole onto the substrate followed by polymerization/aging facilitates the formation of mutually interconnected AgNWs/PPy and a robust freestanding aerogel. This 3D network is well maintained in the PPy nanotube aerogels after the template removal, and in the PCN aerogels after high-temperature air treatment, and welded PCNs with connected inner cavities are frequently observed, a feature that favors mechanical integrity of the 3D structure (Figure S1, Supporting Information). Enlarged view clearly shows the presence of a large amount of 1D tubular nanostructures with uniform diameters and a rough surface, and hollow cavities in the fractured sections (Figure 2b,c). This rough yet clean surface represents a typical morphology of PCNs compared with the smooth surface of PPy nanotubes and other control samples (e.g., the aerogel annealed without adding air, Figure S1, Supporting Information), indicating successful creation of pores in PCNs by air etching. Transmission electron microscopy (TEM) images of individual PCNs reveal



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**Figure 1.** Fabrication of 1D PCNs and 3D PCN aerogels. a) Schematic illustration of the fabrication process in which microscopically PPy was deposited on 1D AgNWs (template) and then converted to PPy nanotubes (by HNO<sub>3</sub> treatment) and PCNs with micro-/mesopores (by carbonization under air), and macroscopically the 3D AgNW/PPy networks were converted to PPy nanotube aerogels and then PCN aerogels (photos in the bottom panel), corresponding to the microstructure change. The schematic illustration of micropore-creation process throughout the entire tube walls both in the axial and radial directions. b) Illustration of the pore-creation process in which a PPy molecule containing C, N, H atoms was transformed into a porous structure containing micro-/mesopores by HNO<sub>3</sub> and air treatments.

an outer diameter of 100–200 nm, an inner cavity of 50–150 nm which is consistent with the AgNW diameters, and a wall thickness of 30–80 nm (Figure 2d). The formation of this tubular nanostructure is owing to the uniform wrapping of PPy outside and that HNO<sub>3</sub> can infiltrate throughout the PPy layer to dissolve the inner nanowires completely. High-resolution TEM images clearly exhibit a highly porous tube wall structure consisting of densely packed pores throughout the entire wall (Figure 2e,f). Compared with previously reported porous carbon

materials mainly in the form of particles, carbon nanotubes (CNTs), and carbon nanofibers,<sup>[23,25–27]</sup> here we have obtained 1D nanotubes with a uniform porous structure along both the axial and radial directions.

X-ray photoelectron spectroscopy (XPS) measurements reveal a large-degree reduction of N and O contents in the air-treated PCNs. The PPy nanotube aerogel after HNO<sub>3</sub> treatment contains 12.18% N and 21.78% O, which drop to 1.2% and 5.6% in the resulting PCNs, respectively, indicating the consumption of







**Figure 2.** Structural characterization of PCNs. a–c) SEM images of a PCN aerogel in different magnifications, showing 3D-interconnected networks of nanotubes with a clean and rough surface. d–f) TEM images of individual PCNs showing highly porous tube walls, in which red circles indicate uniform pores revealed in high-resolution image. g) XPS survey spectra of the PPy nanotubes and PCNs, showing a decrease of N 1s signal. h) N<sub>2</sub> adsorption/ desorption isotherms of PCN aerogels and a control sample without introducing air during annealing. i) The corresponding pore-size distribution in the PCNs. Inset is the contribution to the surface area and pore volume from sub-nanopores and pores between 1 and 4 nm.

both N and O during the reaction with C atoms for pore creation (Figure 2g). Compared to the original AgNW/PPy aerogel, the removal of AgNWs by HNO3 infiltration is accompanied by anion doping to the PPy layer, as proved by the increase of N/C and O/C ratios (Table S1, Supporting Information). Moreover, the HNO3 treatment and low-concentration air etching lead to a synergistic effect on the formation of a highly porous structure. The main function/effect of HNO<sub>3</sub> treatment is to induce NO<sub>3</sub><sup>-</sup> anion doping (therefore introducing N and O) into the PPy aerogel. The presence N and O promotes the formation of uniform microporous structure during subsequent air etching. In order to study whether there is a saturation level of this effect, XPS was used to characterize PPy aerogels after different HNO<sub>3</sub> treatment periods (from 2 min to 24 h). From the deconvoluted spectrum of C 1s, we calculated 1) the ratio of C=C/C-C to C 1s content which indicates the maintenance of original carbon lattice, and 2) the ratio of O 1s to C 1s content which shows the introduction of oxygen by anion doping (Figure S2, Supporting Information). As the HNO<sub>3</sub> treatment time increased, the ratio of C=C/C-C to C 1s content decreased rapidly and the ratio of O 1s to C 1s content increased correspondingly over the first 8 h, and then both the ratios were stabilized without much change, clearly indicating the saturation behavior of HNO3 treatment. In addition to NO<sub>3</sub><sup>-</sup> anion doping, air etching is also very important for creating the porous structure. In this regard, we carried out a comprehensive comparison on the samples with (PCNs) and without air treatment (control sample #2) by more characterizations such as Raman spectra, X-ray diffraction (XRD), XPS (Figure S3, Supporting Information). Analysis of the difference in the crystallinity, structural defects, and other related factors could reveal the effect of air etching. In Raman spectra, the decreased  $I_{\rm G}$  and a higher  $I_{\rm D}/I_{\rm G}$  ratio indicate substantially increased defects mainly existing as micropores created by air etching among the hexagonal carbon lattice in PCN aerogels (as illustrated in Figure 1b). XRD pattern in PCNs show a diminished and broadened band at around 23°, corresponding to (002) diffraction of graphite, indicating a more disordered structure and reduced crystalline degree after air-etching process, consistent with the Raman spectra results. In survey and deconvoluted XPS spectra (Figure S3 and Table S1, Supporting



Information), the main elemental composition includes C, N (3.23 and 1.2 wt%, respectively), and O (5.4 and 5.6 wt%) for the control sample #2 and PCNs, where a significant portion of N and O has been consumed during annealing with or without air. The remaining N element as dopant in carbon materials exists mainly in three types: N-5, N-6, and N-Q. As in PCNs, the control sample #2 is also made from a 3D macroporous network of 1D nanotube units, however, with a rather dense tube wall (Figure S3a,b, Supporting Information). In the nitrogen adsorption/desorption isotherms of PCN aerogels, the hysteresis loop exhibits combined characteristics of type I and type IV isotherms, indicating microporous and mesoporous nanostructures (Figure 2h). The calculated Brunauer-Emmett-Teller (BET) surface area is about 461 m<sup>2</sup> g<sup>-1</sup>, much larger than the PPy aerogel annealed under inertial gas (62 m<sup>2</sup> g<sup>-1</sup>). A pronounced peak centered at 0.808 nm is observed in the pore-size distribution, while the rest of pores are primarily below 3.2 nm (Figure 2i). Those micropores less than 1 nm contribute to about 50% of the surface area and 30% of the total pore volume. The above result indicates that our HNO<sub>3</sub> treatment and airetching methods could effectively produce uniform micro- and mesopores, the majority of which lie under 4 nm with a centralized micropore distribution on 0.8 nm. We considered that the highly centralized pore-size distribution in PCNs was caused by the consumption of a large amount of C and N atoms due to the evenly distributed N sites (pyrrole-N five-membered carbon rings and anion doping) and the uniform micropore sites formed in the PPy tube walls. According to a number of theoretical and experimental studies, micropores smaller than 1 nm could lead to anomalous increase in carbon capacitance.<sup>[16]</sup> We have conducted a series of air-etching experiments and optimized two critical parameters, 1) the air flow rate (1-20 sccm) and 2) the air-etching time (from 10 min to 5–6 h). At a suitable flow rate of 2.5 sccm, we use the second parameter to synthesize PCNs with tailored porous structure. Two control samples #3 (more air-etching time, 4-5 h) and #4 (less air-etching time, ≈20 min) were prepared and their structures were characterized by TEM and BET. In the control sample #3, more porous tube walls than PCNs were observed and the pore-size distribution is more decentralized with pores centered at other sizes (1.7 nm) except the peak at around 0.8 nm (Figure S4a,b, Supporting Information). It indicates that some micropores were enlarged gradually during longer air-etching time. On the other hand, the control sample #4 showed less porous tube walls than PCNs and a similar pore-size distribution yet a much smaller pore volume (Figure S4c,d, Supporting Information). Interestingly, all three PCNs have two major pore size distributions (centered at 0.8 and 1.7 nm, respectively) and relatively large surface areas  $(300-535 \text{ m}^2 \text{ g}^{-1}).$ 

Our 3D PCN aerogels with a well-defined porous structure and high electrical conductivity (3.7 S cm<sup>-1</sup>, by 4-probe measurement) can serve as a freestanding supercapacitor electrode, without the need of mixing with polymer adhesives or conductive fillers. We have systematically tested their supercapacitor performance in a two-electrode configuration using an aqueous 1  $\mbox{M}$  H<sub>2</sub>SO<sub>4</sub> electrolyte, particularly at high scan rates (from 5 mV s<sup>-1</sup> all the way up to 12 V s<sup>-1</sup>) (**Figure 3**a–c). At moderate scan rates (from 100 mV s<sup>-1</sup> to 1 V s<sup>-1</sup>), cyclic voltammetry (CV) curves show nearly perfect rectangular shape, indicating fast charge separation and efficient ion storage. At even higher rates (1–12 V s<sup>-1</sup>), we observe consistent CV evolution, showing a slight deviation from the rectangular shape, but without polarization occurring at the two voltage extremities (0 and 1 V). The CV results demonstrate that the supercapacitor behavior of our PCN electrodes is well maintained at very high scan rates. To further explore their fast-charging properties, we have conducted galvanostatic charge/discharge (GCD) tests and find that the PCN electrodes can be charged over a large span of current densities from 1 to 1000 A  $g^{-1}$  (Figure 3d–f). Under 100 A g<sup>-1</sup>, the GCD curves maintain nearly linear and symmetrical triangular shape, verifying the ideal electrical double layer (EDL) capacitive performance and fast-charging behavior, as shown in CV tests. The IR drop appearing in the GCD curve remains very small (0.047 V) until the current density increases to 100 A g<sup>-1</sup>, and gradually increases at higher current densities (0.231 V at 500 A  $g^{-1}$ , 0.468 V at 1000 A  $g^{-1}$ ). It means that the supercapacitor can store and release energy efficiently within 50 ms (43 ms for 600 A  $g^{-1}$ , 16 ms for 1000 A  $g^{-1}$ ), and this is the highest current density ever achieved in macroscopic porous carbon-based electrodes.

We have calculated the specific capacitances  $(C_s)$  of our PCN electrodes based on the CV and GCD tests, respectively. The corresponding  $C_s$  values are 200.7 F g<sup>-1</sup> (5 mV s<sup>-1</sup>) and 107.2 F g<sup>-1</sup> (12 V s<sup>-1</sup>) in CV tests, and are 193.2 F g<sup>-1</sup> (1 A g<sup>-1</sup>), 177.3 F  $g^{-1}$  (10 A  $g^{-1}$ ), 164.8 F  $g^{-1}$  (50 A  $g^{-1}$ ), 160.0 F  $g^{-1}$ (100 A  $g^{-1}$ ), and 154.8 F  $g^{-1}$  (200 A  $g^{-1}$ ) by GCD tests, respectively (Figure 4a). When the current densities increase to 500 and 1000 A g<sup>-1</sup>, we can still obtain impressive capacitances of 147.6 and 120.4 F g<sup>-1</sup>, respectively. The  $C_{\rm s}$  values obtained in our PCN electrodes are comparable to those of other porous carbon-based materials.<sup>[28-30]</sup> In addition, the measured IR drop at different discharge current densities are relatively low compared with the IR drop in above studies also tested in aqueous electrolyte with a 1 V voltage window (Figure 4b).<sup>[5,11,31,32]</sup> For example, a metal-organic framework-derived porous carbon showed an IR drop of ≈0.2 V at 200 A  $g^{-1}\!,$  and a CNT@micro-C-2 composite structure was 0.1 V at 50 A g<sup>-1</sup>, which are higher than our PCNs. Furthermore, the variation of IR drop shows a linear relationship with the current density over the entire range (up to 1000 A  $g^{-1}$ ), suggesting excellent fast-charging property. In contrast, most of previous studies showed significantly and exponentially increased IR drop when the current density increased.

Based on the above  $C_s$ , we have obtained the capacitance retentions of the PCN aerogels, which are as high as 91.7% (10 A g<sup>-1</sup>), 85.3% (50 A g<sup>-1</sup>), 82.8% (100 A g<sup>-1</sup>), 80.1% (200 A g<sup>-1</sup>), 76.4% (500 A g<sup>-1</sup>), and 62.3% (1000 A g<sup>-1</sup>). In comparison, most of other porous carbon–based two-electrode systems with aqueous or organic electrolytes show lower capacitance retentions tested in a smaller current density range (up to 200 A g<sup>-1</sup>) (Figure 4c and Table S2 (Supporting Information)).<sup>[5,6,11,14,31–36]</sup> Those electrodes were generally tested to current densities of 100 or 200 A g<sup>-1</sup>, with only a few reaching 500 A g<sup>-1</sup> (57% retention of the low-current value),<sup>[7]</sup> and one work reaching 1000 A g<sup>-1</sup> (37% retention) by adding indolebased macromolecules into electrolyte.<sup>[9]</sup> Our PCN electrodes can not only extend to high current density, but also maintain a minimum decrease in the capacitance as the current density



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**Figure 3.** PCN-based supercapacitor electrodes and fast charging behavior. a-c) CV curves of PCN aerogels recorded at various scan rates from 5 mV s<sup>-1</sup> to 12 V s<sup>-1</sup> in a two-electrode configuration, showing well maintained rectangular shape at very high rates. d-f) GCD profiles of PCN aerogels measured at current densities from 1 to as high as 1000 A g<sup>-1</sup>.

increases. These results indicate that our PCN aerogels possess superior rate capability extending to very high current densities, owing to the highly porous nanotube structure prepared by air etching. Annealing without air resulted in aerogels containing dense-wall nanotubes with  $C_{\rm s}$  of 167.3 F g<sup>-1</sup> at 1 A g<sup>-1</sup>, which drops substantially to 116.3 F g<sup>-1</sup> at a modest rate of 25 A g<sup>-1</sup> (Figure S5, Supporting Information), suggesting the important effect of air in producing porous nanotubes with significantly enhanced rate capability.

A study on the structure-property relationship in PCNs could disclose the dominant factor in the high-rate behavior. Here, we studied the capacitive performance of control samples #3 and #4 by CV, GCD tests and compared it with our optimized PCN sample. As shown in Table S3 (Supporting Information), the main difference in the porous structure of these three samples includes: 1) pore volume at 0.8 nm in the PCNs  $(0.06 \text{ cm}^3 \text{ g}^{-1})$  is the largest compared with that of control samples #3 (0.05 cm<sup>3</sup> g<sup>-1</sup>) and #4 (0.037 cm<sup>3</sup> g<sup>-1</sup>); 2) pore volume at 1.7 nm in the PCNs (0.027 cm<sup>3</sup> g<sup>-1</sup>) is relatively low compared with that of control samples #3 (0.04  $\text{cm}^3 \text{ g}^{-1}$ ) and #4  $(0.026 \text{ cm}^3 \text{ g}^{-1})$ ; 3) the PCNs have an intermediate surface area (461 m<sup>2</sup> g<sup>-1</sup>) between control samples #3 (535 m<sup>2</sup> g<sup>-1</sup>) and #4 (301  $m^2 g^{-1}$ ). From the consistent results obtained in CV, GCD, and electrochemical impedance spectroscopy (EIS) tests, both the control samples #3 and #4 showed more rapid degradation at increasing current density, than the PCN sample (Figure S6, Supporting Information). That is to say, the high-rate performance is weakened in the two control samples, which is related to their porous structure. It seems that the surface area is not very critical within a certain range. Therefore, we conclude that a more centralized distribution and higher pore volume of micropores at 0.8 nm are the dominant factors to control the

high-rate performance and allow the PCNs to be charged at 1000 A  $g^{-1}$  without much degradation.

Typically, there are two separate parts contributing to the capacitance, one is surface capacitive effects associated to EDL and the other is diffusion-restricted process related to pseudo-capacitance.<sup>[37]</sup> Each part can be derived through the Trasatti analysis by<sup>[38]</sup>

$$C_{\rm s} = k_1 + k_2 \nu^{-\frac{1}{2}} \tag{1}$$

$$\nu = t^{-1} \tag{2}$$

where  $k_1$  is a rate-independent component attributed to EDL,  $k_2$  is slope of the linear portion fitting, and t is the discharging period at each current density. With a maximum capacitance of 185.8 F g<sup>-1</sup> in the PCNs (Figure S7a, Supporting Information), the derived EDL capacitances ( $k_1$ , by extrapolating  $C_s$  to  $k_2 v^{-1/2}$  at the intercept) according to the CV and GCD results are 158.3 and 165.1 F g<sup>-1</sup>, respectively, consistent with each other (Figure 4d,e). Consequently, the contributions from the EDL and pseudocapacitance are about 85.1% and 14.9%, respectively, indicating an EDL-dominated capacitive behavior that is favorable for achieving high-rate capability. Also, we have adopted the Dunn method<sup>[39]</sup> to study the ratio of EDL capacitance through distinguishing the current arising from the rateindependent or diffusion-controlled processes, and the result (84.5%) is in accordance with the Trasatti analysis (Figure S4b, Supporting Information).

The excellent fast-charging properties of our PCN aerogels as demonstrated above are attributed to a number of structure-related factors including: 1) the freestanding 3D







**Figure 4.** Rate performance of PCN aerogels and analysis of EDL contribution. a) Specific capacitances of PCN aerogel electrodes calculated from GCD and CV tests at various current densities and scan rates. b) Plot of IR drop (experimental values and linear fitting line) of PCNs at different current densities up to 1000 A  $g^{-1}$ , and the IR drop of a number of other porous-carbon materials (refs. [5,11,31,32]) tested in 1 V voltage window are included for comparison. c) Rate capability of PCNs under high charging rates up to 1000 A  $g^{-1}$ . Included are also capacitance retentions of other porous carbon–based EDLC (two-electrode cells, aqueous electrolyte) (up to 100 or 200 A  $g^{-1}$ ) from literature. Trasatti analysis of PCN electrodes including d) plots of the specific capacitance (calculated from CV tests) against reciprocal of the square root of scan rate. The intercept of the fitting line is capacitance from pure EDLC, and e) plots of the specific capacitance (calculated from GCD tests) against the square root of discharge time.

networks consisting of interconnected 1D highly porous nanotubes provide continuous and efficient pathways for electron transport, (2) a high ratio of sub-nanometer pores centered at 0.8 nm further promotes the electrochemical properties, and (3) the porous 3D networks allow the electrolyte to fully infiltrate throughout the electrode and access the hierarchical pores along the PCNs. To theoretically explore the origin of the high electrical conductivity of the PCN aerogels, we have constructed a nanotube by rolling up the PCN-based sheet shown in Figure 1b, and calculated its electronic band structure and total/partial density of states (DOS) based on first-principle calculations. The optimized geometry of the 1D nanotube shows ordered pores, and the calculated band structure and DOS exhibit metallic features as characterized by the high DOS and the bands crossing the Fermi level in the high symmetry k point path of  $\Gamma(0, 0, 0) \rightarrow Z(0, 0, 0.5)$  (Figure S8, Supporting Information). In comparison, previously reported porous carbon materials are mainly in the form of particles with various shapes such as spheres, nanosheets, hollow cages, and other irregular particles.<sup>[6,31,40,41]</sup>

The energy/power densities are important criteria for supercapacitors. The Ragone plot shows that our PCN electrodes possess an outstanding power density of 265.6 kW kg<sup>-1</sup> at an energy density of 1.2 Wh kg<sup>-1</sup>, and an energy density of 6.7 Wh kg<sup>-1</sup>



at a power density of 500 W kg<sup>-1</sup> (Figure 5a). For pure porous carbon-based EDLCs, one of the major advantages is their superior power density, and our performance (265.6 kW kg<sup>-1</sup>) is among the highest values reported in porous-carbon electrodes with aqueous electrolytes,<sup>[4,5]</sup> owing to the ultrafast charging at a time scale of tens of milliseconds. Furthermore, cycling stability at high rates is a key parameter to evaluate fast-charging supercapacitors. Our PCNs with optimized porous structure show outstanding cycling performance at a very high rate (1000 A  $g^{-1}$ ), with a capacitance retention of 88.2% after 10<sup>5</sup> cycles and an average 0.12% decay per 10<sup>3</sup> cycles (Figure 5b). This is attributed to the large amount of uniformly distributed micropore defects (caused by air etching) on the surface PCN tube walls. After cycling tests, we have characterized the PCN electrode by TEM (Figure S9, Supporting Information). One can hardly observe changes in the 1D nanotube morphology and the porous tube wall structure in the same sample before and after 10<sup>5</sup> cycles, suggesting that the PCNs can maintain a stable microstructure under high-rate testing.

EIS has been carried out to investigate the kinetics in our porous electrodes. The Nyquist plots of the original PCN electrode and after 30k, 55k, 100k cyclic tests at 1 V s<sup>-1</sup> are plotted, where the steep slopes at low-frequency regions indicate an efficient ion-transport process within the hierarchical porous structure (Figure 5c). With increasing cycle numbers, the slight evolution (enlarging) of the semicircles at high-frequency sections indicates a rather stable charge transfer resistance ( $R_{ct}$ ) at the electrode–electrolyte interface over 1 × 10<sup>5</sup> cycles (Figure 5c, inset). The  $R_{ct}$  of PCNs is also smaller than the control sample with a dense wall prepared without air

etching, which means that the micro- and mesoporous tube walls are favorable for electrolyte infiltration, leading to reduced ion-transport resistance and diffusion distance (Figure S5c, Supporting Information). Significantly, a very small time constant  $\tau_0$  of 0.057 s ( $\tau_0 = 1/f_0$ ,  $f_0$  is the frequency at a phase angle of 45°, which locates at the point of equal capacitive and resistive impedances) for PCNs could be derived from the Bode phase plot, and an increased  $\tau_0$  of 0.43 s for the dense-wall sample (Figure 5d and Figure S5d (Supporting Information)). This constant represents the minimum time required to set free all the energy from the supercapacitors with an efficiency higher than 50%, and corresponds to a superior rate capability in our PCNs with a unique 1D porous structure.<sup>[42]</sup> In comparison, other typical porous-carbon electrodes usually exhibit  $\tau_0$  in the range of 0.08–0.6 s.<sup>[4,6]</sup>

#### 3. Conclusions

In summary, we demonstrated controlled fabrication of 1D porous-carbon nanotubes having uniform micro- and mesopores throughout the entire tube walls, with desired pore size distribution for supercapacitor applications. Our pore-creation method, by combining HNO<sub>3</sub> treatment and airetching processes, could be extended to other N-containing precursors to fabricate various porous-carbon structures with tunable hierarchical pores. In addition to AgNWs, other metal/inorganic nanowires and organic molecules may also serve as (soft) templates for synthesizing 1D PCNs in a more economical way for practical applications. As a macroscopic, freestanding



**Figure 5.** Power density and cycling stability of PCN aerogel electrodes. a) Ragone plot of PCNs. b) Cyclic stability of PCNs at 1000 A g<sup>-1</sup> for 10<sup>5</sup> cycles. c) Nyquist plots of PCNs before and after cycling tests. Inset shows the high frequency section of the Nyquist plots. d) Bode phase plot of PCNs. The horizontal line highlights the frequency  $f_0$  (1/ $\tau_0$ ) at the phase angle of -45°.

supercapacitor electrode, the 3D PCN aerogels exhibited exceptional rate performance including, 1) maintaining rectangular CV curves at high scan rates (up to 12 V s<sup>-1</sup>), 2) can be charged at very high current densities (up to 1000 A g<sup>-1</sup>), 3) superior cycling stability at high charging rates (88% capacitance retention after  $10^5$  cycles at 1000 A g<sup>-1</sup>). Our highly porous 1D nanotube structure has the potential to develop microelectronic and power-supply devices that require fast charging/ discharging capability (e.g., within 0.1 s).

### 4. Experimental Section

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*Chemicals*: Polyvinylpyrrolidone (PVP), AgNO<sub>3</sub>, ethylene glycol (EG), NaCl, Py, HNO<sub>3</sub>, ethanol. All chemicals were used without further purification.

Synthesis of AgNW/PPy Aerogels: AgNW/PPy aerogels were prepared according to literature (ref. [18]), and described briefly as follows: first, 6.9 mg NaCl and 2.652 g PVP were added to 90 mL EG slowly at 90 °C under constant stirring (solution A). Second, 1.022 g AgNO<sub>3</sub> was dissolved in 60 mL of EG under 90 °C by stirring (solution B). Then, solution B was added dropwise to solution A in about 15 min. The obtained solution was treated at 160 °C for 6 h and the AgNW products were purified by centrifugation with ethanol for 5 times. The obtained AgNWs possess diameters of 50–150 nm and lengths of tens of micrometers. After the AgNWs were dispersed in solvent consisting of H<sub>2</sub>O and ethanol (1:1 in volume), Py (0.5 mL) was added into the suspension and stirred for 30 min. Then, 1.23 g AgNO<sub>3</sub> was added and agitated for 10 min. Next, the above solution was laid in shade for gelation over 7 days to form a AgNW/PPy hydrogel, which was then purified by water and transformed into an aerogel through freeze-drying.

Synthesis of PPy Nanotube Aerogels: The AgNW/PPy aerogels were immersed in diluted HNO<sub>3</sub> for several hours to fully dissolve the AgNW template. After the purification and freeze-drying processes, the  $NO_3^{-1}$ -doped PPy nanotube aerogels were obtained.

Synthesis of PCN Aerogels and Control Samples: The PCN aerogels were produced through annealing the NO<sub>3</sub><sup>-</sup>doped PPy nanotube aerogels at 1000 °C in Ar atmosphere (200 sccm) with 2.5 sccm air flow for 1–2 h (air etching as mentioned in the text). Four control samples were also prepared. The AgNW/PPy aerogels were directly annealed without HNO<sub>3</sub> treatment at 1000 °C accompanying Ar/air treatment for 1–2 h to obtain the control sample #1. Specially, there was a part of AgNWs consumed by air. The control sample #2 was produced by annealing the PPy nanotube aerogels (after dissolving AgNWs by HNO<sub>3</sub>) at 1000 °C in Ar without air for 1–2 h. The control samples #3 and #4 were produced under the same condition of PCN, but with more air treatment time (4–5 h) and less treatment time (=20 min), respectively. In brief, #1 (without HNO<sub>3</sub> treatment), #2 (without air treatment), #3 (more air treatment time), #4 (less air treatment time). All the sample weights were measured before and after annealing.

Characterization: SEM was conducted on a Hitachi S-4800 operating at an accelerating voltage of 10 kV. TEM was conducted on FEI Tecnai T20 and FEI Tecnai F30 at accelerating voltages of 200 and 300 kV. XPS was measured on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al K $\alpha$  radiation (150 W). The pore structure was determined by the N<sub>2</sub> adsorption using an ASAP 2020 volumetric sorption analyzer. The BET surface area was calculated from the isotherm by the BET equation. Pore size distribution was calculated according to the Barrett–Joyner–Halenda (BJH) model. Cumulative pore volume was obtained based on density function theory (DFT).

*Electrochemical Measurements*: All tests were carried out using a two-electrode system with a CHI 660 electrochemical workstation. The supercapacitor cells contained two identical freestanding aerogels as electrode materials without additives or binders, a filter paper as separator, two Pt foils as current collectors, and a poly tetrafluoroethylene (PTFE) clamp as fixation. The PCN aerogels had a measured thickness

of about 200  $\mu$ m and calculated density of  $\approx$ 60 mg cm<sup>-3</sup>. CV and GCD tests were conducted at a voltage window of 0–1 V, with scan rates from 5 mV s<sup>-1</sup> to 12 V s<sup>-1</sup>, and current densities of 1–1000 A g<sup>-1</sup>. Specific capacitance (*C*<sub>s</sub>) was calculated according to Equations (3) and (4)

$$C_{\rm s} = \frac{4l}{m\,\Delta V/\Delta t} \tag{3}$$

$$C_{\rm s} = \frac{2\int l/m \, \mathrm{d}V}{v \, U} \tag{4}$$

where *I* (A) is the applied current density, *m* (g) is the total mass of both electrodes,  $\Delta t$  (s) represents the discharge time,  $\Delta V$  corresponds to the voltage change excluding the IR drop during discharge,  $\nu$  is the scan rate, and *U* is the potential window. The energy density (*E*) and power density (*P*) of the supercapacitor cells normalized on the two electrodes were calculated according to Equations (5) and (6)

$$E = \frac{C_s U^2}{8 \times 3.6} \tag{5}$$

$$P = \frac{3600E}{\Delta t} \tag{6}$$

Theoretical Computation: All the first-principle calculations were in the framework of the DFT implemented in Vienna Ab initio Simulation Package (VASP)<sup>[43]</sup> within the projector augmented-wave approach. The valance electron wavefunctions were expanded using plane-wave basis sets<sup>[44]</sup> with a kinetic energy cutoff of 550 eV. The electronic exchange-correlation functional was in the Perdew–Burke–Ernzerhof (PBE)<sup>[45]</sup> form. Based on the convergence test, the first Brillouin zone was represented by *k* points sampled using Monkhorst–Pack scheme<sup>[46]</sup> with a grid density of  $2\pi \times 0.02$  Å<sup>-1</sup>. The conjugated gradient method was adopted to optimize the structure, and convergence criteria of total energy and force components were set to be  $1 \times 10^{-4}$  eV and 0.001 eV Å<sup>-1</sup>, respectively.

# **Supporting Information**

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

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# **Conflict of Interest**

The authors declare no conflict of interest.

#### **Keywords**

air etching,  $HNO_3$  treatment, porous-carbon nanotube, supercapacitor electrode, ultrafast charging

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