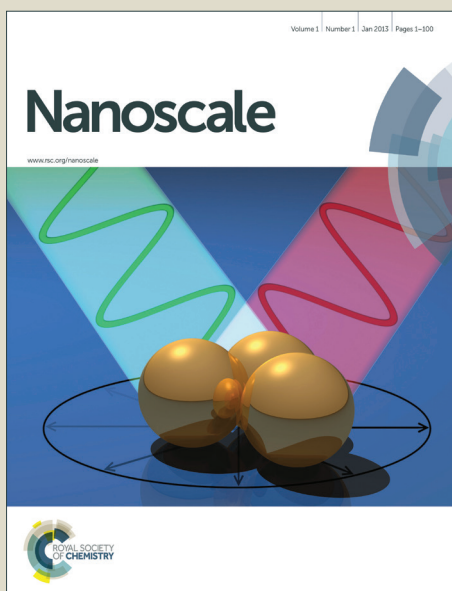


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# Making Commercial Carbon Fiber Cloth Having Comparable Capacitances to Carbon Nanotube and Graphene in Supercapacitors through a “Top-Down” Approach

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**Abstract:** A “top-down” and scalable approach for processing carbon fiber cloth (CFC) into flexible and all-carbon electrodes with remarkable areal capacity and cyclic stability was developed. CFC is commercially available in large quantity but its use as electrode materials in supercapacitors is not satisfactory. The approach demonstrated in this work is based on sequential treatment of CFC with KOH activation and high temperature annealing that can effectively improve its specific surface area to a remarkable 2780 m<sup>2</sup>/g while at the same time achieving a good electrical conductivity to 320 S/m without sacrificing its intrinsic mechanical strength and flexibility. The processed CFC can be directly used as electrode for supercapacitors without any binders, conductive additives and current collectors while avoiding elaborate electrode processing steps to deliver specific capacitance of ~ 0.5 F/cm<sup>2</sup>

and  $\sim 197$  F/g with remarkable rate performance and excellent cyclic stability. The properties of these processed CFC cloth are comparable or better than graphene and carbon nanotube based electrodes. We further demonstrate symmetric solid-state supercapacitors based on these processed CFC with very good flexibility. This “top-down” and scalable approach could be readily applied to other types of commercially available carbon materials and therefore could have substantial significance for high performance supercapacitor devices.

## Introduction

Supercapacitors are unique energy storage devices with remarkable properties. They have substantially higher power densities and much better cyclic stability compared with rechargeable batteries; and they are widely recognized as one of the most promising technologies for the next-generation energy storage.<sup>1,2</sup> Over the past few years, They have been under intensive research and substantial achievements, in particular, on the synthesis and processing of advanced electrode materials, design and fabrication of novel electrode architectures, and integration with energy generation and other energy storage systems, have been demonstrated.<sup>3-9</sup> Most of the supercapacitor devices developed by far, however, are based on electrode materials that are expensive and difficult for large scale production and/or require elaborate processes to fabricate electrodes; and hence, may not be readily adaptable for practical applications. Therefore, developing effective strategies to fabricate electrodes with low cost materials and scalable methods are highly desired and are actively pursued in recent years.

Electrical double-layer capacitor (EDLC) is one important type of supercapacitors; and it generally uses high surface area carbon or its derivatives as the electrode materials.<sup>10,11</sup> In general, carbon materials such as activated carbon, carbon nanotubes and graphene are extensively used for EDLC.<sup>12-21</sup> However, most of these materials are in powder form and assembling them into electrodes usually requires uses of binders, conducting additives and current collectors.<sup>15,16,22</sup> The drawbacks of using these additional components, in that it brings significant processing cost and substantial compromises in electrode-level performance

metrics, have now been recognized. It has been suggested that fabrication of binder-free and freestanding electrodes is an effective approach to resolve this problem,<sup>23-25</sup> but the methods developed by far for this approach usually involve substantial amount of carbon nanotubes and/or graphene that are expensive and difficult for large scale production. Therefore, developing simple processing methods to fabricate carbon-only electrode without using advanced nanomaterials are highly desired for real applications. Several recent works devoted to carbon cloth have shown its great potentials for practical applications, including preparation of carbon fiber cloth material from cotton textile, chemical activation of carbon fiber cloth for high rate EDLC electrode.<sup>26,27</sup>

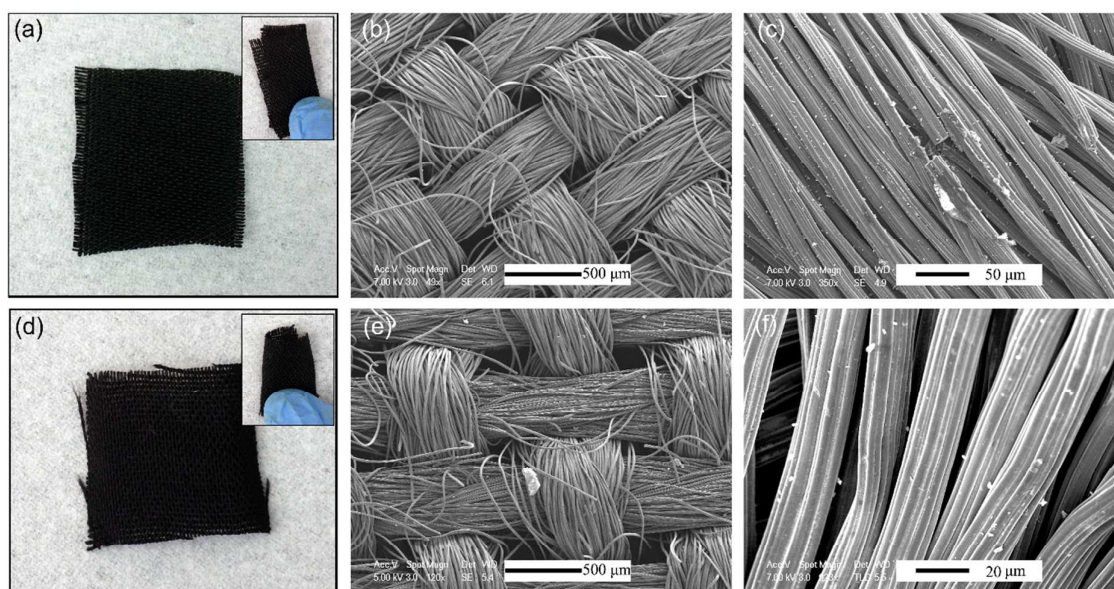
In this paper we report a top-down and scalable approach to fabricate flexible and all-carbon electrodes with remarkable performance for EDLC supercapacitors. We used activated carbon fiber cloth (CFC) as our carbon material because it is inexpensive and commercially available in large quantities and it also has excellent mechanical strength with superior flexibility. This type of material has been used extensively for several commercial applications such as air purification and wastewater treatment, however, it has been rarely used as supercapacitor electrode materials presumably due to its relatively low surface area ( $\sim 1000 \text{ m}^2/\text{g}$ ) and moderate electrical conductivity ( $\sim 100 \text{ S/m}$ ). The approach demonstrated in this work is based on sequential treatment of CFC with KOH activation and high temperature annealing. This approach can effectively increase the specific surface area of CFC to a remarkable value of  $2780 \text{ m}^2/\text{g}$  (three times increase) and electrical conductivity to  $320 \text{ S/m}$ , while not sacrificing its intrinsic mechanical strength and flexibility. These physiochemical properties of processed CFC make them capable of being directly used as

supercapacitor electrode without involving any binders, conductive additives, current collectors and any elaborative electrode processing steps. As EDLC electrodes, the processed CFC materials had excellent capacitive properties in a variety of aqueous electrolytes and overall were able to deliver specific capacitance of  $\sim 0.5 \text{ F/cm}^2$  and  $\sim 197 \text{ F/g}$ , remarkable rate performance and very good cyclic stability (99% retention for 15000 cycles). Noticeably, these performance values are comparable or better than graphene and carbon nanotube based electrodes. Furthermore, we demonstrate that symmetric solid-state supercapacitors assembled with processed CFC electrodes have superior flexibility and excellent capability for storing energy. This “top-down” and scalable approach developed here could be readily applied to other types of commercially available carbon materials and therefore could have substantial significance for high performance supercapacitor devices.

## Results and Discussions

All experimental details can be found in supporting information. The CFC material purchased from Chemviron Carbon (Calgon Carbon Corporation, PA, USA) is very flexible and can be folded and unfolded many times without losing its mechanical integrity as can be seen from the set of photographs shown in Figure 1a. The intrinsically outstanding mechanical property, together with moderate electrical conductivity, makes CFC suitable as supercapacitor electrodes directly without elaborate electrode preparation processes. SEM characterization of the as-purchased CFC (Figure 1b) suggests that it has a textile structure consisting of interwoven carbon fibers with diameters ranging from 15 to 20  $\mu\text{m}$  (Figure 1c). However, BET measurement revealed that its specific surface area is  $\sim 1034 \text{ m}^2/\text{g}$  (Figure 2a), which is relatively low compared with other carbon materials used for EDLC application. In order to make CFC materials suitable for EDLC application, we developed a top down and

scalable approach consisting of KOH activation and thermal annealing for improving its specific surface area as well as the electrical conductivity.



**Figure 1: Morphology of CFC before (top three images) and after (bottom three images) KOH activation: (a and d) photograph of raw and KOH activated CFC, insets show that both of them have good structural integrity and are highly flexible; SEM images of raw (b and c) and KOH activated (e and f) CFC at different magnifications.**

KOH activation is a well-developed approach for preparing porous carbon materials,<sup>28, 29</sup> but its effect on the flexibility and mechanical strength of the CFC is not clear. KOH activation is a complicated process and involves various chemical/physical reaction schemes. The mechanism is generally accepted as starting with the following reaction:<sup>30, 31</sup>



The KOH derived potassium compounds such as  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{O}$  and metallic K could act as agents for etching carbon framework. Under higher temperature conditions, the intermediate reaction products such as  $\text{H}_2\text{O}$  and  $\text{CO}_2$  can also react with carbon to generate pores for

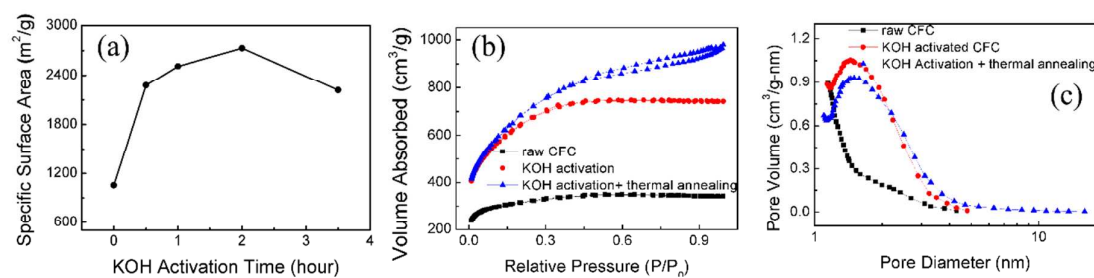
improved porosity. In this work, we systematically studied the effect of the KOH activation conditions on the properties of the CFC and discovered reaction conditions that could increase the specific surface area while retaining its mechanical properties (Figure 1d). The retained mechanical flexibility and strength of activated CFC could attribute to the facts that KOH activation generates small-sized micropores in the carbon framework.<sup>31</sup> The uniformly distributed micropores will not significantly damage the macrostructure of the carbon frame when controlled properly. SEM images of the activated CFC (Figure 1e and f) suggest that it has similar textile morphology as the pristine CFC and the diameters of the carbon fibers were comparable. Therefore, the activated CFC textile still has well-connected carbon fibers, which is one of the key factors for maintained mechanical strength and flexibility (Figure S1). The good mechanical properties of activated CFC were also evidenced by repeated bending test (2 bends per second) of single CFC electrode and CFC supercapacitor devices. After this test, no obvious changes in morphology and no broken fibers, cracks, and peeled carbon chips were observed under SEM. Furthermore, no obvious reduction in the specific capacity was measured as well (Figure S2 and S3). These results suggest that KOH activation did not obviously change the morphology and mechanical properties of carbon cloth.

The variation of BET specific surface area for KOH activated CFC as a function of activation time is shown in Figure 2a. Overall, the highest specific surface area of 2720 m<sup>2</sup>/g was obtained with 2 hours activation, which is a significant increase from the 1034 m<sup>2</sup>/g of the as-purchased CFC. Samples activated for longer times were found to have lower specific surface area, presumably due to higher degree of damage to the carbon framework.<sup>31</sup> To investigate the pore characteristics, N<sub>2</sub> adsorption/desorption isotherm measurements were

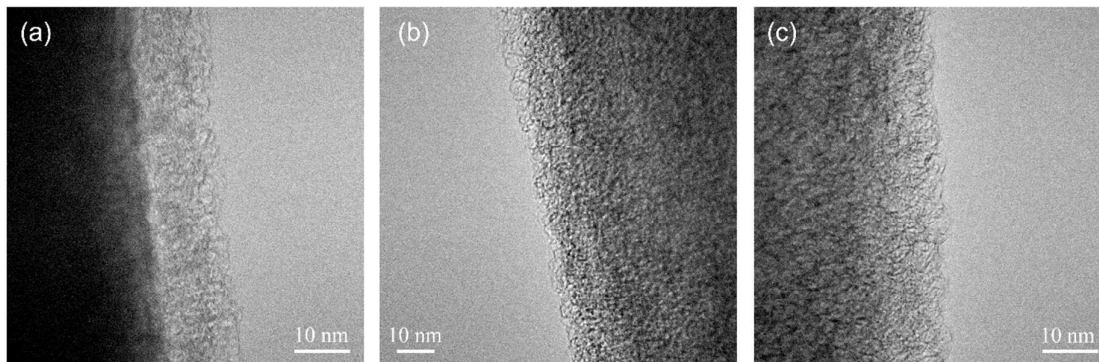


performed (figure 2b and 2c). The as-received CFC showed typical type-I isotherm, suggesting it mainly has micropores that are smaller than 1 nm (Figure 2c). The isotherm of KOH activated CFC also showed type-I isotherm but the specific surface area was substantially increased. Figure 2c compares the pore diameter distribution of CFC before and after KOH activation. It can be seen that after activation, the volume of pores was noticeably increased and mesopores with diameter at  $\sim 2.5$  nm was produced on the evidence of broad peak occurred at 1~3nm. Such bigger pores could be beneficial for improving EDLC performance because electrolyte ions transportation within bigger pores and channels is much easier.

Figure 3a and b show typical high-resolution TEM images of individual carbon fibers before and after KOH activation. These images show that after KOH activation (Figure 3b), the surface of carbon cloth became rough and a significant amount of well-defined pores was observed. Such changes in surface roughness are presumably due to KOH activation since KOH activate carbon material mainly through etching reactions.<sup>32</sup>



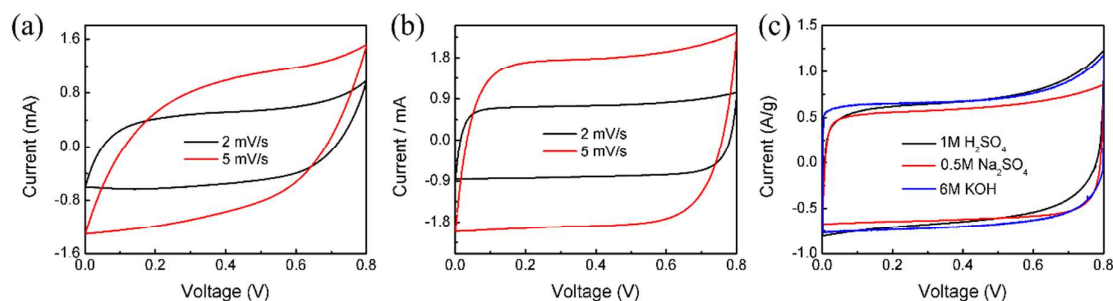
**Figure 2: (a) Changes in BET specific surface area of CFC upon KOH activation as a function of activation time. (b) Nitrogen adsorption/desorption isotherm and (c) pore size distribution of raw CFC, KOH activated CFC and CFC with both KOH activation and thermal annealing.**



**Figure 3: TEM characterization of CFC with different treatments: (a) as-received; (b) KOH activation and (c) both KOH activation and thermal annealing.**

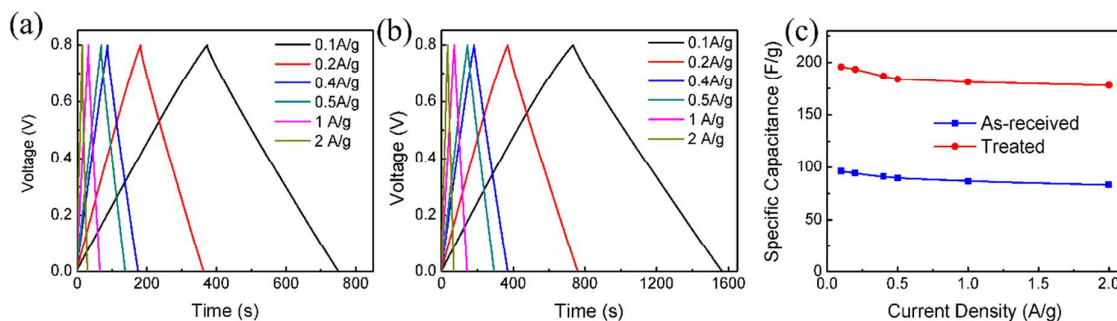
Electrical conductivity of the electrode is critically important in determining the overall EDLC performance and highly conductive materials are highly desired. Chemical activation of carbon (such as KOH activation used here), however, usually damages its graphitic structure and hence compromises its electrical conductivity. As a result, the KOH activated CFC showed a high electrical resistivity of  $\sim 1.5 \Omega \cdot \text{cm}$ . To increase its conductivity, thermal annealing under inert atmosphere was used to improve its graphitic structure integrity. Through a systematic study we identified that a  $1100^\circ\text{C}$  treatment for 2 hours was effective to decrease the resistivity to  $0.31 \Omega \cdot \text{cm}$  ( $322 \text{ S/m}$ ), which is 5 times better than the activated CFC. Thermal annealing at elevated temperatures noticeably improved the electrical conductivity because it can remove most of the surface functional groups and impurities that were introduced during KOH activation. It can also improve the degree of carbon graphitization that is also beneficial for higher conductivity (Figure S1). Overall, it is evident that thermal annealing can improve the electrical conductivity of CFC as well as maintain its mechanical strength.<sup>33</sup>

Moreover, the thermally processed CFC was found to have a BET specific area of 2780  $\text{m}^2/\text{g}$ , which is actually slightly higher than the KOH activated CFC (2720  $\text{m}^2/\text{g}$ , Figure 2), suggests that the thermal annealing treatment did not significantly change the surface area of CFC. This slight increase in specific surface area may attribute to the elimination carbon surface functional groups that were introduced during KOH activation.<sup>34</sup> Further comparisons of the  $\text{N}_2$  absorption/desorption isotherm (Figure 2b) and the pore size distribution (Figure 2c) suggest that the thermal treatment was able to increase the diameter of pores, as evidenced by the broadening of the peak at 1.6nm and the appearance of the shoulder at  $\sim 2.5$  nm. On the basis of these results, it is clear that combined treatments of KOH activation for 2 hours and thermal annealing for another 2 hours were effective for producing high surface area and conductive CFC, and therefore were used as standard procedures in this work for preparing EDLC electrodes. It should be noted that the area density of processed CFC was decreased from the 12  $\text{mg}/\text{cm}^2$  of raw CFC to 5.8  $\text{mg}/\text{cm}^2$ . For simplicity, CFC processed with these two processes is termed as processed CFC for discussions below.



**Figure 4: Comparison of the CV profiles acquired in 6M KOH electrolyte of (a) raw CFC and (b) processed CFC. (c) CV of processed CFC in different aqueous electrolyte (black: 1M  $\text{H}_2\text{SO}_4$ , red: 0.5M  $\text{Na}_2\text{SO}_4$ , blue: 6M KOH) at 2 mV/s. The processed CFC electrodes have ideal EDLC performance in a variety of electrolytes.**

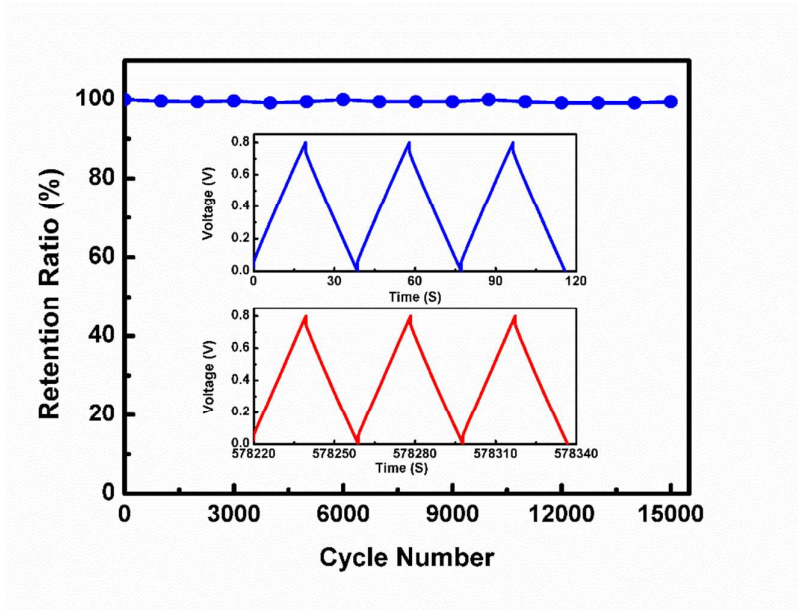
The EDLC performance of raw and processed CFC electrodes was studied using the two-electrode configuration (as coin cells) in a variety of electrolytes. Figure 4a and 4b compare typical CV curves collected from these two materials at different scan rates. In comparison to raw CFC, the processed CFC electrodes showed ideal rectangular shape and increased areas of CV curves, indicating their charge-storage capabilities were substantially improved. As the scan rate was increased, the processed CFC electrodes had much better capacitive behavior as evidenced by the retention of square shaped CV curves. Specific capacitance calculated from CV curves acquired at 2 mV/s suggests that the processed CFC was able to deliver a specific capacitance of 187 F/g. In contrast, the original CFC only has a specific capacitance of 98 F/g under the same condition, and therefore suggests that the electrode treatment procedure developed in this work can nearly double the EDLC capacitance of CFC. Figure 4c shows the CVs of processed CFC electrodes acquired at 2 mV/s in a variety of aqueous electrolytes, including 6M KOH, 1M H<sub>2</sub>SO<sub>4</sub> and 0.5M Na<sub>2</sub>SO<sub>4</sub>. A solid-state electrolyte made with H<sub>3</sub>PO<sub>4</sub> and polyvinyl alcohol (PVA) was also used and the results from this electrolyte will be discussed below. These electrolytes were chosen because they are typical aqueous electrolytes used for supercapacitors and the fact that the processed CFC electrodes can operate nicely in these electrolytes suggests that they have great potential for integration into full supercapacitor devices by combining with other types of supercapacitor chemistry (such as pseudocapacitor). Interestingly, it was found that the specific capacitances of processed CFC depends on the electrolyte and has the order of KOH > H<sub>2</sub>SO<sub>4</sub> > Na<sub>2</sub>SO<sub>4</sub>. Such difference could originate from the differences of the ion-carbon interaction and ionic radius of different ions.



**Figure 5: Galvanostatic charge-discharge curves of (a) raw and (b) processed CFC electrodes at increasing current densities from 0.1 A/g to 2 A/g; and (c) comparison of specific capacitance (F/g) determined from data shown in (a) and (b) for raw and processed CFC. It can be seen that the processed CFC have substantially higher specific capacitance under all conditions examined.**

The ability to retain high capacitance during fast charge-discharge processes is a critical requirement for high performance and practical EDLCs. The rate performance of processed CFC was studied using the galvanostatic charge-discharge method conducted at different current densities in 6.0 M KOH and typical results are shown in Figure 5b. For comparison, the behavior of raw CFC was also tested under identical conditions and the results are shown in Figure 5a. The processed CFC exhibited symmetric and linear charge-discharge profiles, suggesting that it has excellent double layer capacitive behavior. Figure 5c compares the specific capacitance of CFC electrodes with and without treatment obtained at different current densities. Overall, the processed CFC showed a capacitance of 197 F/g at 0.1 A/g and 180 F/g (91% retention) as the current density was increased 20 times to 2 A/g. Tests conducted at even higher rates suggest that the specific capacitance of CFC can retain as high as 166 F/g and 156 F/g at the current rate of 6 A/g and 10 A/g, respectively (Figure S4). At the rate of 6 A/g, the calculated specific energy density was 12.3 Wh/kg whereas the specific power density was 2.1 KW/kg. Noticeably, the energy storage capability of CFC is much better

than the supercapacitor devices based on carbon nanomaterials such as graphene, carbon nanotube, activated carbon, as well as their nanocomposites (commonly, < 10 Wh/kg and 1 KW/kg).<sup>35-40</sup> In strong contrast, the raw CFC only had ~ 100 F/g at 0.1 A/g and 90 F/g at 2 A/g. This obvious increase in specific capacitance from galvanostatic charge-discharge further proved that the KOH activation and thermal treatment process were able to substantially improve the EDLC performance of CFC.



**Figure 6:** Cyclic stability of processed CFC electrodes for 15000 charge-discharge cycles tested in 6.0M KOH, the inset shows the first three and the last three charge-discharge profiles.

Cyclic stability is another key factor in evaluating performance of EDLC electrodes. The stability of the processed CFC electrode was studied using a charge-discharge current density of 3.3 A/g for 15000 cycles and the results are shown in Figure 6. The electrode was remarkably stable (>99% capacitance retention) and no obvious decay in specific capacitance was observed in this long term test. The inset shows the first three and last three charge-discharge cycles, and all of them show characteristic symmetric and triangular EDLC curves.

This outstanding cyclic stability further demonstrate that the processed CFC electrode could be promising electrode materials for practical applications.

Table 1 compares the performance of processed CFC electrodes fabricated in this work with typical carbon materials reported in literature on the basis of parameters that are of practical significance, including specific capacitance, amount of additives, use of current collector, flexibility, cyclic stability, and projected material and manufacture cost. From these comparisons, it is evident that electrodes fabricated with processed CFC are able to provide excellent EDLC performances without uses of any additives and current collectors. The CFC electrodes are also highly flexible and are low cost. It is therefore expected that the materials developed in this work could have particular practical values.

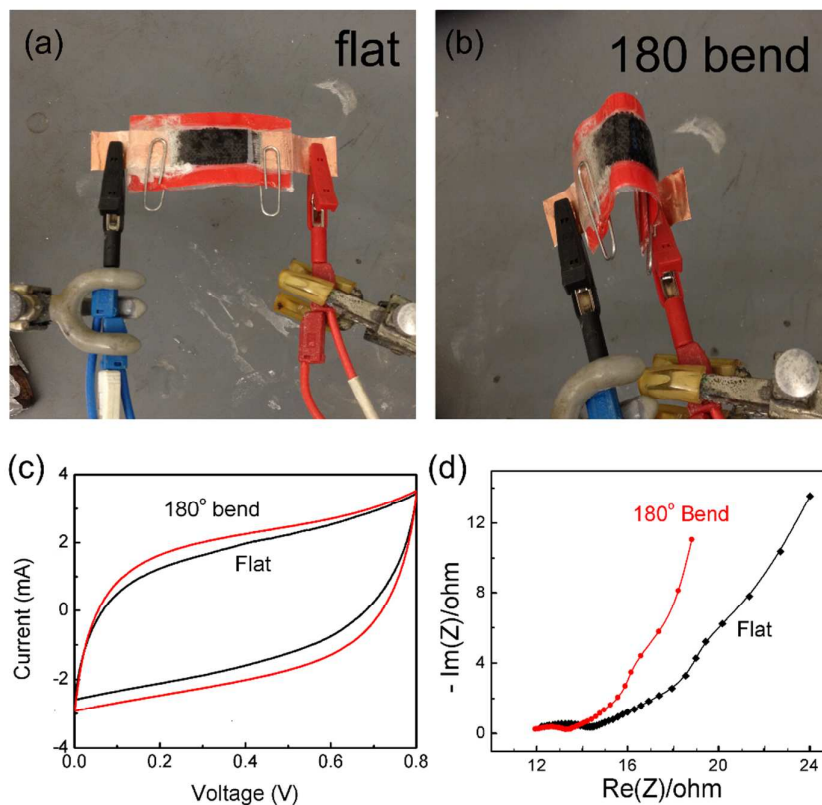
**Table 1: Comparison of electrochemical and mechanical properties of the processed CFC with typical carbon materials reported in the literature.**

Material	capacitance (F/g)	additive (w/w%)	current collector	flexibility	current rate (sweep rate)	cycling stability /cycles	cost	Ref.
graphene hydrogel	175	None	no	N/A	10 mV/s	N/A	high	5
mesoporous carbon	173	15%	yes	no	~ 0.2 A/g	98% /1000	high	41
carbide – derived carbon	190	> 5%	yes	no	5 mV/s	N/A	high	42
seaweeds-derived carbon	198	10%	yes	no	2 mV/s	85% /10000	low	43
carbon sphere	173	10%	yes	no	2 mV/s	N/A	low	44
N-enriched carbon	198	20%	yes	no	0.05 A/g	Stable /10000	high	45
N-doped carbon fiber	202	20%	yes	no	1 A/g	97% /3000	moderate	35
ordered mesoporous carbon	206	>5%	yes	no	5 mV/s	N/A	high	36
graphene/carbon black	138	None	no	no	10 mV/s	96.2% /2000	high	46
carbon nanotubes	167	15%	no	no	50 mV/s	93.3% /5000	high	47
<b>CFC</b>	<b>197</b>	<b>None</b>	<b>no</b>	<b>excellent</b>	<b>0.1 A/g</b>	<b>99% /15000</b>	<b>low</b>	<b>this work</b>



Flexible solid state supercapacitors were then fabricated using processed CFC electrodes in order to examine their performance as flexible full devices. Solid-state supercapacitors hold great promises for many applications because they are easier to fabricate and have remarkable safety advantages.<sup>37,48</sup> A photograph of the fabricated flexible device is shown in Figure 7a, and Figure 7b is a photograph of the same device bent at 180 degree to show its flexibility. The performance of the CFC SC was analyzed using CV (Figure 7c) and EIS (Figure 7d) methods, both for the flat device and for the device bent at 180 degrees. The calculated areal capacitance based on the CV measurements was as high as 0.5 F/cm<sup>2</sup>. CV results and EIS testing show that there was no significant difference for the device under flat and bent conditions. In fact, from the CV results it appears that the bent device actually exhibited better performance, most likely due to the fact that the act of bending forces was able to bring the two CFC electrodes closer, which decreased the inner resistance of the device. This was also supported by EIS results (Figure 7b), as evidenced by the smaller diameter of semi-circle and the tilted straight line at low frequency range. The cyclic stability of the device under repeated 180° bending test was shown in Figure S3 and the results suggest that the device had excellent flexibility and stability and no noticeable capacity loss was measured. It is noteworthy to mention that the applied bending rate was very fast and was around 1 bend per second. These results testified superior flexibility and mechanical strength of the processed CFC electrodes developed in this work.





**Figure 7: Photographs of the fabricated solid-state supercapacitor using processed CFC electrode when (a) laid flat and (b) bent for 180 degree. The 180 degree bend test was used to check the flexibility of the devices. Comparisons of (c) CV (sweep rate: 5mV/S) and (d) EIS of the devices under flat and bent configurations.**

## Conclusions

In conclusion, a novel top down and scalable approach was developed in this work for fabricating flexible supercapacitor electrodes with remarkable areal capacity and cyclic stability. This approach is based on sequential treatment of KOH activation and thermal annealing and was successfully applied on low cost carbon fiber cloth. As a result, supercapacitor electrodes with properties that are of real significance such as high mechanical

strength and superior flexibility without using any additives were readily obtained. The fabricated electrodes were able to deliver high specific capacitances of 197 F/g and 0.5 F/cm<sup>2</sup>. They also exhibited excellent rate capability (~ 90% capacity retention) and long-term cyclic stability (nearly no capacity loss for 15000 cycles). Noticeably, the performance values are comparable or better than electrodes based on carbon nanotube and/or graphene. We further demonstrated symmetric solid-state supercapacitors that have superior flexibility and excellent capability. This “top-down” and scalable approach could be readily applied to other types of commercially available carbon materials and therefore could have substantial significance for high performance supercapacitor devices.

#### **Acknowledgements**

This work is in-part supported by grants from NSF (EECS-1344745) and NSF (CHE-1213469). The authors also acknowledge the support from Duke University SMIF (Shared Materials Instrumentation Facilities). T.Z. is supported by the Duke Center for the Environmental Implications of NanoTechnology (CEINT) summer research program.

## References

1. P. Simon and Y. Gogotsi, *Nature Materials* 2008, 7, 845-854.
2. Z. G. Yang, J. L. Zhang, M. C. W. Kintner-Meyer, X. C. Lu, D. W. Choi, J. P. Lemmon and J. Liu, *Chem. Rev.* 2011, 111, 3577-3613.
3. Y. Zhu, S. Murali, M. Stoller, K. Ganesh, W. Cai, P. Ferreira, A. Pirkle, R. Wallace, K. Cychosz, M. Thommes, D. Su, E. Stach, R. Ruoff, *Science* 2011, 332, 1537-1541.
4. Z. Weng, Y. Su, D.W. Wang, F. Li, J. Du and H.M. Cheng, *Adv. Energy Mater.* 2011, 1, 917-922.
5. Y. Xu, K. Sheng, C. Li and G. Shi, *ACS Nano* 2010, 4, 4324-4330.
6. G. H. Yu, X. Xie, L. J. Pan, Z. N. Bao and Y. Cui, *Nano Energy* 2013, 2, 213-234.
7. Y. W. Cheng, H. B. Zhang, C. V. Varanasi and J. Liu, *Energy Environ. Sci.* 2013, 6, 3314-3321.
8. H. Wang, H. S. Casalongue, Y. Liang, and H. Dai, *J. Am. Chem. Soc.* 2010, 132, 7472-7477.
9. P. Yang, X. Xiao, Y. Li, Y. Ding, P. Qiang, X. Tan, W. Mai, Z. Lin, W. Wu, T. Li, H. Jin, P. Liu, J. Zhou, C. P. Wong and Z. L. Wang, *ACS Nano* 2013, 7, 2617-2626.
10. A. Pandolfo and A. Hollenkamp, *J. Power Sources* 2006, 157, 11-27.
11. L. L. Zhang and X. S. Zhao, *Chem. Soc. Rev.* 2009, 38, 2520-2531.
12. T. Y. Kim, H. W. Lee, M. Stoller, D. R. Dreyer, C. W. Bielawski, R. S. Ruoff and K. S. Suh, *ACS Nano* 2011, 5, 436-442.
13. X. Yang, J. Zhu, L. Qiu and D. Li, *Adv Mater.* 2011, 23, 2833-2838.
14. Y. W. Cheng, H. B. Zhang, S. T. Lu, C. V. Varanasi and J. Liu, *Nanoscale* 2013, 5, 1067-1073.
15. Z. Fan, J. Yan, L. Zhi, Q. Zhang, T. Wei, J. Feng, M. Zhang, W. Qian and F. Wei, *Adv. Mater.* 2010, 22, 3723-3728.

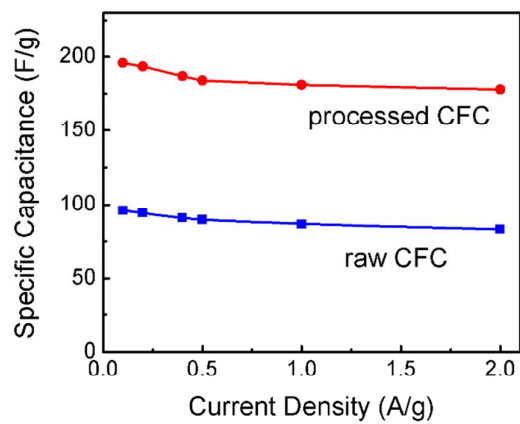
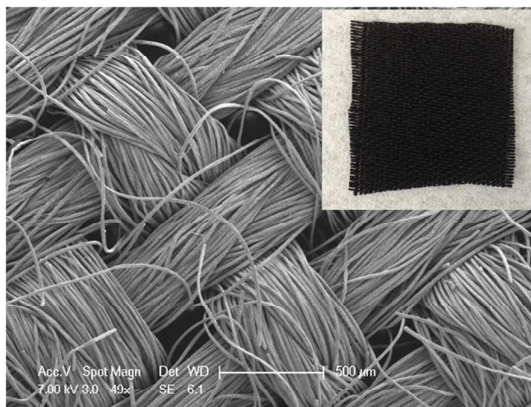
16. J. Gamby, P. L. Taberna, P. Simon, J. F. Fauvarque and M. Chesneau, *J. Power Sources* 2001, 101, 109-116.
17. M. G. Hahm, A. Reddy, D. P. Cole, M. Rivera, J. A. Vento, J. Nam, H. Y. Jung, Y. L. Kim, N. T. Narayanan, D. P. Hashim, C. Galande, Y. J. Jung, M. Bundy, S. Karna, P. M. Ajayan and R. Vajtai, *Nano Lett.* 2012, 12, 5616-5621.
18. Y. Huang, J. Liang and Y. Chen, *Small* 2012, 8, 1805–1834.
19. B.R. Stoner, A. S. Raut, B. Brown, C. B. Parker and J. T. Glass, *Appl. Phys. Lett.* 2011, 99, 183104.
20. A. S. Raut, C. B. Parker, B.R. Stoner and J. T. Glass, *Electrochem. Commun.* 2012, 19, 138-141.
21. D. Yu and L. Dai, *J. Phys. Chem. Lett.*, 2010, 1, 467–470.
22. T. E. Rufford, D. Hulicova-Jurcakova, K. Khosla, Z. Zhu, G. Q. Lu, *J. Power Sources* 2010, 195, 912–918.
23. C. Meng, C. Liu, L. Chen, C. Hu and S. Fan, *Nano Lett.* 2010, 10, 4025-4031.
24. Y. W. Cheng, S. T. Lu, H. B. Zhang, C. V. Varanasi and J. Liu, *Nano Lett.* 2012, 12, 4206-4211.
25. L. Hu, J. W. Choi, Y. Yang, S. Jeong, F. L. Mantia, L. F. Cui and Y. Cui, *PANS*, 2009, 106, 21490–21494.
26. L. Bao and X. Li, *Adv. Mater.* 2012, 24, 3246–3252.
27. G. Wang, H. Wang, X. Lu, Y. Ling, M. Yu, T. Zhai, Y. Tong and Y. Li, *Adv. Mater.* 2014, 26, 2676-2682.
28. T. Otowa, Y. Nojima and T. Miyazaki, *Carbon* 1997, 35, 1315-1319.
29. Z. Zapata-Benabithé, F. Carrasco-Marin and C. Moreno-Castilla, *J. Power Sources* 2012, 219, 80-88.
30. J. Wang and S. Kaskel, *J. Mater. Chem.* 2012, 22, 23710-23725.

31. Y. Lv, F. Zhang, Y. Dou, Y. Zhai, J. Wang, H. Liu, Y. Xia, B. Tu and D. Zhao, *J. Mater. Chem.* 2012 22, 93-99.
32. M. A. Lillo-Rodenas, D. Cazorla-Amoros and A. Linares-Solano, *Carbon* 2003, 41, 267-275.
33. D. Mattia, M. P. Rossi, B. M. Kim, G. Korneva, H. H. Bau and Y. Gogotsi, *J. Phys. Chem. B* 2006, 110, 9850-9855.
34. B. M. Kim, S. Sinha and H. H. Bau, *Nano Lett.* 2004, 4, 2203-2208.
35. L. F. Chen, X. D. Zhang, H. W. Liang, M. G. Kong, Q. F. Guan, P. Chen, Z. Y. Wu and S. H. Yu, *ACS Nano* 2012, 6, 7092-7102.
36. W. Xing, S. Z. Qiao, R. G. Ding, F. Li, G. Q. Lu, Z. F. Yan and H. M. Cheng, *Carbon* 2006, 47, 216-224.
37. Y. X. Xu, Z. Y. Lin, X. Q. Huang, Y. Liu, Y. Huang and X. F. Duan, *ACS Nano* 2013, 7, 4042-4049.
38. Q. T. Qu, L. Li, S. Tian, W. L. Guo, Y. P. Wu and R. Holze, *J. Power Sources* 2010, 195, 2789-2794.
39. C. Yu, C. Masarapu, J. Rong, B. Wei and H. Jiang, *Adv. Mater.* 2009, 21, 4793-4797.
40. Y. J. Kang, H. Chung, C.H. Han and W. Kim, *Nanotechnology* 2012, 23, 065401.
41. X. L. Yu, J. G. Wang, Z. H. Huang, W. C. Shen and F. Y. Kang, *Electrochem. Commun.* 2013, 36, 66-70.
42. J. Chmiola, G. Yushin, R. Dash and Y. Gogotsi, *J. Power Sources* 2006, 158, 765-772.
43. E. Raymundo-Pinero, F. Leroux and F. Beguin, *Adv. Mater.* 2006, 18, 1877-1882.
44. X. H. Xia, L. Shi, H. B. Liu, L. Yang and Y. D. He, *J. Phys. Chem. Solids* 2012, 73, 385-390.
45. D. Hulicova-Jurcakova, M. Kodama, S. Shiraishi, H. Hatori, Z. H. Zhu and G. Q. Lu, *Adv. Funct. Mater.* 2009, 19, 1800-1809.

46. G. K. Wang, X. Sun, F. Y. Lu, H. T. Sun, M. P. Yu, W. L. Jiang, C. S. Liu and J. Lian, *Small* 2012, 8, 452-459.
47. G. Lota, K. Lota and E. Frackowiak, *Electrochem Commun.* 2007, 9, 1828-1832.
48. L. Yuan, X. Lu, X. Xiao, T. Zhai, J. Dai, F. Zhang, B. Hu, X. Wang, L. Gong, J. Chen, C. Hu, Y. Tong, J. Zhou and Z. L. Wang, *ACS Nano* 2012, 6, 656–661.



## Table of Contents



A “Top-Down” approach prepared carbon fiber cloth with superior mechanical strength and flexibility shows high specific capacity and excellent cycleability