<table>
<thead>
<tr>
<th>Title</th>
<th>Functionalized highly porous graphitic carbon fibers for high-rate supercapacitive electrodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Wang, Huanwen; Yi, Huan; Zhu, Changrong; Wang, Xuefeng; Fan, Hong Jin</td>
</tr>
<tr>
<td>Date</td>
<td>2015</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10220/25651">http://hdl.handle.net/10220/25651</a></td>
</tr>
<tr>
<td>Rights</td>
<td>© 2015 Elsevier. This is the author created version of a work that has been peer reviewed and accepted for publication by Nano Energy, Elsevier. It incorporates referee’s comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<a href="http://dx.doi.org/10.1016/j.nanoen.2015.03.033">http://dx.doi.org/10.1016/j.nanoen.2015.03.033</a>].</td>
</tr>
</tbody>
</table>
Functionalized Highly Porous Graphitic Carbon Fibers for High-Rate Supercapacitive Electrodes

Huanwen Wang, Huan Yi, Changrong Zhu, Xuefeng Wang, Hong Jin Fan

PII: S2211-2855(15)00129-9
DOI: http://dx.doi.org/10.1016/j.nanoen.2015.03.033
Reference: NANOEN782

To appear in: Nano Energy

Received date: 11 January 2015
Revised date: 22 March 2015
Accepted date: 23 March 2015

Cite this article as: Huanwen Wang, Huan Yi, Changrong Zhu, Xuefeng Wang, Hong Jin Fan, Functionalized Highly Porous Graphitic Carbon Fibers for High-Rate Supercapacitive Electrodes, Nano Energy, http://dx.doi.org/10.1016/j.nanoen.2015.03.033

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Article type: Rapid Communications

**Functionalized Highly Porous Graphitic Carbon Fibers for High-Rate Supercapacitive Electrodes**

Huanwen Wang\textsuperscript{a}, Huan Yi\textsuperscript{a}, Changrong Zhu\textsuperscript{b}, Xuefeng Wang\textsuperscript{a,*} Hong Jin Fan\textsuperscript{b,*}

\textsuperscript{a} Department of Chemistry, Key Laboratory of Yangtze River Water Environment, Ministry of Education, Tongji University, Shanghai 200092, China.

\textsuperscript{b} School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

* Authors to whom correspondence should be addressed.

_E-mail address:_ xfwang@tongji.edu.cn (X. F. W) fanhj@ntu.edu.sg (H. J. F)
Abstract

Combining high specific surface area (SSA) and superior electrical conductivity together at bulk state is very important for carbon materials in capacitive energy storage applications. Herein, by applying molten sodium metal to activate natural cotton at a relatively low processing temperature (800 °C), we have obtained hierarchically porous graphitic carbon fibers (HPGCFs) with SSA up to 1716 m² g⁻¹ and a high degree of graphitization in the bulk state. This is advantageous compared to amorphous carbon fibers obtained by conventional thermal annealing and KOH-activation. The obtained HPGCFs show remarkable energy storage capability (61% capacitance retention from 1 to 60 A g⁻¹). To further increase the capacitance value, anthraquinone (AQ) molecules have been selected to functionalize HPGCFs via π-π stacking interactions. Asymmetric supercapacitors have been assembled using HPGCFs as the positive electrode and AQ-HPGCFs as the negative electrode in aqueous H₂SO₄ solution. The device presents a large energy density (19.3 Wh kg⁻¹ in the applied potential range between 0–1.2 V) and ultrahigh power capability (up to 120 A g⁻¹, a full charge-discharge within 0.8 sec).

Keywords: carbon fiber, graphitic, ultrahigh-rate, anthraquinone, supercapacitor
1. Introduction

The ever worsening energy depletion and global warming issues call for not only urgent exploitation of renewable and clean energy sources (e.g., solar and wind power), but also development of green and advanced energy storage devices [1–3]. Supercapacitor has emerged as a promising candidate for electrochemical energy storage due to its faster charge-discharge processes, in seconds, than batteries [4, 5]. However, the existing carbon material based supercapacitors still suffer from relatively low energy density compared to commercial batteries [6]. To solve this low energy density problem, asymmetric supercapacitors (ASCs) have been extensively explored by combining a Faradic electrode (as energy source) and a capacitive electrode (as power source) to increase the operation voltage [7–9]. The keys to high energy and power densities of ASCs are to develop appropriate materials for facilitating fast kinetic balance between the two electrodes [2, 10, 11].

Activated carbon (AC) has been the most widely used capacitive electrode in ASCs [12]. However, the capacitance value is limited particularly at high current densities. The major reason is the limited ion transport kinetics through the microtunnels (with a size typically <0.5 nm), and consequently the insufficient surface accessibility of ions during electrochemical charges and discharges [13, 14]. In addition, carbon nanotubes [15] and mesoporous graphene [9] have also been reported as the capacitive electrodes of ASCs. With a high conductivity and tubular nanostructure, carbon nanotubes have exhibited high rate capability, but their capacitance values (tens of F g\(^{-1}\)) are rather low due to the relatively small SSA of typically hundreds of m\(^2\) g\(^{-1}\) [16, 17]. Although higher capacitance performance is achieved for mesoporous graphene, its high synthesis cost is an unfavorable factor for commercialization. Therefore, the development of a hierarchical carbon material with a large surface area, high conductivity, suitable pore size distribution, low cost and regular structure, is highly desirable for high performance ASCs.

Recent reports have shown that there are some organic molecules with reversible electrochemical redox couples that can generate pseudocapacitance [18–22]. The storage capacities of redox-active organic molecules may even outperform those of conventional metal
oxides because of the multi-electron reactions in a low-molecular-weight moiety. For instance, decoration of carbon onions with quinones can increase the energy density from 0.5 to 4.5 Wh kg\(^{-1}\) [23]. More importantly, these organic compounds are free from resource restrictions and potentially environmentally benign. Consequently, it would be a green, low-cost and effective strategy to involve redox-active organic materials in ASCs to enhance the supercapacitor properties.

Based on the above considerations, we prepare cheap but high performance carbon fiber-based electrodes from natural cotton materials, and also develop environmentally benign full supercapacitor devices. We firstly employ molten sodium metal to restructure the cheap natural cotton for obtaining hierarchical porous hollow graphitic carbon fibers (HPGCFs). Sodium activation enables HPGCFs with high SSA, hierarchical porous texture and high graphitization combined together, which would promise facile ion diffusion and fast electron transport. Secondly, anthraquinone (AQ) as the electrochemically active molecule is immobilized onto the HPGCFs through non-covalent modification, which can superimpose the additional pseudocapacitance (−0.13 V vs. SCE) on the electric double-layer capacitance (EDLC). Finally, an aqueous electrolyte based ASC integrating HPGCFs as the positive electrode and AQ-HPGCFs as the negative electrode is successfully fabricated to demonstrate ultrahigh capacitive performance in a fully packaged supercapacitor cell.

2. Experimental section
2.1 Synthesis of HPGCFs

The cotton was obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, P. R. of China. HPGCFs were synthesized by a two-step process. In the first step, the cotton was directly carbonized at 800 °C with a heating rate of 2 °C min\(^{-1}\) for 1 h under a nitrogen atmosphere, which leads to the formation of carbon fibers (CFs). In the second step, the obtained CFs (1 g) and sodium metal (3 g) were placed in an alumina crucible with a cover in an N\(_2\)-filled glove box and then the crucible was put into a tube furnace and heated in nitrogen atmosphere at 800 °C for 6 h at a heating rate of 2 °C min\(^{-1}\). After that, the activated mixtures were washed with dilute HCl solution (1 M) and
deionized water until the filtrate became neutral. The HPGCFs were finally dried in a vacuum oven at 60 °C for 24 h. The final carbon yield of HPGCFs was about 25%.

For comparison, the CFs from the first step were also activated by heating (at a heating rate of 2 °C min⁻¹) a KOH/CF mixture (at KOH/CF weight ratio of 4) under nitrogen to a final temperature of 800 °C for 6 h. The obtained samples were then thoroughly washed with HCl (1 M) to remove any inorganic salts, and then with distilled water until neutral pH and finally dried in an oven (60 °C). The resultant sample was denoted as KOH-CFs.

2.2 Synthesis of AQ-HPGCFs

AQ molecules were introduced onto HPGCFs by the solvothermal reaction. Typically, AQ (0.05 g) was dissolved in 70 mL dimethylformamide (DMF) and then HPGCFs (0.1 g) were added under vigorous stirring. The mixture was ultrasonic agitation for 60 minutes and kept stirring for another 12 hours. Finally, the dark homogeneous solution was transferred into 100 ml Teflon-lined stainless steel autoclave and heated at 180 °C for 12 hours. The products, namely AQ-HPGCFs, were washed with deionized water several times and then dried at 60 °C for 24 hours.

2.3 Material characterization

The products were characterized by field emission scanning electron microscopy (FESEM; Philips XSEM30, Holland) and transmission electron microscopy (TEM; JEOL, JEM-2010, Japan). The structure of the samples was examined by X-ray diffraction (XRD; Philips PC-APD) with Cu Kα radiation (λ=1.5418 Å) operating at 40kV, 60mA. Raman spectra were collected using a 514 nm laser with RM100 under ambient conditions, with a laser spot size of about 1 mm. FT-IR spectra were recorded at 0.5 cm⁻¹ resolution on a Bruker Vertex 70 V with 0.1 cm⁻¹ accuracy using a three-reflection attenuated total reflection (ATR) accessory with a ZnSe internal reflection element (Harrick Scientific Products). Nitrogen adsorption/desorption isotherms were measured at the liquid nitrogen temperature using a Micromeritics Tristar 3000 analyzer.

2.4 Electrochemical measurement

The working electrodes were prepared by pressing mixtures of the as-prepared powder samples and polytetrafluoroethylene (PTFE) binder (weight ratio of 90:10) onto a piece of carbon fiber paper (1 × 1 cm², 0.1 mm thick). A three-electrode system was firstly used to measure the electrochemical performance of the HPGCFs and AQ-HPGCFs as the working electrodes in 1 M H₂SO₄ aqueous solution, with a platinum foil as the counter electrode.
and a saturated calomel electrode (SCE) as the reference electrode, respectively. Each working electrode contained about 1 mg of electroactive material and had a geometric surface area of about 1 cm$^{-1}$.

The asymmetric supercapacitor was measured with a two-electrode system, where the HPGCFs were the positive electrode, and the AQ-HPGCFs were the negative electrode. The loading mass ratio of the active materials (AQ-HPGCFs : HPGCFs) was estimated to be 0.8 according to the specific capacitance and the potential window obtained from their galvanostatic charge–discharge curves. The HPGCFs and AQ-HPGCFs working electrodes were pressed together with a polypropylene membrane as separator under the optimized mass loading (for charge equality, the mass loading of the 1×1 cm$^2$ electrodes was chosen as AQ-HPGCFs: $\approx 0.8$ mg, HPGCFs mass: $\approx 1$ mg). All electrochemical measurements were carried out in 1 M H$_2$SO$_4$ aqueous solution on a CHI660D electrochemical working station. For comparison, the HPGCFs//HPGCFs symmetric supercapacitor was also assembled by pressing the two same HPGCF electrodes together with a polypropylene membrane as separator in 1 M H$_2$SO$_4$. The calculation method of specific capacitance, energy density and power density in different electrode configurations was shown in supporting information.

3. Results and discussion

![Schematic illustration of the preparation of highly porous graphitic carbon fibers (HPGCFs) and anthraquinone-functionalized HPGCF (AQ-HPGCFs).]

**Figure 1** Schematic illustration of the preparation of highly porous graphitic carbon fibers (HPGCFs) and anthraquinone-functionalized HPGCF (AQ-HPGCFs).
3.1 The formation process of HPGCFs and AQ-HPGCFs

In the present work (Figure 1), natural cotton is selected as raw materials due to the unique hollow cellulose fiber structure and the green nature. Compared with other synthetic routes, fabricating value-added carbon through natural plant or waste biomass has the advantages of high-yield, low-cost and less pollution to the environment. Until now, a series of natural materials, such as tea-leaves [24], banana [25], rice husk [26], enteromorpha prolifera [27], cow dung [28], human hair [29] and dead leaves [30], have been studied as the precursors to prepare carbon materials for supercapacitor application. Despite these progresses, the plant/biomass-based carbon materials usually suffer from imperfections, such as low degree of graphitization and crystallization as well as severe aggregation. For electrochemical applications, high degree of graphitization is generally preferred to reduce the internal resistance and enhance the power performance. However, either the reported physical activation (using steam [31], CO₂ [32], etc.) or chemical activation (using KOH [33, 34], NaOH [34, 35], Ca(OH)₂ [36], K₂CO₃ [37], H₃PO₄ [38], ZnCl₂ [25], etc.) seem not very effective in improving the graphitization. High temperature treatment of amorphous carbon around 3000 °C can produce well-developed graphitic structure, as demonstrated previously [39]. More recently, highly graphitic and crystalline graphene oxide (GO)-based graphene aerogels have been prepared via heat treatment at temperatures up to 2500 °C [40]. Obviously, it is very practical if the processing temperatures can be lowered. In addition, transition metals can be used to catalyze the graphitization of amorphous carbon at lower temperatures (1000~1200 °C). For instance, Moreno-Castilla’s group prepared graphitized domains with three-dimensional stacking order by heating Fe-, Co-, Ni-, or Cr- doped carbon aerogels higher than 1000 °C [41]. However, the above metal catalysis could not generate microscale pores, and the obtained carbon has low surface areas. Therefore, it is highly desirable to develop a low-temperature method to synthesize carbon materials with high surface areas and a high graphitization.

In this work, we introduce sodium activation at a relatively low temperature (800 °C) and the resultant HPGCFs show high degree of graphitization. The functional hollow cellulose fiber
structure is well reserved after carbonization and activation by molten sodium. In addition, the material is highly porous with a large surface area (1716 m\(^2\) g\(^{-1}\)). Furthermore, the highly graphitized carbon derived from cotton could act as \(\pi-\pi\) stack with the benzene ring, which should lead to a higher immobilization of the AQ on the surfaces of HPGCFs.

![Figure 2](image)

**Figure 2** XRD patterns (a) and Raman spectra (b) of three types of carbon fibers. CFs: normal fibers after only thermal carbonization of pristine cotton, KOH-CFs: KOH-activated carbon fibers. HPGCFs: molten Na-activated hierarchical porous graphitic carbon fibers.

### 3.2 Physical characterization

Both X-ray diffraction (XRD) and Raman spectra characterization are conducted for studying the structure of HPGCFs and comparison samples (CFs and KOH-CFs). When comparing with CFs and KOH-CFs in XRD patterns (**Figure 2a**), the diffraction peaks of HPGCFs sample is obviously sharper than that of CFs and KOH-CFs. This indicates that the as synthesized HPGCFs sample has more perfection of graphitic crystalline structure. Besides, the patterns of the CFs and KOH-CFs exhibit a very broad d\(_{002}\) diffraction profile at 23.6° (corresponding to d spacing of 0.38 nm), indicating the formation of a poorly ordered and amorphous structure while the 2θ value shifted from 23.6° to 26.1° which means d\(_{002}\) value changed from 0.38 to 0.34 nm, suggesting a better crystallization. Thus, it proves the advantage of using molten sodium instead of KOH activation.
Raman spectroscopy is applied to gain more information about the microstructure of the samples. The comparison of Raman spectra between the CFs, KOH-CFs and HPGCFs is shown in Figure 2b. In the case of CFs, the intensity of D-band peak is nearly same as that of G-band and these two peaks are not separated, indicating that carbons are in an amorphous style. The spectrum of KOH-CFs is similar to that of CFs, albeit the D (defect) and G (graphitic) peaks are slightly separated. Comparatively, the Raman spectrum of HPGCFs displays a decreased intensity of D-band, an increased intensity of G-band and the abrupt appearance of G’-band, which implies a better graphitization [42]. In addition, the position of G-band shows a red-shift from KOH-CFs (1598 cm\(^{-1}\)) to HPGCFs (1572 cm\(^{-1}\)), further verifying that sodium activation causes an increase in the average size of the sp\(^2\) domains. Therefore, this highly graphitic structure is expected to exhibit an enhanced electric conductivity of HPGCFs.

The surface morphologies of the as-synthesized samples were characterized by field-emission scanning electron microscopy (FESEM). The pristine cotton consists of numerous cellulose fibers with the diameter of ca. 15 \(\mu\)m (Figure S1). After carbonization at 800 °C, the cotton fibers transformed into helical carbon fibers (Figure 3a). Meanwhile, the diameter of the fiber was reduced to ca. 9 \(\mu\)m (Figure 3b), due to the thermal decomposition of some organic components. From the FESEM images (Figure 3c), it can be clearly seen that carbonized CFs are partially unzipped during the activation process. The cross section view of one fractured fiber (Figure 3d) shows that the HPGCF has a hollow microtubular structure. The inner diameter and the wall thickness of the HPGCF tube are about 3 and 1.5 \(\mu\)m, respectively. When used as the supercapacitor electrodes, the hollow structure of the HPGCFs could buffer electrolyte ions within the tube for facilitating the charge storage inside the inner surface.
To further reveal the difference in the microstructure of HPGCFs and KOH-CFs as a possible reason for their supercapacitor performance difference, high-resolution transmission electron microscopy (HRTEM) measurement was carried out (Figure 4). Usually, the activation with KOH could generate nanoscale pores in the final carbon product and this can be clearly seen in Figure 4a. The resultant micropores may originate from the combustion of carbon with KOH, proceeding as $6\text{KOH} + \text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3$, followed by decomposition of $\text{K}_2\text{CO}_3$ and/or reaction of $\text{K}/\text{K}_2\text{CO}_3/\text{CO}_2$ with carbon [43]. However, there is little, if no, signal of graphite formation after KOH activation (Figure 4a, b). In contrast, for HPGCFs, the sodium activation induces regular rearrangement of carbon slices and the formation of graphene ribbons in a
three-dimensional stacking order (Figure 4d). The lattice fringes can be clearly observed. The interplanar spacing is measured to be 0.34 nm, corresponding to the graphitic (002) plane, which is in agreement with XRD analysis.

![Figure 4 TEM images of the KOH-CFs (a, b) and HPGCFs (c, d).](image)

The graphitic structure of HPGCFs could form π–π stack with the benzene ring for the immobilization of AQ molecules. FT-IR measurements have revealed the detailed interaction between HPGCFs and AQ in the resultant AQ-HPGCFs sample. Data of FTIR and specific discussion are presented in Figure S2. This result strongly confirms the presence of AQ onto HPGCFs and the existence of π–π stacking interaction between AQ and HPGCFs.
The pore size and distribution of the HPGCFs and KOH-CFs were studied with N\textsubscript{2} adsorption/desorption isotherms (data presented in Figure S3 and Table S1). The HPGCFs and KOH-CFs possess both mesopores peaked at 3.37 nm and micropores at 1.84 nm. The specific surface areas of HPGCFs and KOH-CFs were determined to be 1716 and 1290 m\textsuperscript{2} g\textsuperscript{-1}, while the pore volumes are 0.92 and 0.65 cm\textsuperscript{3} g\textsuperscript{-1}, respectively. In addition, the mesopore ratio in the total pore volume is larger for the HPGCFs (10\%) than for the KOH-CFs (5\%). The higher surface area and pore volume as well as the larger mesopore ratio of HPGCFs are advantageous in charge storage.

The electronic conductivity of the samples was measured using a four-probe method. KOH-activated carbon fibers (KOH-CFs) sample exhibit a conductivity of around 1.4 S cm\textsuperscript{-1}. The molten Na-activated HPGCFs sample show a higher value of 3.1 S cm\textsuperscript{-1}. The increase in the electronic conductivity for HPGCFs is in agreement with the XRD, Raman and TEM results. The packing densities of KOH-CFs and HPGCFs electrodes are about 0.51 and 0.43 g cm\textsuperscript{-3}, respectively. The reduction of the packing density for HPGCFs is related with the obvious increase in the pore volume. We also conducted the wetting propertie of the fiber electrodes (Figure S4). It is found that the H\textsubscript{2}SO\textsubscript{4} electrolyte droplet can easily spread into the surface of both KOH-activated carbon fibers (KOH-CFs) and molten Na-activated HPGCFs, which is indicative of the good wetting behavior of these fiber electrodes and the benefit to ion transport.

3.3 On the activation mechanism

In our work, sodium activation of natural cotton at 800 °C could both generate nanopores and also induce graphitization. However, when the temperature is reduced to 500 °C (still higher than the MP of metal sodium, ~100 °C), no graphitization can be observed and carbons are still in an amorphous state (see Figure S5a). In addition, there is no sodium impurities remained in the HPGCFs after washing in HCl solution (see XPS in Figure S5b). These results indicate that the mechanism of sodium activation is different from the catalytic graphitization of traditional metal (Fe, Co, Ni), where a higher temperature than MP is needed. The activation mechanism is
proposed as follows. Sodium as an alkali metal can infiltrate into carbon matrix, which causes a rearrangement of amorphous carbons under the appropriate thermodynamic condition. Annealing cotton fibers at 500 °C (or lower) results in an insufficient infiltration of sodium, thus forming the irregular arrangement of carbon slices and no obvious graphitization is observed. At 800 °C, a sufficient infiltration of sodium metal in carbon skeletons can be achieved, which leads to a regular rearrangement of carbon textures and the formation of graphene ribbons in the stacking order. This activation mechanism is also in agreement with reduction of graphene oxide (GO) by Li in molten LiCl-KCl [44], where the sufficient solubility of Li and GO in molten LiCl is very critical for achieving the lower $I_D/I_G$ value and the presence of 2D band in Raman spectra. Besides, the surface area and pore volume of graphitic carbons are often dependent on the graphitization temperature. For instance, highly crystalline graphene was reported to have the surface area of 345 m$^2$ g$^{-1}$ at 2500 °C, much lower than 1200 m$^2$ g$^{-1}$ at 1050 °C [40]. As for HPGCFs in our study, the generation of micro- and meso-pore volume may be attributed to the lower graphitization temperature. Furthermore, molten sodium can provide active spots within the carbon matrix and responsible for the formation of a series of nanopores in graphitic carbon layers.

3.4 Electrochemical properties

To evaluate the properties of the prepared samples as supercapacitor electrodes, we perform measurements of cyclic voltammogram (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS).

**HPGCFs and KOH-CFs**

We first check CV curves of KOH-CFs and HPGCFs within the potential range from -0.2 to 0.7 V at different scan rates (data presented in Figure 5). Obviously, CV profiles of HPGCFs retain a rectangular shape at all scan rates between 10 and 200 mV s$^{-1}$, whereas the CV curves of KOH-CFs recorded at 200 mV s$^{-1}$ are obviously distorted. These results indicate a superior ion response of HPGCFs.
Figure 6 presents the GCD curves and capacitance values of KOH-CFs and HPGCFs at different current densities. It can be seen that all the curves are highly linear and symmetrical at each current density. However, at high current densities (Figure 6a, 6b), the IR drop is much smaller for HPGCFs than for KOH-CFs (for instance, the IR drop of HPGCFs and KOH-CFs at 12 A g\(^{-1}\) is 0.05 and 0.14 V, respectively (Figure 6c)). The specific capacitance values calculated from the discharging curves at 1 A g\(^{-1}\) are 175 and 140 F g\(^{-1}\) for HPGCFs and KOH-CFs, respectively. As shown in Figure 6d, the HPGCF electrode exhibits a capacitance of 107 F g\(^{-1}\) at 60 A g\(^{-1}\) with the capacitance retention of 61 % relative to 1 A g\(^{-1}\). In contrast, the KOH-CF electrode delivers a much lower capacitance value of 46 F g\(^{-1}\) at 60 A g\(^{-1}\) with only 32% retention in comparison with 1 A g\(^{-1}\). The volumetric capacitance for KOH-CFs and HPGCFs electrodes are 48 and 24 F cm\(^{-3}\), respectively, at 60 A g\(^{-1}\).

Figure 5 CV curves of KOH-activated carbon fibers (KOH-CFs) and Na-activated hierarchical porous graphitic carbon fibers (HPGCFs) at four different scan rates.
Although understanding the exact mechanism of ion/electron transport in this porous texture needs more detailed investigations, we believe that the shortened diffusion distance from the external electrolyte to the interior surfaces through ion-buffering reservoirs of the hollow fiber and the minimized transport resistance in the mesoporous region contribute synergistically to the high-rate performance. In particular, the high graphitization of HPGCFs results in a lower equivalent series resistance (ESR) of 2.6 Ω smaller than that of KOH-CFs (3.9 Ω) (Figure S7), which also reduces the electrode IR drop for efficient charge storage.

**Figure 6** Comparison between KOH-activated carbon fibers (KOH-CFs) and Na-activated graphitic carbon fibers (HPGCFs). GCD curves of (a) KOH-CFs and (b) HPGCFs at different current densities. (c) GCD curves at 12 A g⁻¹. (d) Capacitance values at different current densities.
**AQ-HPGCFs**

The inset of **Figure 7a** illustrates the CV curve of AQ-HPGCFs in the potential range from -0.35 to 0.25 V at a scan rate of 10 mV s⁻¹ in 1 M H₂SO₄ solution. The CV curve shows well-defined and reversible redox peaks at -0.13 V and -0.16 V on the top of EDLC, which is well suited for the negative electrode in aqueous acid. These peaks have symmetric wave-shapes and a small peak separation of 30 mV, which is expected for surface confined redox species. The electrochemical process can be described as a two electrons and two protons process as follows [18]:

![Chemical reaction diagram](image-url)
Figure 7 Electrochemical properties of the AQ-functionalized HPGCFs. (a) CV curves at different scan rates. (b) Variation of anodic and cathodic peak current with scan rate. (c) Capacitance values versus current density. The insets show the GCD curves at different current densities from 2 to 60 A g\(^{-1}\).

For comparison, the CV curve of pure AQ was also measured in the same condition. As shown in Figure S9, the peak separation at 10 mV s\(^{-1}\) is up to 145 mV, and the anode/cathode peaks show extremely asymmetric shapes. This confirms the importance of combining AQ with HPGCFs for fast charge storage.

Furthermore, quantitative analysis of the relationship between the peak current (\(i_p\)) and the
scan rate (v) can provide a better understanding on the kinetic of the electrode material. According to the CV curves at different scan rates (Figure 7a), it presents a plot of peak current versus scan rate on the applied scan rate for the AQ-HPGCFs (Figure 7b). A linear relationship is observed between the peak current and the scan rate with R²=0.9645 and 0.9546 for the anodic and cathodic curves, respectively, which suggests that the redox process is controlled by the surface reaction and also reveals fast kinetics for the AQ-HPGCF electrode. It can be pointed out that this electrochemical behavior of the AQ-HPGCFs is different from most metal oxides, where the \( i_p \) vs. \( v^{1/2} \) plot gives a reasonable linear relationship, indicating a diffusion-limited reaction [45, 46].

The inset of Figure 7c exhibits the GCD curves of AQ-HPGCFs. Obviously, the combination of EDLC and pseudocapacitance is responsible for the charge/discharge duration. The specific capacitance can achieve a maximum of 347 F g\(^{-1}\) at a low current density of 2 A g\(^{-1}\), which can still retain 198 F g\(^{-1}\) (about 57% retention) even at a current density as high as 60 A g\(^{-1}\) (Figure 7c). The higher capacitance values and excellent rate capability are tightly related with fast kinetics of the AQ-HPGCF electrode, which helps to provide high energy and power for the following ASC.

**HPGCFs//AQ-HPGCFs asymmetric supercapacitor**

As shown in Figure 8a, a novel ASC using AQ-HPGCFs as the negative electrode and HPGCFs as the positive electrode has been developed in aqueous H\(_2\)SO\(_4\) solution. To obtain a satisfactory capacitive performance, the charge balance between the two electrodes should follow the relationship \( Q^+ = Q^- \) [9]. The stored charge is related to the specific capacitance (C), the potential window in the GCD process (\( \Delta V \)), and the mass of the electrode (m), which follows the equation: \( Q = C \times \Delta V \times m \). According to the above analysis of the specific capacitance value and potential window for the HPGCFs and AQ-HPGCFs (Figure 8b), the optimal mass ratio between the two electrodes is expected to be \( m_{\text{AQ-HPGCF}}/m_{\text{HPGCFs}} = 0.8 \) in the ASC.
Figure 8 Schematics (a) of the HPGCFs//AQ-HPGCFs asymmetric supercapacitor. (b) CV curves of individual HPGCFs and AQ-HPGCFs electrodes at 10 mV s\(^{-1}\). (c) CV curves of the ASC at various scan rates in 1 M H\(_2\)SO\(_4\). (d) Specific capacitance of the ASC as a function of current density, the insets show GCD curves of the ASC at various current densities (ranging from 1 to 120 A g\(^{-1}\)). (e) Cycling performance of the ASC measured at 20 A g\(^{-1}\) for 5000 cycles.

Figure 8c presents typical CV curves for the HPGCFs//AQ-HPGCFs ASC at various scan rates between 0.0 and 1.2 V. The broad peaks centred at ca. 0.8 V are due to the reduction (positive scan) and oxidation (negative scan) of the AQ groups on the surface of the AQ-HPGCFs electrode. Over the wide range of scan rates from 10 to 200 mV s\(^{-1}\), the shapes of these CV curves are unchangeable, indicating the ideal capacitive behavior and fast
charging–discharging characteristics. The GCD curves at different current densities from 0.5 A g$^{-1}$ to 120 A g$^{-1}$ are shown in the insets of Figure 8d. All the discharge curves are almost symmetric to their corresponding charging counterparts, suggesting an excellent electrochemical reversibility and a good coulombic efficiency. The relationship between specific capacitance (based on the total mass of the active materials of the two electrodes) and current density is illustrated in Figure 8d. The specific capacitance reaches a maximum of 96 F g$^{-1}$ at 1 A g$^{-1}$ and retains 48 F g$^{-1}$ (~50% capacitance retention) at a ultrahigh current density of 120 A g$^{-1}$ (a full charge-discharge within 0.8 s). To the best of our knowledge, such prominent rate capability is superior to the best results reported for ASCs in the literature. In addition, when the geometric area of working electrodes in ASC is changed from 1×1 cm$^2$ to 2×2 cm$^2$, there is only 5% capacitance loss (Figure S10). The cycling stability of the HPGCFs//AQ-HPGCFs ASC device was tested at a constant scan rate of 20 A g$^{-1}$ for 5000 cycles. As shown in Figure 8e, 89% of the initial capacitance is retained, indicating a good long-term stability of the ASC.

The energy density (E) and power density (P) are two important parameters that characterize the performance of supercapacitors. The GCD curves were used to evaluate the two values of our HPGCFs//AQ-HPGCFs ASC devices (detailed information is described in the Supporting Information). Figure 9 shows the Ragone plot of specific E versus P values. The maximum P value of 72 kW kg$^{-1}$ (with E = 9.6 Wh kg$^{-1}$) and E of 19.3 Wh kg$^{-1}$ (with P= 0.3 kW kg$^{-1}$) have been achieved with an operating potential of 1.2 V. These values are higher than those of the symmetric supercapacitors based on HPGCFs (5.3 Wh kg$^{-1}$), as shown in Figure S11, hydrazine reduced graphene hydrogels (5.7 Wh kg$^{-1}$) [47], nitrogen and boron co-doped graphene aerogels (8.7 Wh kg$^{-1}$) [48], and hydroquinone functionalized graphene hydrogels (11.3 Wh kg$^{-1}$) [49]. In addition, the HPGCFs//AQ-HPGCFs ASC also outperforms some ASCs in literature such as graphene/MnO$_2$//graphene (7 Wh kg$^{-1}$ at 5 kW kg$^{-1}$) [12], CoO@PPy nanowire array//AC (11.8 Wh kg$^{-1}$ at 5.5 kW kg$^{-1}$) [50], Graphene-NiCo$_2$O$_4$//AC (7.6 Wh kg$^{-1}$ at 5.6 kW kg$^{-1}$) [51], graphene/MnO$_2$//ACN (8.2 Wh kg$^{-1}$ at 16.5 kW kg$^{-1}$) [52], and RGO–RuO$_2$//RGO–PANI (6.8 Wh kg$^{-1}$ at 49.8 kW kg$^{-1}$) [53]. Most importantly, the highest
power density (72 kW kg\(^{-1}\)) for our HPGCFs//AQ-HPGCFs ASC could meet the power demands of the PNGV (Partnership for a New Generation of Vehicles) [54–56]. Furthermore, the energy density (19.3 Wh kg\(^{-1}\)) of the our ASC device is also superior to most aqueous electrolyte based EDLCs (3–6 Wh kg\(^{-1}\)) [57, 58].

![Ragone plot](image)

**Figure 9** Ragone plot of the HPGCFs//AQ-HPGCFs ASC (solid square). Scatter dots refer to the power densities and the corresponding energy densities reported in the literature (the reference numbers are indicated in the figure).

On the basis of above experimental results, the advantageous features of the HPGCFs//AQ-HPGCFs ASC device can be summarized as follows:

*Low cost, safe and green nature.* The preferred energy storage devices are composed of inexpensive and easily acquired materials and fabricated through a relatively simple scalable process. In our system, the cotton that we used is being manufactured in ton quantity at low cost. The AQ molecules are one of the most common organic materials, which have the low-cost
advantage. Furthermore, the cotton and AQ raw materials used here are highly renewable. Thus excessive consumption would not cause environmental problems. As for safety issue, our HPGCFs//AQ-HPGCFs device operates in aqueous electrolytes and is free of flammable organic electrolytes. It can be processed under ambient conditions without the necessity of an oxygen- or humidity-free environment.

High power density. This is a key requirement for supercapacitors. The maximum power density of the HPGCFs//AQ-HPGCFs ASC is 72 kW kg\(^{-1}\), which means a full charge-discharge within 0.8 s. The ultrahigh power should be related to the favorable ions/electrons transport kinetics of HPGCFs, namely, 1D hollow fiber architecture as ion-buffering reservoirs, hierarchical porous texture for fast ion accommodation, and highly graphitic structure for enhanced electric conductivity. The AQ molecules are also of pseudocapacitive nature without diffusion limitation.

4. Conclusions

We have demonstrated a new strategy to fabricate hierarchical porous graphitic carbon fibers (HPGCFs) via a molten sodium activation route from natural cotton precursor. Through a further functionalization of the HPGCF scaffold by AQ molecules, the composite can deliver even higher capacitive performance. Detailed electrochemical characterization has demonstrated the advantage of both HPGCFs and AQ-HPGCFs compared to conventional CFs and KOH-activated CFs. It is believed that the hierarchical porosity and high graphitization degree could provide effective pathways for rapid ionic and electronic transport. The integration of HPGCFs and AQ-HPGCFs into an ASC device enables the combination of ultrahigh power density, comparable energy density, and excellent structural stability, as well as high safety, low cost and green nature. In particular, even at a power density of 72 kW kg\(^{-1}\) (a full charge-discharge within 0.8 s), an energy density of 9.6 Wh kg\(^{-1}\) has been obtained. In addition to the high application potential in ultrahigh-rate charge storage, this interesting porous graphitic carbon fibers could also be useful in applications in fuel cells, nanocomposites for mechanical enhancement, and
air-pollution filters.

Supporting information

Supplementary data associated with this article can be found in the online version: Calculations of specific capacitance, energy density and power density based on the galvanostatic charge–discharge curves. SEM images of natural cotton, FTIR spectra of the AQ-HPGCFs and pure AQ, Nitrogen adsorption-desorption isotherms and pore size distributions, electrochemical properties of pure AQ, comparison of capacitance at various current densities for two cell sizes (1×1 cm², 2×2 cm²), electrochemical properties of HPGCFs//HPGCFs symmetric supercapacitor.

Acknowledgment

The authors gratefully acknowledge the financial support offered by NSFC Grants (21173158, 21373152). H. J. Fan thanks the support by SERC Public Sector Research Funding (Grant number 1121202012), Agency for Science, Technology, and Research (A*STAR), , and MOE AcRF Tier 1 (RG104/14).
References


Huanwen Wang received a B.S. degree from the Northwest Normal University in 2008, and Ph.D degree from Tongji University in 2014 under supervision of Prof. Xuefeng Wang. He was a visiting student from Dec 2013 to Mar 2014 to the School of Physical and Mathematical Sciences, Nanyang Technological University (NTU). Currently he is a postdoc fellow at School of Materials Science and Engineering of NTU. His research is focused on synthesis of novel nanomaterials and energy storage and conversion.

Huan Yi received his B.S. degree in 2011 from Northeast Normal University, China. He is currently pursuing his Ph.D. under the Supervision of Prof. Xuefeng Wang at Tongji University. His research focuses on design and synthesis of advanced functional materials for energy applications.

Changrong Zhu received her B. S. degree (2012) in School of Material Science and Engineering from Sichuan University. She is currently pursuing her Ph.D degree (since 2012) in School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore. Her research interests are the fabrication of nanostructure materials for application in energy storage systems.

Dr. Xuefeng Wang is a distinguished professor at the Department of Chemistry in Tongji University. Before joining Tongji University in 2009, he was a senior scientist at the Department of Chemistry University of Virginia. He received a B.S. degree from the Northwest Normal University in 1983 and Ph.D. from Fudan
University in 1996. Dr. Wang's research interests include metal reactions with hydrogen, designing particles in composites and related advanced materials, and their potential applications in energy storage.

Dr. Hong Jin Fan is currently an associate professor at Nanyang Technological University (NTU). He received PhD from National University of Singapore in 2003, followed by postdoc at Max-Planck-Institute of Microstructure Physics, Germany and University of Cambridge. He joined in NTU since 2008. His research interests include semiconductor nanowires and heterostructured nanomaterials, atomic layer deposition in energy applications, and battery and solar energy conversion materials and technologies. He is an editorial board member of Nanotechnology and Scientific Reports, advisory board member of Advanced Science, and Associate Editor of Materials Research Bulletin.
Highlights

- Natural cottons are activated using molten sodium metal at 800 °C. The obtained carbon fibers are demonstrated as good candidate for supercapacitive electrode materials.
- The molten sodium activation is found more effective than conventional KOH activation.
- Asymmetric supercapacitors show outstanding performance.
Graphic Abstract

[Diagram showing the process of carbonization and sodium activation, followed by modifying with small organic molecules.]