

(43) International Publication Date
16 March 2017 (16.03.2017)

(51) International Patent Classification:

D01F 9/22 (2006.01) *B01F 9/14* (2006.01)
B29C 47/00 (2006.01) *H01M 4/86* (2006.01)

(21) International Application Number:

PCT/US2016/050899

(22) International Filing Date:

9 September 2016 (09.09.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/217,154 11 September 2015 (11.09.2015) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: USING SODIUM CHLORIDE FOR HIGH ENERGY DENSITY ELECTRODES IN SUPERCAPACITORS

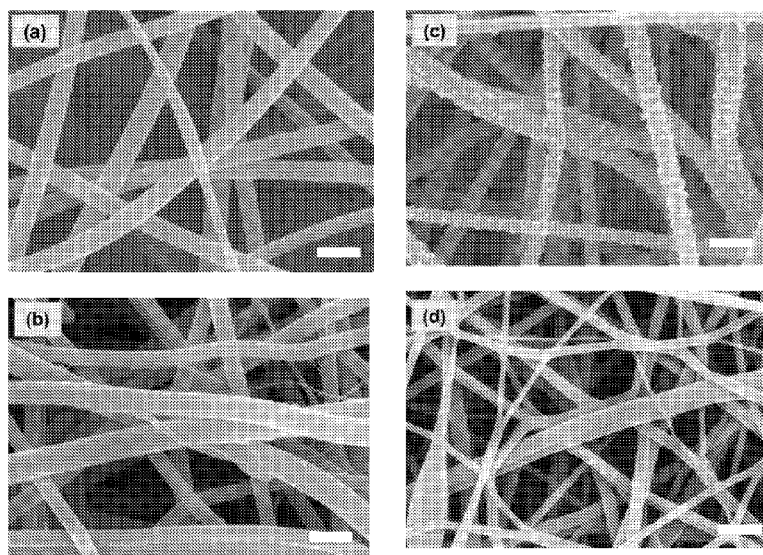


Figure 1

(57) Abstract: The invention concerns methods of producing an electrode suitable for use in supercapacitors and batteries, a method comprising forming a shaped body from a mixture of a carbon precursor and sodium chloride, heating the shaped body to a temperature of at least 600 °C in an inert atmosphere to produce a carbonized shaped body with heteroatom functional groups, and contacting the carbonized shaped body with an acid solution to extract excess sodium chloride. The introduction of functional groups is correlated to an increase in energy density of ~5 -fold.

USING SODIUM CHLORIDE FOR HIGH ENERGY DENSITY ELECTRODES IN
SUPERCAPACITORS

GOVERNMENT RIGHTS

[0001] This invention was made with government support under NSF- CAREER-CBET 1150528 and NSF-1236466 awarded by the National Science Foundation. The government has certain rights in the invention.

RELATED APPLICATIONS

[0002] This application claims benefit of U.S. Patent Application No. 62/217,154 filed September 11, 2015, the disclosure of which is incorporated herein in its entirety.

TECHNICAL FIELD

[0003] The invention concerns free-standing, device-ready sodium chloride based carbon nanofibers have been fabricated for application as electrodes in supercapacitors and batteries.

BACKGROUND

[0004] Supercapacitors, or ultracapacitors, with higher power density and longer cycle life than batteries and conventional capacitors, are an important class of energy storage devices, with growing range of applications including portable electronics, hybrid electric vehicles, and industrial power management. Supercapacitors store energy either using ion adsorption at the electrode/electrolyte interface (double layer capacitors) or using fast Faradaic redox reactions between the electrolyte and electrode (pseudocapacitors). The most studied pseudocapacitive materials are transition metal oxides such as RuO₂, MnO₂, etc. and conducting polymers such as polyaniline, polypyrrole. See, G. Wang, L. Zhang, J. Zhang, Chemical Society Reviews 41 (2012) 797-828, J. Zang, S.-J. Bao, C.M. Li, H. Bian, X. Cui, Q. Bao, C.Q. Sun, J. Guo, K. Lian, The Journal of Physical Chemistry C 112 (2008) 14843-14847, G. Yu, X. Xie, L. Pan, Z. Bao, Y. Cui, Nano Energy 2 (2013) 213-234 and T. Liu, L. Finn, M. Yu, H. Wang, T. Zhai, X. Lu, Y. Tong, Y. Li, Nano Letters (2014). These materials, however, present some important drawbacks such as they are expensive, operate in low voltage window, cause decomposition of electrolyte, and have poor stability. An alternative approach is the surface modification of carbon materials to include functional groups, which can participate in pseudo-faradaic charge transfer reactions and maintain the high cyclability of supercapacitors. See, D. Hulicova-Jurcakova, M. Kodama,

S. Shiraishi, H. Hatori, Z.H. Zhu, G.Q. Lu, *Advanced Functional Materials* 19 (2009) 1800-1809, Z. Zhou, Z. Zhang, H. Peng, Y. Qin, G. Li, K. Chen, *RSC Advances* 4 (2014) 5524-5530, and L.-F. Chen, X.-D. Zhang, H.-W. Liang, M. Kong, Q.-F. Guan, P. Chen, Z.-Y. Wu, S.-H. Yu, *ACS Nano* 6 (2012) 7092-7102.

[0005] In the last decade, a number of studies have shown the high performance of heteroatom (nitrogen, oxygen, sulfur, etc.) -enriched carbons for supercapacitors. Yun, *et al* (*Materials* 5 (2012) 1258-1266) have shown nitrogen- and micropore- containing carbon nanotubes ($200 \text{ m}^2 \text{ g}^{-1}$) had a capacitance of 190.8 F g^{-1} , much higher than pristine carbon nanotubes ($218 \text{ m}^2 \text{ g}^{-1}$, 48.4 F g^{-1}), which was attributed to the pseudocapacitance from nitrogen groups. A recent study by Zhou *et al* (*RSC Advances* 4 (2014) 5524-5530) have reported nitrogen and oxygen containing activated carbon nanotubes, synthesized by activating polypyrrole nanotubes with KOH, with a surface area of $705.9 \text{ m}^2 \text{ g}^{-1}$ exhibit high capacitance of 384.9 F g^{-1} at 0.5 A g^{-1} current density, attributed to high surface area and interfacial functional groups. Chen, *et al* (*ACS Nano* 6 (2012) 7092-7102) have synthesized nitrogen-doped porous carbon nanofibers by carbonization of carbonaceous nanofibers coated with polypyrrole. The composite nanofibers have a surface area of $562.51 \text{ m}^2 \text{ g}^{-1}$ and specific capacitance of 202 F g^{-1} at current density of 1 A g^{-1} . Zhang, *et al* (*applied materials & interfaces* (2014)) reported that the incorporation of nitrogen and sulfur into the carbon framework enhanced the capacitance as well as improved the conductivity of the ordered mesoporous carbons. Most studies employ porous carbons with high surface area as supercapacitor electrodes and thus, the double layer capacitance contribution is higher and the contribution of pseudocapacitance is not clear. In addition, for the incorporation of heteroatoms, these techniques utilize either activation processes, which produce carbons with poor mechanical strength and lower electrical conductivity, costly templating methods, or complex treatment processes (D. Hulicova-Jurcakova, M. Kodama, S. Shiraishi, H. Hatori, Z.H. Zhu, G.Q. Lu, *Advanced Functional Materials* 19 (2009) 1800-1809 and D. Hulicova-Jurcakova, M. Seredych, G.Q. Lu, T.J. Bandoz, *Advanced Functional Materials* 19 (2009) 438-447). Moreover, most of these works fabricate powder-based carbons, which need to be blended with insulating binders (such as PTFE, PVDF) to form electrodes. The incorporation of binders reduces the conductivity of the electrode and the effective available surface area in addition to adding to the weight of the device (C. Tran, V. Kalra, *Journal of Power Sources* 235 (2013) 289-296).

[0006] There is a need in the art for electrodes and methods of making electrodes that overcome these deficiencies.

SUMMARY

[0007] In some embodiments, the invention concerns methods of producing an electrode comprising (i) forming a shaped body from a mixture comprising a carbon precursor and sodium chloride; (ii) heating the shaped body to a temperature of at least 600 °C (at least 700 °C or at least 800 °C in some methods) in an inert atmosphere to produce a carbonized shaped body. In some embodiments, the method additionally comprises contacting the carbonized shaped body with an acid solution and/or water to extract excess sodium chloride. The carbonized shaped body can function as the body of the electrode. In certain embodiments, the method additionally comprising heating the shaped body to a temperature of 150-350 °C (200-350 °C in some embodiments) in air or an oxygen-containing gas prior to heating the shaped body to a temperature of at least 600 °C. The mixture comprising a carbon precursor and sodium chloride may optionally comprise a solvent.

[0008] While any suitable acid may be used, sulfuric acid (H_2SO_4) is preferred in some embodiments. While a range of acid concentrations may be used, in one preferred embodiment the acid solution has a concentration of 0.01 to 2 moles/liter (0.2 to 2 moles/liter in some embodiments), although higher concentrations may be used in some embodiments.

[0009] Any suitable carbon precursor may be utilized with the invention. Such precursors are known in the art. One preferred carbon precursor is polyacrylonitrile (PAN).

[0010] Numerous methods are known in the art for producing formed bodies that can be used as electrodes. The invention can utilize these methods. One preferred method, however is electrospinning. The mixture of a carbon precursor and sodium chloride can be used to electrospin fibers to produce the shaped body. This technique typically is used to produce a shaped body that is a mat of nanofibers. A solvent may be used in the electrospinning process. In some embodiments, the carbon precursor and the sodium chloride are dissolved in dimethylformamide solution for the mixture used in electrospinning. In some embodiments, the carbon precursor may be present in an amount of 0.01-50% or 3-30% by weight in the dimethylformamide solution. In certain embodiments, the sodium chloride is present in an amount of 0.01-15% or 0.01-25% by weight in the dimethylformamide solution.

[0011] One advantage of producing the shaped body by electrospinning is that a free-standing body may be produced without the need to use a binder. As such, in some embodiments, the electrode is free of or substantially free of binder.

[0012] After contacting the carbonized shaped body with an acid solution to dissolve out excess sodium chloride, the carbonized shaped body may be washed with water. Purified or deionized water is preferred in some embodiments.

[0013] The invention also concerns electrodes and other shaped bodies made by the inventive process. Some electrodes have a surface with at least 5 atomic % nitrogen, at least 2 atomic % sulfur and at least 5 atomic % oxygen content. Some electrodes have a specific surface area of at least 0.01 or 0.1 or 1 m² g⁻¹. In some embodiments, the electrode has a porosity of 10-95% (30-95% in some embodiments).

[0014] Certain electrodes of the inventions have a specific capacitance of at least 70 F g⁻¹. In terms of surface composition, some electrode have a surface oxygen to carbon ratio of 1-35 (8-35 or 12-35 in some embodiments) atomic %. In other embodiments, the electrodes have a surface nitrogen to carbon ratio of 1-17 (10-17 or 13-17, in some embodiments) atomic %.

[0015] An advantage of the instant invention is the incorporation of sodium chloride in the nanofibers enhances the capacitance of nanofibers by five-fold by inducing pseudocapacitance. The fabrication method is very simple and sodium chloride is incorporated in the fabrication process itself (*i.e.* electrospinning in some embodiments). The sodium chloride helps in creating reactive sites on the surface of carbon during the carbonization process. The heteroatom (*e.g.* oxygen, sulfur, etc.) functional groups can easily attach to these reactive sites, which can participate in the pseudofaradaic charge transfer reactions, thereby providing high capacitance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The present application is further understood when read in conjunction with the appended drawings. For the purpose of illustrating the subject matter, there are shown in the drawings exemplary embodiments of the subject matter; however, the presently disclosed subject matter is not limited to the specific methods, devices, and systems disclosed. In addition, the drawings are not necessarily drawn to scale. In the drawings:

[0017] **Figure 1** presents SEM images of (a) as-made, (b) stabilized, (c) carbonized, and (d) treated CNF-13 nanofibers. Scale bar is 200 nm.

[0018] **Figure 2** shows cyclic voltammograms of the treated carbon nanofibers in 1 mol L⁻¹ H₂SO₄ using two-electrode test cell at a scan rate of 5 mV s⁻¹.

[0019] **Figure 3** presents XRD patterns of electrospun CNF-13 fibers at different stages of fabrication.

[0020] **Figure 4** presents deconvoluted C1s, N1s, and O1s XPS peaks for carbonized and treated CNF-13 samples.

[0021] **Figure 5** shows a schematic diagram of the nitrogen and oxygen functionalities.

[0022] **Figure 6** presents XPS S2p peak distribution for treated CNF-13 sample.

[0023] **Figure 7** presents cyclic voltammograms of the treated CNF-13 nanofibers in 1 mol L⁻¹ H₂SO₄ using a three-electrode test cell at different scan rates.

[0024] **Figure 8** shows galvanostatic charge-discharge profiles of treated CNF-13 at different current densities in 1 mol L⁻¹ H₂SO₄ electrolyte in a three-electrode test cell.

[0025] **Figure 9** shows Nyquist impedance plots of CNF-0 and CNF-13 measured in a three-electrode test cell in 1 mol L⁻¹ H₂SO₄ electrolyte.

[0026] **Figure 10** presents CV curves of treated CNF-13 from 1st to 1000th cycle at a scan rate of 100 mV s⁻¹ in 1 mol L⁻¹ H₂SO₄ in a three electrode test cell.

[0027] **Figure 11** is a schematic of an electrospinning apparatus.

[0028] **Figure 12** presents SEM images of carbonized (a) CNF-0, (b) CNF-4, and (c) CNF-7 nanofibers. Scale bar is 200 nm. The fabricated carbon nanofibers are denoted as CNF – X, where X is the weight percent of NaCl in the original solution used to electrospin the fibers.

[0029] **Figure 13** presents EDS mapping of carbonized CNF-13 nanofibers showing uniform distribution of sodium and chlorine on the surface of nanofibers.

[0030] **Figure 14** presents nitrogen adsorption-desorption isotherms for (a) carbonized and (b) treated CNF-13.

[0031] **Figure 15** shows comparison of specific capacitance data of treated CNF-13 with 2-electrode and 3-electrode test cells at different scan rates in 1 M H₂SO₄.

[0032] **Figure 16** presents a schematic of (a) 2-electrode and (b) 3-electrode setup.

[0033] **Figure 17** presents cyclic voltammograms of treated CNF-13 (solid) and CNF-0 (dotted) in different pH electrolytes in 2-electrode cells

[0034] **Figure 18** presents XPS elemental scans of CNF-13 before and after re-heat treatment.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0035] The present disclosure may be understood more readily by reference to the following description taken in connection with the accompanying Figures and Examples, all of which form a part of this disclosure. It is to be understood that this disclosure is not limited to the specific products, methods, conditions or parameters described and / or shown herein, and

that the terminology used herein is for the purpose of describing particular embodiments by way of example only and is not intended to be limiting of any claimed disclosure. Similarly, unless specifically otherwise stated, any description as to a possible mechanism or mode of action or reason for improvement is meant to be illustrative only, and the invention herein is not to be constrained by the correctness or incorrectness of any such suggested mechanism or mode of action or reason for improvement. Throughout this text, it is recognized that the descriptions refer both to methods of operating a device and systems and to the devices and systems providing said methods. That is, where the disclosure describes and/or claims a method or methods for operating a flow battery, it is appreciated that these descriptions and/or claims also describe and/or claim the devices, equipment, or systems for accomplishing these methods.

[0036] In the present disclosure the singular forms “a,” “an,” and “the” include the plural reference, and reference to a particular numerical value includes at least that particular value, unless the context clearly indicates otherwise. Thus, for example, a reference to “a material” is a reference to at least one of such materials and equivalents thereof known to those skilled in the art, and so forth.

[0037] When a value is expressed as an approximation by use of the descriptor “about,” it will be understood that the particular value forms another embodiment. In general, use of the term “about” indicates approximations that can vary depending on the desired properties sought to be obtained by the disclosed subject matter and is to be interpreted in the specific context in which it is used, based on its function. The person skilled in the art will be able to interpret this as a matter of routine. In some cases, the number of significant figures used for a particular value may be one non-limiting method of determining the extent of the word “about.” In other cases, the gradations used in a series of values may be used to determine the intended range available to the term “about” for each value. Where present, all ranges are inclusive and combinable. That is, references to values stated in ranges include every value within that range.

[0038] It is to be appreciated that certain features of the invention which are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. That is, unless obviously incompatible or specifically excluded, each individual embodiment is deemed to be combinable with any other embodiment(s) and such a combination is considered to be another embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination. Finally, while an embodiment may be described

as part of a series of steps or part of a more general structure, each said step may also be considered an independent embodiment in itself.

[0039] When a list is presented, unless stated otherwise, it is to be understood that each individual element of that list and every combination of that list is to be interpreted as a separate embodiment. For example, a list of embodiments presented as “A, B, or C” is to be interpreted as including the embodiments, “A,” “B,” “C,” “A or B,” “A or C,” “B or C,” or “A, B, or C.”

[0040] Numerous methods are known in the art for producing formed bodies that can be used as electrodes. The invention can be applied to any existing carbon-based electrode material (of any form including nanofibers, particles, powder etc.). Some of these methods may involve the use of binder to produce a free-standing shaped body. Machining may optionally be used to alter the shape of the shaped body. Importantly, sodium chloride can be mixed with any carbon precursor and then processed and treated using any existing method to improve capacitance. The instant method may also be used in combination with existing activation methods to further enhance capacitance.

[0041] Electrospinning is used to produce the shaped body in some methods of the invention. This technique is a novel and facile technique for fabricating free-standing (binder-free) heteroatom-enriched carbon nanofibers with high supercapacitance using common salt (*i.e.* sodium chloride (NaCl)). To the best of our knowledge, this is the first time NaCl has been reported to enhance capacitance by modifying carbon surface functionality. Electrospinning is a simple and versatile technique for fabricating free standing (binder-free) carbon nanofibers that can be applied to polymers loaded with nanoparticles or active agents. See, A. Greiner, J.H. Wendorff, *Angewandte Chemie International Edition* 46 (2007) 5670-5703 and T. Wang, S. Kumar, *Journal of Applied Polymer Science* 102 (2006) 1023-1029. NaCl and polyacrylonitrile (PAN) were electrospun together to form a free-standing mat of carbon nanofibers. PAN acted as precursor to both carbon as well as nitrogen while NaCl helped in oxidizing the carbon surface after carbonization. The oxygen was further enhanced and sulfur was incorporated by post-treatment of carbonized nanofibers with aqueous acidic solution. Thus synthesized nanofibers have low surface area but demonstrate excellent supercapacitive properties attributed to pseudocapacitance of oxygen and sulfur surface functional groups, comparable to high surface area heteroatom-doped carbons.

[0042] A solvent may be used in the electrospinning process. In some embodiments, the carbon precursor and the sodium chloride are dissolved in dimethylformamide solution for the mixture used in electrospinning. In some embodiments, the carbon precursor may be present

in an amount of 3-30% by weight in the dimethylformamide solution. In certain embodiments, the sodium chloride is present in an amount of 0.01-15% by weight in the dimethylformamide solution.

[0043] One advantage of producing the shaped body by electrospinning is that a free-standing body may be produced without the need to use a binder. As such, in some preferred embodiments, the shaped body and the electrode are free of or substantially free of binder.

[0044] The carbon fiber may be electrospun so as to form a body having at least one cross-sectional dimension in the range of from about 10 micrometers to about 1 cm, or from about 50 micrometers to about 0.5 cm. Bodies formed according to these disclosed methods are suitably fibrous layers in form. The fibrous layers may then be cut to conform to a shape that a user desires.

[0045] A typical electrospinning setup consists of a metallic spinneret, a syringe pump, a high-voltage power supply, and a grounded collector in a humidity controlled chamber. A representative example of a electrospinning setup is presented in **Figure 11**. A polymer solution, polymer melt or a sol-gel solution is continuously pumped through the spinneret at a constant rate, while a high voltage gradient is applied between the spinneret tip and the collector substrate. The solvent continuously and rapidly evaporates while the jet stream is whipped and stretched by electrostatic repulsion forming solidified continuous nanofibers (diameters ~ 50-500 nm) on the grounded collector. Carbon nanofiber (CNFs) mats can be fabricated by subjecting electrospun nanofibers of an appropriate polymer precursor to stabilization and calcination processes. Cellulose, phenolic resins, polyacrylonitrile (PAN), polybenzimidazol, and pitch-based materials have been electrospun to produce CNFs. Among them, PAN is widely used as a precursor for CNFs due to its excellent electrospinnability and relatively high carbon yield. CNFs produced from electrospinning PAN have been subjected to different chemical or physical activation processes using steam, CO₂, or NaOH to create pores within nanofibers. The activation process further increases the specific surface area of carbon nanofibers thereby enhancing the specific capacitance. These activation processes, however, add an extra step to the fabrication procedure and also deteriorate mechanical strength by creation of physical pores.

[0046] Advantages of the instant invention include:

1. The fabrication technique doesn't involve any extra steps to enhance capacitance, sodium chloride can be incorporated in the carbon precursor itself. Whereas other methods usually use an extra step such as activation to improve capacitance.

2. The precursor for creating pseudocapacitance is an inexpensive compound, common salt or sodium chloride so it could be easily used in existing processes without adding any extra costs.

3. High supercapacitance comparable to current state-of-art high surface area carbons is obtained.

4. The fabricated materials (*i.e.* sodium chloride based carbon nanofibers) are free-standing or device-ready eliminating the need for further processing steps to form electrodes. In addition, in some embodiments, no binder is needed to form electrodes. These binders are known to deteriorate conductivity and performance of current capacitor/battery electrodes.

5. This method can be used with any other existing carbon materials to enhance capacitance. In other words, sodium chloride can be mixed with any carbon precursor and then processed and treated using any existing method to improve capacitance. Note this method (of mixing with sodium chloride) can also be used in combination with existing activation methods to further enhance capacitance.

6. The fabricated materials have a high number of surface functional groups, which could be advantageous for other applications such as in batteries.

7. This method fabricates electrodes with high mechanical strength. The existing activation based processes of the art create physical pores in the electrodes and deteriorates mechanical strength.

Definitions

[0047] As used herein, the term “surface” refers to the first 10 nm of the exterior of the electrode. In some embodiments, the depth of what is considered surface is the first 5 nm.

[0048] The term “capacitance” is measured as described in the “electrochemical measurements” section of the specification.

[0049] “Specific surface area” is determined as described in the “characterization” section of the specification.

[0050] The term “atomic percent” is defined by the equation below.

$$\text{Atomic percent} = (N_i/N_{\text{tot}}) \times 100\%$$

where N_i is the number of atoms of interest and N_{tot} is the total number of atoms.

[0051] The term “atomic ratio” is defined by the following equation.

Atomic ratio = atomic percent of the atoms of interest / atomic percent of the comparison atoms. When expressed in percent, the atomic ratio is multiplied by 100%.

[0052] Surface oxygen to carbon ratio is defined by the equation:

$$(N_{\text{oxygen}}/N_{\text{carbon}})*100$$

where N_{oxygen} is the number of oxygen atoms and N_{carbon} is the number of carbon atoms.

[0053] Surface nitrogen to carbon ratio is defined by the equation:

$$(N_{\text{nitrogen}}/N_{\text{carbon}})*100$$

where N_{nitrogen} is the number of nitrogen atoms and N_{carbon} is the number of carbon atoms.

[0054] The phrase “substantially free” means having less than 1 weight percent of the material and preferably less than 0.1 percent by weight.

[0055] As required, detailed embodiments of the present invention are disclosed herein; it is to be understood that the disclosed embodiments are merely exemplary of the invention that may be embodied in various forms. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limits, but merely as a basis for teaching one skilled in the art to employ the present invention. The specific examples below will enable the invention to be better understood. However, they are given merely by way of guidance and do not imply any limitation.

Experimental

Materials

[0056] Polyacrylonitrile (PAN, MW = 150,000, Sigma-Aldrich Co., Ltd., USA) and N,N-dimethylformamide (DMF, Sigma-Aldrich Co., Ltd., USA) were used without any purification. Sodium chloride (NaCl, Sigma-Aldrich Co., Ltd., USA), was ground into fine powder and dried overnight under vacuum to remove any absorbed water.

Synthesis of carbon nanofibers

[0057] PAN (10 wt%) and NaCl (4, 7 & 13 wt%) were dissolved in DMF and stirred at room temperature for 4-5 hours. Nanofibers were electrospun at room temperature with humidity below 20% using a 22 gauge stainless steel needle (Hamilton Co.). The distance between the needle tip and the grounded collector (aluminum foil) was 15 cm, and the applied voltage of 13-14 kV was used to obtain a stable Taylor cone. The electrospinning was carried out in batches of 2 mL solution and replaced with stirred solution to minimize precipitation of sodium chloride in the syringe while electrospinning. The electrospinning was carried out for long enough time to obtain ~3-4 mg 3/8” disc electrodes for electrochemical measurements. The electrospun nanofibers were stabilized in an air oven by heating to 280 °C at a rate of 5 °C min⁻¹ for 5 hours.

The stabilized nanofibers were then carbonized under nitrogen flow of 400 ml min^{-1} in a horizontal tube furnace at a heating rate of $2 \text{ }^{\circ}\text{C min}^{-1}$ to the temperature of $800 \text{ }^{\circ}\text{C}$ and held for 1 h. The carbonized NaCl-PAN nanofibers were then treated with $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution to dissolve out excess sodium chloride and then thoroughly washed with distilled water to remove excess sulfuric acid. The resultant nanofibers are denoted as CNF -X, where X is the weight percent of NaCl in the original solution used to electrospun the fibers.

Characterization

[0058] The morphology and microstructure of the samples were characterized using a Zeiss Supra 50VP scanning electron microscope (SEM). A Quadrasorb (Quantachrome Instruments, USA) was used to conduct gas sorption measurements. Samples were tested at 77 K (liquid nitrogen baths were used for coolant) isotherms, using nitrogen gas as adsorbate. Brunauer-Emmett-Teller (BET) formula was used to calculate specific surface areas in the P/Po range between 0.05-0.10. For X-Ray diffraction (XRD) analysis, the samples were characterized using a Rigaku SmartLab X-ray diffractometer in Bragg-Brentano mode ($\text{Cu K}\alpha$ radiation, voltage 40 kV, current 30 mA, scanning range $10\text{--}90^{\circ}$ and step size of 0.02°). X-ray photoelectron spectroscopy (XPS) measurements were performed on Physical Electronics VersaProbe 5000 spectrometer using monochromated $\text{Al K}\alpha$ excitation source. The binding energy scales were calibrated with respect to the C1s peak position (285.0 eV). The quantitative analysis was performed using CASAXPS software after Shirley background subtraction. The mixed 30% Gaussian-Lorentzian line shapes were used for peak fitting.

Electrochemical measurements

[0059] The carbon nanofiber mats were directly used as binder-free electrodes for electrochemical measurements. For two-electrode cyclic voltammetry analysis, a symmetric cell was assembled by placing two $3/8''$ diameter discs of the fabricated CNFs, separated by a Whatman glass fiber separator, sandwiched between two graphite current collectors one on each side. The electrodes were immersed in the electrolyte $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ overnight before measurements to ensure complete wetting of carbon electrodes. For three electrode analysis, an aqueous Ag/AgCl electrode was used as the reference electrode in the 2-electrode test-cell. The capacitive performances of the samples were investigated by using cyclic voltammetry (CV),

galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) techniques, which were performed using Gamry Reference 3000 potentiostat. A schematic of electrode

[0060] The specific capacitance per unit mass of one electrode in a 2-electrode setup was calculated according to the equation: $C = \int I \Delta t / (m \Delta V)$, where I is the response current (A), Δt is the discharging time (s), m is the average mass of the carbon nanofiber electrodes (g) and ΔV is the voltage window. For a three-electrode capacitance measurement, the above equation was modified as: $C = \int I \Delta t / (m \Delta V)$ [20].

[0061] The galvanostatic charge-discharge tests were performed at current densities ranging from 0.5 to 20 A g⁻¹. The specific capacitance per electrode from galvanostatic charge-discharge experiments was calculated from the discharge curves after 3 charge-discharge cycles. EIS measurements were carried out applying a sine wave with an amplitude of 10 mV over the frequency range of 100 kHz to 0.1 Hz.

Results and Discussion

[0062] Nanofibers with varying concentrations of NaCl (0-13.3%) were electrospun and Figure 1 (a)-(d) shows the SEM images of CNF-13 at various stages i.e. as-made (after electrospinning), after stabilization, after carbonization (pyrolysis) and after treatment. As discussed in the experimental section, treated nanofibers refer to the samples obtained after treating the carbonized nanofibers with 1 mol L⁻¹ H₂SO₄ solution and then washed with distilled water. Smooth nanofibrous structure with very few beads was obtained on electrospinning, which was retained after the heat treatment processes. The carbonized CNF-13 (Figure 1c) shows the appearance of nanocrystals on the surface of nanofibers, which were removed on treatment. The SEM images of carbonized CNF-0, CNF-4, and CNF-7, as shown in Figure 12, show a similar morphology to that of CNF-13 except the nanocrystal concentration on the surface of carbonized carbon nanofibers reduced with decreasing NaCl concentration (Figure 13).

[0063] The cyclic voltammograms of treated CNF-0, CNF-4, CNF-7 and CNF-13 samples in a two-electrode test cell at 5 mV s⁻¹ scan rate are shown in Figure 2. The specific capacitance increased with increasing NaCl concentration and is highest for CNF-13 nanofibers (182 F g⁻¹). The specific capacitances of CNF-0, CNF-4, and CNF-7 were determined as 35.94, 70.2 and 111.6 F g⁻¹ respectively. Thus, specific capacitance is enhanced 5-fold on adding 13 wt% NaCl (CNF-13) to PAN (CNF-0). It was observed that on further increasing NaCl concentration beyond 13 wt%, because of precipitation of NaCl in the electrospinning solution,

no significant improvement in specific capacitance of the prepared nanofibers was obtained. Hence, CNF-13 nanofibers were chosen for further study and are discussed below.

[0064] The specific surface area (SSA), and pore volume determined by BET surface area method for CNF-13 and CNF-0 (control) nanofibers are listed in Table 1. The SSA slightly improves from $14 \text{ m}^2 \text{ g}^{-1}$ for CNF-0 to $21 \text{ m}^2 \text{ g}^{-1}$ for CNF-13 nanofibers. On treatment, the SSA is $24 \text{ m}^2 \text{ g}^{-1}$. Since there is no significant improvement in the surface area due to NaCl, it shows that NaCl behaves differently from the previously reported zinc chloride and tin chloride. Both of them served as activating agents to create high surface area porous carbons. Based on the BET data, we can also conclude that the five-fold improvement in the capacitance of CNF-13 (vs. CNF-0) is not a result of the double layer capacitance. To better understand the effect of NaCl on capacitance, detailed chemical analysis was conducted as discussed below.

Table 1 BET surface area and total pore volume calculated from nitrogen adsorption-desorption isotherms

Sample	BET SSA, $\text{m}^2 \text{ g}^{-1}$	Total pore volume, $\text{cm}^3 \text{ g}^{-1}$
Carbonized CNF-13	21	0.017
Treated CNF-13	24	0.017
Carbonized CNF-0	14	0.011

[0065] In order to identify the nano-crystals formed on the surface of carbon nanofibers on carbonization, X-ray diffraction (XRD) was used. Figure 3 compares the XRD spectrum of as-made, stabilized, carbonized, and treated CNF-13 samples. XRD spectrum of as-made CNF-13 nanofibers shows a broad diffraction peak at 17° , which is commonly observed in the fiber diffraction patterns of PAN with hexagonal packing. On heat-treatment, the diffraction peak at 17° disappeared with the evolution of a broad peak at 2θ of $\sim 25^\circ$ attributed to the (002) crystallographic plane of graphite crystallites. The broad peak is characteristic of the amorphous nature of carbon ascribed to the turbostratic structure, which are not as ordered as graphite. In addition to the carbon peak, XRD patterns display the major NaCl peaks at 2θ of 31.62° , 45.44° , 56.72° , 66.28° and 75.52° corresponding to (200), (220), (222), (400) and (420) miller indices. These peaks disappear in the treated CNF-13 suggesting the removal of NaCl nanocrystals, as also seen via SEM (Figures 1(c) and 1(d)). Based on the XRD and SEM data, NaCl doesn't undergo any chemical reaction during the stabilization and carbonization processes.

[0066] X-ray photoelectron spectroscopy (XPS) was used to study the surface functional groups. In order to understand the role of sodium chloride and the effect of dilute acid treatment on the fabricated nanofibers, we compared the surface functional groups of four samples – carbonized CNF-13, treated CNF-13, carbonized CNF-0 and treated CNF-0. The surface elemental compositions and oxygen-to-carbon (O/C) and nitrogen-to-carbon (N/C) ratios from XPS data analysis of carbonized and treated CNF-13 and CNF-0 (as control) samples are summarized in Table 2. The elemental analysis shows high oxygen to carbon (O/C) content on the surface of carbonized CNF-13 (19.8%), almost twice that of the control sample, carbonized CNF-0 (7.8%). To understand the origin of additional oxygen, we conducted XPS of PAN/NaCl (13 wt% NaCl) and pure PAN nanofibers after the air stabilization step, a process step prior to carbonization, where samples were exposed to oxygen. We found that both samples exhibit similar fractions of surface oxygen (14-17%). Given that the carbonization step occurs in inert environment and there is no other source of oxygen, it is interesting to see significant enhancement of oxygen functional groups in the carbonized CNF-13 compared to carbonized CNF-0. Again, without wanting to be bound by theory, we hypothesize the following mechanism taking place during carbonization in CNF-13 nanofibers– at high temperatures, sodium chloride reacts with the hydrogen radicals formed during dehydrogenation reactions during carbonization to form sodium metal as follows:

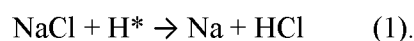


Table 2 Elemental composition (at.%) of carbonized and treated CNF-0 and CNF-13 nanofibers determined from XPS

	Carbonized CNF-0 (%)	Treated CNF-0 (%)	Carbonized CNF-13 (%)	Treated CNF-13 (%)
O	6.22	7.07	13.51	18.63
C	80.08	78.59	68.3	64.3
N	13.69	13.49	9.51	10.65
Na	—	—	4.93	0.31
Cl	—	—	3.75	—
S	—	0.84	—	6.11
O/C	7.8	9.0	19.8	29.0
N/C	17.1	17.2	13.9	16.6

[0067] The conversion is though not complete, since we detect sodium chloride after carbonization via XRD and XPS. The HCl gas diffuses into the nitrogen gas flowing through the furnace. The sodium atoms, thus, etch the carbon surface leaving reactive carbon sites. A portion of that sodium can reconvert into sodium chloride, since chlorine species is present in the gas. In addition, it is also expected that at $\sim 800^\circ\text{C}$, sodium chloride melts and blocks the carbon surface including the remaining functionalized sites from the stabilization step (during stabilization, oxidation and cyclization reactions take place to form a ladder PAN structure). Thus, complete carbonization of PAN is inhibited leaving the functional groups intact on carbon nanofibers that provide the pseudocapacitance.

[0068] On acidic treatment, the oxygen content is further enhanced from 13.51% to 18.63% for CNF-13 nanofibers due to surface oxidation by sulfuric acid. Almost all sodium and chlorine is removed from the surface of carbonized CNF-13 and 6.11% of sulfur is added on acidic treatment. Note the samples were thoroughly washed with DI water prior to any characterization, so, we do not expect any residual H_2SO_4 . The sulfur addition is, thus, due to the adsorption of sulfur functional groups on the surface of nanofibers. However, the XPS of treated CNF-0 nanofibers show only 0.84% of sulfur on the surface and no significant enhancement of surface oxygen was seen. This indicates that the surface of carbonized CNF-13 allowed for improved adsorption of oxygen and sulfur groups (compared to CNF-0). We further analyzed the surface species by deconvolution of various elemental peaks.

[0069] The deconvoluted C1s, O1s & N1s peaks for carbonized and treated CNF-13 are shown in Figure 4. Analogous data was collected for CNF-0. The contribution from each species obtained after peak fitting is listed in Table 3. The deconvolution of C 1s spectra yields four peaks: C-1 (284.6 eV) due to graphitic carbon ($-\text{C}=\text{C}-$) and/or $-\text{C}-\text{C}-$; C-2 (285.5-285.7 eV) due to carbon in $\text{C}=\text{N}$, $\text{C}-\text{O}$ (phenol, hydroxyl, ether groups); C-3 (287.6-287.8 eV) due to $\text{C}=\text{O}$ bonds (carbonyl, quinone groups), and C-4 (288.4-289 eV) due to carbon in carboxyl or ester groups. On comparing the C1s peak distribution in Table 3, we note that while the carbonized CNF-0 sample shows no C-4 peak (carboxyl/ester), the carbonized CNF-13 sample exhibits a prominent C4 peak showing the presence of a significant fraction (22%) of carboxyl and/or ester groups on its surface. This C-4 peak disappears after acid treatment as seen in the treated CNF-13 C1s peak distribution data. Figure 5 is a schematic showing the oxygen and nitrogen functional groups. The nitrogen containing functionalities are assigned to pyridinic (N-6, 398.1 ± 0.2 eV); pyrrolic/pyridone (N-5, 399.9 ± 0.3 eV), quaternary (N-Q, 400.9 ± 0.17 eV), and N-oxide (N-X, 402-404 eV) groups [27, 28]. N-6 and N-5 are the dominant peaks in both

carbonized and treated CNF-0. Appearance of N-X (N-oxide) peak is seen due to acid treatment in treated CNF-0. The N1s spectrum of CNF-13 shows all four peaks. N-6 is the dominant peak in carbonized CNF-13, however, on treatment, the contribution from N-6 peak reduces and N-5 peak increases possibly due to the increase in pyridone nitrogen (N-5(1) in Figure 5). The deconvolution of O1s peak in carbonized and treated CNF-0 gives two peaks – O-1 at 531.40 eV assigned to oxygen in quinone and/or carbonyl groups, and O-2 at 532.5 eV assigned to oxygen in phenol/ether groups [28]. However, the carbonized CNF-13 shows two additional peaks, O-3 at 533.4 eV assigned to oxygen in carboxylic groups and O-4 at 536.4 eV, corresponding to adsorbed oxygen or water. The treated CNF-13 shows only O-1 and O-2 peaks, with O-2 being the dominant one. The absence of O-3 peak indicates the elimination of carboxylic groups on acidic treatment, as also seen from the disappearance of the C-4 peak in the C1s spectrum of treated CNF-13. These observations suggest a reaction between sulfuric acid and carboxylic groups that also results in the adsorption of sulfur groups on the surface of treated CNF-13. The sulfur S2p XPS spectrum for treated CNF-13 is shown in Figure 6. The deconvolution of S2p peak gives two doublet peaks at 168 eV and 169 eV assigned to the $-\text{SO}_3\text{H}$ and $-\text{OSO}_3\text{H}$ groups respectively. Sodium (Na1s) peak for carbonized CNF-13 occurs at 1072.3 eV corresponding to Na-Cl bond.

Table 3a. XPS core level peak analysis of C1s, N1s and O1s peaks for carbonized and treated CNF-0 and CNF-13.

Sample	C1s peaks				N1s peaks			
	C-1 ^a	C-2 ^b	C-3 ^c	C-4 ^d	N-6 ^e	N-5 ^f	N-Q ^g	N-X ^h
Carbonized CNF-0	39.3	39.54	21.16	—	41.49	58.51	—	—
Treated CNF-0	39.96	38.77	21.27	—	34.66	50.39	—	14.95
Carbonized CNF-13	29.99	47.99	—	22.01	46.03	14.74	15.91	23.33
Treated CNF-13	39.46	38.01	22.53	—	31.5	26.32	19.59	22.59

Table 3b. XPS core level peak analysis of C1s, N1s and O1s peaks for carbonized and treated CNF-0 and CNF-13.

O1s peaks

O-1 ⁱ	O-2 ^j	O-3 ^k	O-4 ^l
56.77	43.23	—	—
40.4	59.6	—	—
—	35.4	39.66	24.94
38.63	61.37	—	—

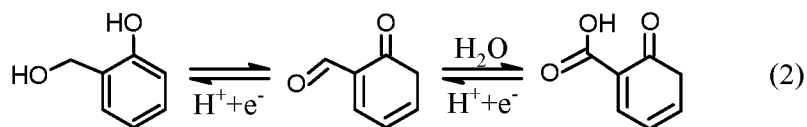
^a284.6 eV, ^b285.6 ± 0.12 eV, ^c287.7 ± 0.1 eV, ^d288.9 eV, ^e398.1 ± 0.2 eV, ^f399.9 ± 0.3 eV, ^g400.9 ± 0.17 eV, ^h402.5 ± 1.64 eV, ⁱ531.4 ± 0.1 eV, ^j532.3 ± 0.2 eV, ^k533.4 eV, ^l536.4 eV.

[0070] The results of XPS can be summarized as: (1) The oxygen on the surface of carbonized CNF-13 is almost double that of CNF-0. Thus, the presence of NaCl leads to increased oxygen content on CNF-13 by etching carbon surface during carbonization. (2) Presence of NaCl also modifies the surface functional groups as is indicated by the presence of carboxylic groups and adsorbed oxygen and absence of carbonyl groups (3) The sulfuric acid treatment further enhances the oxygen content as well as incorporates sulfur by the adsorption of sulfonic and sulfate groups on carbonized CNF-13. 4. The surface nitrogen content decreased a little from 13.69% for CNF-0 to 9.51% for carbonized CNF-13. The N1s spectrum of CNF-13 show two additional peaks, N-Q and N-X, along with N-6 and N-5, which were not observed for carbonized CNF-0. It has been reported that while N-6 and N-5 nitrogen atoms mainly contribute to pseudo-capacitive effect, N-Q and N-X groups improve the electron transfer through the carbon framework thereby providing better capacitance retention. Thus, we expect that oxygen and sulfur functional groups are responsible for enhanced capacitance of CNF-13 nanofibers, while nitrogen functional groups improves the charge transfer leading to better capacitance retention.

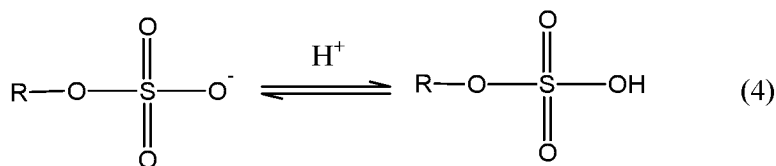
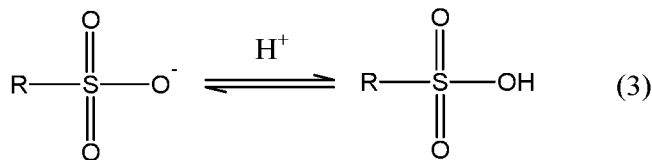
[0071] The specific capacitance was determined from both two electrode (practical performance measurement) and three electrode cells (for studying faradaic reactions) and are compared in Figure 15. The three-electrode specific capacitances were slightly higher than two-electrode capacitances at low scan rates (<50 mVs⁻¹) but similar at high scan rates. The electrode loading was kept in the range from 8–11 mgcm⁻² in accordance with the best practices for measuring capacitor performance reported by Ruoff and coworkers. Figure 7 shows the cyclic voltammetry (CV) curves for different scan rates varying from 5 mVs⁻¹ to 500 mVs⁻¹ for treated CNF-13 nanofibers in a three-electrode test cell. The CV curves show a near-rectangular shape even at high scan rates indicating good capacitive behavior. We do not see any redox peaks despite huge pseudocapacitive contributions indicating that charging and discharging occur at a

pseudo-constant rate over the entire voltammetry cycles. Similar behavior has previously been reported for low-surface area, nitrogen-enriched carbons with high supercapacitance. A high specific -capacitance of 193 F g^{-1} was obtained at a scan rate of 5 mV s^{-1} in a 1 V voltage window. As expected, the capacitance reduced with increasing scan rates due to mass transfer limitations at high scan rates. Nevertheless, we retain 66% of capacitance at 100 mVs^{-1} scan rate and 38.3% at 500 mVs^{-1} indicating high power handling capability due to the open pore structure (inter-fiber spacing) in nanofiber mats resulting in faster electrolyte/ion diffusion. The galvanostatic charge–discharge profiles at different current densities are shown in Figure 8. A high specific capacitance of 204 Fg^{-1} was obtained at 0.5 Ag^{-1} . We retain 57% of this capacitance (116 Fg^{-1}) even at a current density of 20 Ag^{-1} .

[0072] As discussed above, the five-fold capacitance enhancement in CNF-13 (vs. CNF-0) is attributed to the additional oxygen and sulfur functional groups. The following continuous reversible oxidation/reduction reactions between hydroxyl, carbonyl and carboxyl groups occur in acidic medium (see, X. Fan, Y. Lu, H. Xu, X. Kong, J. Wang, Journal of Materials Chemistry 21 (2011) 18753-18760):



[0073] Thus, transition of hydroxyl and carboxyl groups involve two-electron transition, thereby contributing to twice the charge storage. Kim et al. [29] have shown that sulfuric acid treatment on PAN based hard carbons increases the reversible capacity by up to ~20%. The sulfur functionalities contribute to pseudocapacitance by the redox reactions involving sulfone groups such as:



[0074] To further elucidate the high performance of the fabricated carbon nanofibers, the capacitance values reported in literature for functionalized carbons have been compared with the present work (Table 4). It is to be noted that most works had employed high surface area

carbons ($>200 \text{ m}^2 \text{ g}^{-1}$), thus the contribution from the electric double layer capacitance is expected to be significant, and the contribution from the pseudocapacitive effect is not evident. Despite a low surface area of only $24 \text{ m}^2 \text{ g}^{-1}$, the capacitance of our PAN/NaCl carbon nanofibers, which is 193 F g^{-1} at 5 mV s^{-1} , is two-fold higher than that reported for carbon nanotube/PAN blend-based carbon nanofibers with $200 \text{ m}^2 \text{ g}^{-1}$ surface area. Chen et al (L.-F. Chen, X.-D. Zhang, H.-W. Liang, M. Kong, Q.-F. Guan, P. Chen, Z.-Y. Wu and S.-H. Yu, ACS Nano, 2012, 6, 7092–7102) recently reported the fabrication and electrochemical characterization of nitrogen doped porous carbon nanofibers in supercapacitors. They followed a multistep synthesis procedure that involved coating of pre-formed carbon nanofibers with polypyrrole followed by recarbonization to obtain N-doped porous carbon nanofibers with a surface area of $>550 \text{ m}^2 \text{ g}^{-1}$. They reported a capacitance of 202 F g^{-1} at 1 A g^{-1} . The capacitance of the material fabricated in the present work is comparable despite the low surface area and with the additional advantages of a simpler fabrication procedure, inexpensive materials and potentially higher mechanical strength due to the low pore volume/surface area. Comparing with low surface area functionalized carbons reported in the literature, nitrogen-enriched carbons derived from melamine–mica composites with a surface area of $28 \text{ m}^2 \text{ g}^{-1}$ have almost half the capacitance (115 F g^{-1}) at an order of magnitude lower current density compared to our material.

Table 4a. Comparison of gravimetric capacitances of heteroatom-enriched carbons in the literature.

Carbon type	Surface area, $\text{m}^2 \text{ g}^{-1}$	Electrolyte
(1) Carbonized carbon nanotube/PAN blend ⁴⁶	130	1 M H_2SO_4
(2) Oxygen enriched seaweed biopolymer ¹³	270	1 M H_2SO_4
(3) Nitrogen-enriched carbon from silk fibroins ⁴⁷	2600	1 M TEABF ₄ /PC
(4) Nitrogen-enriched carbons derived from melamine–mica composites ¹⁴	28	1 M H_2SO_4
(5) Nitrogen- and oxygen-containing microporous activated carbon ¹⁷	829	1 M H_2SO_4
(6) Oxygen-containing electrochemically modified graphite electrode ³	6	2.3 M H_2SO_4
(7) Nitrogen-doped carbon nanotubes ⁴⁸	200	1 M H_2SO_4
(8) Nitrogen-doped carbon monolith ³⁶	679	6 M KOH
(9) Nitrogen-doped porous carbon nanofibers ¹⁶	562.51	6 M KOH
(10) Sulfur-doped activated carbons ⁴⁵	3010	0.5 M H_2SO_4
(11) Nitrogen- and oxygen-containing activated carbon nanotubes ¹⁵	706	1 M H_2SO_4
(12) Nitrogen-doped activated porous carbons ⁴⁹	1463	1 M H_2SO_4
Present work	24	1 M H_2SO_4

Table 4b. Comparison of gravimetric capacitances of heteroatom-enriched carbons in the literature.

Carbon type	Scan rate/current density	Capacitance, $F\ g^{-1}$
(1) Carbonized carbon nanotube/PAN blend ⁴⁶	5 $mV\ s^{-1}$	100
(2) Oxygen enriched seaweed biopolymer ¹³	2 $mV\ s^{-1}$	198
(3) Nitrogen-enriched carbon from silk fibroins ⁴⁷	1 $mV\ s^{-1}$	52
(4) Nitrogen-enriched carbons derived from melamine-mica composites ¹³	0.05 $A\ g^{-1}$	115
(5) Nitrogen- and oxygen-containing microporous activated carbon ¹⁷	0.05 $A\ g^{-1}$	~200
(6) Oxygen-containing electrochemically modified graphite electrode ⁴	50 $mV\ s^{-1}$	179.7
(7) Nitrogen-doped carbon nanotubes ⁴⁸	5 $mV\ s^{-1}$	190.8
(8) Nitrogen-doped carbon monolith ³⁶	1 $mV\ s^{-1}$	246
(9) Nitrogen-doped porous carbon nanofibers ¹⁶	1 $A\ g^{-1}$	202
(10) Sulfur-doped activated carbons ⁴⁵	1 $mV\ s^{-1}$	200
(11) Nitrogen- and oxygen-containing activated carbon nanotubes ¹⁵	0.5 $A\ g^{-1}$	384.9
(12) Nitrogen-doped activated porous carbons ⁴⁹	0.1 $A\ g^{-1}$	363
Present work	5 $mV\ s^{-1}$	193
	0.5 $A\ g^{-1}$	204

[0075] Figure 9 compares the Nyquist plots of treated CNF-13 and CNF-0 nanofibers. At high frequencies, while the CNF-0 nanofibers do not show any semi-circle, CNF-13 show clear semi-circle associated with the charge transfer process arising from pseudocapacitance. The semicircular part in the high frequency region represents the electron-transfer-limiting process with its effective diameter equal to the faradaic charge transfer resistance. Furthermore, in the low frequency region, the straight line corresponding to diffusion limiting process is less inclined for CNF-13 suggesting more capacitive behavior compared to CNF-0 nanofibers. The equivalent circuit model shown in the inset of Figure 9 was used to fit the Nyquist plots and analyze them. Here, R_S was the solution resistance, R_F corresponded to the charge-transfer resistance through the pseudo-capacitive process, CPE_1 denotes the double-layer capacitance at the electrode/electrolyte interface, CPE_2 denotes the pseudocapacitance and the factor α , is an adjustable parameter that lies between 0 and 1, and is 1 for an ideal capacitor. The fitting parameters of the experimental data are given in Table 5. The significantly high value of CPE_2 compared to CPE_1 for CNF-13 shows the higher contribution of pseudocapacitance in the overall capacitance. While for CNF-0, $CPE_1 \gg CPE_2$, showing the dominance of double layer capacitance contribution. Thus, Nyquist plots further confirm that the dominant charge storage mechanism in CNF-13 is pseudocapacitance and in CNF-0, it is double-layer capacitance.

Table 5. Values of fitting parameters of equivalent circuit (inset) to Nyquist plots.

Parameters	RS (Ω)	CPE1 (mF)	α_1	RF (Ω)	CPE2 (mF)	α_2
CNF-0	0.255	25.5	0.658	0.703	3.94	1
CNF-13	0.3639	4.09	0.803	0.466	357.5	0.73

[0076] The cyclability is an important parameter for the practical application of supercapacitors. The cycle life of the treated CNF-13 nanofibers was examined at the scan rate of 100 mV/s for 1000 charge-discharge cycles in a three-electrode test cell (Figure 10). The specific capacitance for the 2nd cycle was 129 F g⁻¹ and 130.5 F g⁻¹ after 1000 cycles. Thus, there was no change in specific capacitance even after 1000 cycles. This shows the good stability and high cyclability of the fabricated materials.

[0077] Achieving high gravimetric capacitance is not sufficient for the practical application of nanomaterials as electrodes for supercapacitors. Good areal (per unit geometric area) and volumetric (per unit volume) capacitance is also necessary to compete with existing technology. Thus, the volumetric and areal capacitance was also determined for our materials in a two-electrode test cell. The areal capacitance of 1.15 F cm⁻² was obtained. The volumetric capacitance of 52.33 F cm⁻³ was obtained for 240 mm thick treated CNF-13 electrodes, which is similar to that of a $\approx$ 300 mm electrode made from porous carbon powders ($\sim$ 50 F cm⁻³). Since, the carbon nanofiber mats are compressible, the volumetric capacitance can be further increased. Hence, the PAN–NaCl electrospun fibers were compressed in a hydraulic press by applying a pressure of 1500 lbs at 60 °C for 1 min, followed by the regular stabilization, carbonization, and acid treatment processes. A higher volumetric capacitance of 63.03 F cm⁻³ for the 198 mm electrode for compressed CNF-13 nanofibers was obtained.

Supplementary Tests

[0078] To further confirm that the high capacitance in CNF-13 arises from the pseudocapacitive functional groups, additional experiments were conducted to better understand the charge-storage mechanism in treated CNF-13 nanofibers. Firstly, the tests were conducted in electrolyte solutions of varying pH: 1M H₂SO₄ (acidic), 1M KOH (alkaline) and 3M NaCl (neutral). The CVs conducted in a 2-electrode setup for treated CNF-13 and CNF-0 at 20 mV s⁻¹ in each of these electrolytes are compared and shown in Figure 17. The specific capacitance of CNF-13 reduces in the order: acidic > alkaline > neutral, which is expected as less functional groups would contribute to charge storage in alkaline and neutral electrolytes because of proton deficiency in these electrolytes. This confirms that charge-storage reactions involving the transfer of protons contribute significantly to the capacitance of CNF-13 in acidic electrolytes.

On the other hand, the specific capacitance does not change much with a change in the electrolyte for CNF-0, thereby showing that double layer charge storage is the dominant mechanism in CNF-0. It is however also noted that the CNF-13 capacitance reduces to half its value in neutral electrolyte compared to the acidic electrolyte, but the reduction is not as significant as expected since it has a similar surface area as CNF-0, and the EDLC contribution should be negligible. Thus, we conclude that some surface functionalities would still be active in alkaline and neutral electrolytes although the mechanism is not clear at this point and more investigation will be required.

[0079] Next, we also conducted tests to potentially remove the functional groups from CNF-13 and re-evaluate them. The oxygen-containing functional groups can be removed from carbon surfaces by heat treatment over 500 K resulting in CO and CO₂ evolution. Thus, treated CNF-13 nanofibers were re-heat treated in an inert atmosphere (N₂) at 800°C for 1 h. For comparison, CNF-0 nanofibers were also subjected to the same treatment process. The capacitances of re-heat treated CNF-13 and CNF-0 were measured in a three-electrode cell (with Pt as a counter electrode) in 1M H₂SO₄ solution as shown in Figure 18. The results obtained in acidic and neutral electrolytes at 5 mVs⁻¹ and 20 mVs⁻¹ are listed in Table 2.6. A significant reduction in capacitance is observed for re-heat treated CNF-13 approaching that of CNF-0. While, for CNF-0 the capacitances remain similar since they have none/negligible surface functional groups, to begin with. XPS was conducted to further confirm the reduction in surface functional groups after the re-heat treatment process. The XPS results are summarized in Table 6. The results clearly indicate a lowering of oxygen and sulfur content in the re-treated CNF-13. Thus, successful removal of surface functional groups was achieved via thermal decomposition that leads to a significant lowering of capacitance. This confirms that the five-fold increase in capacitance shown earlier for treated CNF-13 nanofibers was due to the pseudocapacitance added by surface functionalities, induced via NaCl.

Table 6. Summary of XPS data before and after re-heat treatment.

	Carbonized CNF (%)	Treated CNF- 13 (%)	Re-heat treated CNF-0 (%)	Re-heat treated CNF- 13 (%)
O1s	6.22	18.63	6.36	7.84
C1s	80.08	64.3	84.76	84.4
N1s	13.69	10.65	8.88	7.38
S2p		6.11		0.38
O/C	7.8	29.0	7.5	9.3
N/C	17.1	16.6	10.5	8.7

Materials

[0080] Polyacrylonitrile (PAN, MW = 150 000, Sigma-Aldrich, USA) and N,N-dimethylformamide (DMF, Sigma-Aldrich, USA) were used without any purification. Sodium chloride (Sigma-Aldrich, USA) was ground into fine powder and dried overnight under vacuum to remove any absorbed water.

Synthesis of carbon nanofibers

[0081] PAN (10 wt%) and NaCl (4, 6.7 & 13.3 wt%) were added to DMF and stirred at room temperature for 4–5 hours. Nanofibers were electrospun at room temperature with a relative humidity below 20% using a 20 gauge stainless steel needle (Hamilton Co.). The distance between the needle tip and the grounded collector (aluminum foil) was 15 cm, and the applied voltage of 13–14 kV was used to obtain a stable Taylor cone. The electrospinning was carried out in batches of 2 mL solution to minimize settling of sodium chloride in the syringe while electrospinning. The electrospun nanofibers were stabilized in air by heating to 280 °C at a rate of 5 °Cmin⁻¹ for 5 hours. The stabilized nanofibers were then pyrolyzed (carbonized) under a nitrogen flow of 400mLmin⁻¹ in a horizontal tube furnace at a heating rate of 2 °C min⁻¹ to the temperature of 800 °C and held for 1 h. The carbonized NaCl–PAN nanofibers were then treated with 1 M H₂SO₄ solution and then thoroughly washed with distilled water to remove excess sulfuric acid.

Characterization

[0082] The morphology and microstructure of the samples were characterized using a Zeiss Supra 50VP scanning electronmicroscope. A Quadrasorb (Quantachrome Instruments, USA) was used to conduct gas sorption measurements. Samples were tested at 77 K (liquid nitrogen baths were used as coolant) isotherms, using the nitrogen gas as the adsorbate. The Brunauer–Emmett–Teller (BET) formula was used to calculate specific surface areas in the P/Po range between 0.05 and 0.10. For XRD analysis, the samples were characterized using a Rigaku SmartLab X-ray diffractometer in Bragg–Bentano mode (Cu Ka radiation, voltage 40 kV, current

30 mA, scanning range 10–80° and step size 0.02°). XPS measurements were performed on a Physical Electronics VersaProbe 5000 spectrometer using a monochromated Al Ka excitation source. The binding energy scales were calibrated with respect to the C1s peak position (284.6 eV). The quantitative analysis was performed using CASAXPS software after Shirley background subtraction. The mixed 30% Gaussian–Lorentzian line shapes were used for peak fitting.

Electrochemical measurements

[0083] The carbon nanofiber mats were directly used as binder-free electrodes for electrochemical measurements. The capacitive performances of the samples were investigated by using cyclic voltammetry (CV), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS) techniques, which were performed using a Gamry Reference 3000 potentiostat. For two-electrode analysis, a symmetric cell was assembled by placing two 3–4 mg each, 3/800 diameter discs of the fabricated carbon nanofibers separated by a Whatman glass fiber separator, sandwiched between two graphite current collectors one in each side in a swagelok cell. The carbon nanofiber electrodes were immersed in the aqueous electrolyte, 1 M H₂SO₄ overnight before measurements to ensure complete wetting of carbon electrodes. For three electrode analysis, an aqueous Ag/AgCl electrode was used as the reference electrode in the two-electrode test-cell. Thus, in a three-electrode cell, the potential difference is measured with reference to Ag/AgCl.

[0084] The specific capacitance per unit mass of one electrode in a two-electrode setup was calculated according to the equation: $C = \int 2I \Delta t / (m \Delta V)$, where I is the response current (A), t is the discharge time (s), m is the average mass of the carbon nanofiber electrodes (g), and ΔV is the voltage window. For a three-electrode capacitance measurement, the above equation was modified as: $C = \int I \Delta t / (m \Delta V)$. The galvanostatic charge–discharge tests were performed at current densities ranging from 0.5 to 20 Ag⁻¹. The specific capacitance per electrode from galvanostatic charge–discharge experiments was calculated from the discharge curves after three charge–discharge cycles. EIS measurements were carried out by applying a sine wave with an amplitude of 10 mV over the frequency range of 100 kHz to 0.1 Hz.

Conclusions

[0085] Heteroatom-enriched free-standing (binder-free) carbon nanofibers for supercapacitors have been successfully synthesized using a simple fabrication technique. The surface area of the fabricated materials was very low (<25 m²g⁻¹), which allowed us

to better understand the effect of surface functional groups. A high specific capacitance of 204 F g^{-1} , areal capacitance of 1.15 F cm^{-2} and volumetric capacitance of 63.03 F cm^{-3} were obtained in $1 \text{ M H}_2\text{SO}_4$, which are comparable to carbons with a high surface area ($\sim 2000 \text{ m}^2 \text{ g}^{-1}$). Such a high capacitance in the reported materials is attributed to the surface functional groups participating in pseudocapacitive redox reactions. Electrospun PAN–NaCl nanofibers on carbonization showed higher oxygen content mainly in the form of carboxyl groups than those without NaCl. On mild acid treatment, these carboxyl groups react with sulfuric acid leading to adsorption of sulfate and sulfonate functional groups, which further add to the capacitance. Hence, NaCl played a major role in modifying the carbon surface to incorporate oxygen and sulfur functionalities. The fabricated fibers showed good capacitance retention at high current densities (57% at 20 Ag^{-1}). Moreover, no capacitance fade was observed after 1000 cycles showing good stability and high cyclability of the material. The method demonstrated in this work to generate pseudocapacitive surface functionalities can be integrated with our previously published work (C. Tran and V. Kalra, *J. Power Sources*, 2013, 235, 289–296) on creating high surface area porous carbon nanofibers to generate heteroatom enriched-high surface area carbon nanofibers with further enhanced specific capacitance.

What is Claimed:

1. A method of producing an electrode comprising:
 - forming a shaped body from a mixture comprising a carbon precursor and sodium chloride; and
 - heating the shaped body to a temperature of at least 600 °C in an inert atmosphere to produce a carbonized shaped body.
2. The method of claim 1 further comprising contacting the carbonized shaped body with at least one of an acid solution and water to extract excess sodium chloride.
3. The method of claim 1 or 2, additionally comprising heating the shaped body to a temperature of 150-350 °C in air or an oxygen-containing gas prior to heating the shaped body to a temperature of at least 600 °C.
4. The method of anyone of claims 1-3, wherein the acid is H₂SO₄.
5. The method of anyone of claims 1-4, wherein said mixture of a carbon precursor and sodium chloride is electrospun to produce the shaped body prior to heating to a temperature of at least 600 °C.
6. The method of claim 5, wherein the shaped body is a mat of nanofibers.
7. The method of anyone of claims 1-6, wherein the acid solution has a concentration of 0.1 to 2 moles/liter.
8. The method of anyone of claims 1-7, wherein said carbon precursor is polyacrylonitrile (PAN).
9. The method of claim 5 or 6, wherein the carbon precursor and the sodium chloride are dissolved in dimethylformamide solution for the mixture used in electrospinning.

10. The method of claim 9, wherein the carbon precursor is present in an amount of 0.01-50% by weight in the dimethylformamide solution.
11. The method of claim 9 or 10, wherein the sodium chloride is present in an amount of 0.01-25% by weight in the dimethylformamide solution.
12. The method of anyone of claims 1-11, wherein after contacting the carbonized shaped body with an acid solution to dissolve out excess sodium chloride, the carbonized shaped body is washed with water.
13. The method of anyone of claims 1-12, wherein the electrode has a specific surface area of at least $0.01 \text{ m}^2 \text{ g}^{-1}$.
14. The method of anyone of claims 1-13, wherein the electrode has a surface oxygen to carbon ratio of 1-35 atomic %.
15. The method of anyone of claims 1-14, wherein the electrode has a surface nitrogen to carbon ratio of 1-17 atomic %.
16. The method of anyone of claims 1-15, wherein the electrode is substantially free of binder.
17. The method of anyone of claims 1-16 where the electrode has a porosity of 10-95%.
18. The method of anyone of claims 1-17, wherein additional functional groups are formed on the surface of the electrode.
19. An electrode made by the method of any of claims 1-18 and 20-26.
20. A method of forming free-standing carbon nanofibers comprising
 - forming a mixture comprising carbon precursor and sodium chloride;
 - electrospinning said mixture to form a spun product, and
 - pyrolyzing said spun product.

21. The method of claim 20, further contacting said pyrolyzed product with mild acid.
22. The method of claim 20 or claim 21, wherein the carbon precursor is polyacrylonitrile.
23. The method of any one of claims 20-22, wherein the carbon precursor is present in an amount of 0.01-50% by weight in the mixture.
24. The method of any one of claims 20-23, wherein the sodium chloride is present in an amount of 0.01-25% by weight in the mixture.
25. The method of any one of claims 20-24, wherein the mixture comprises dimethyl formamide.
26. The method of claim 21, wherein said mild acid is 0.01 to 2 M H₂SO₄.

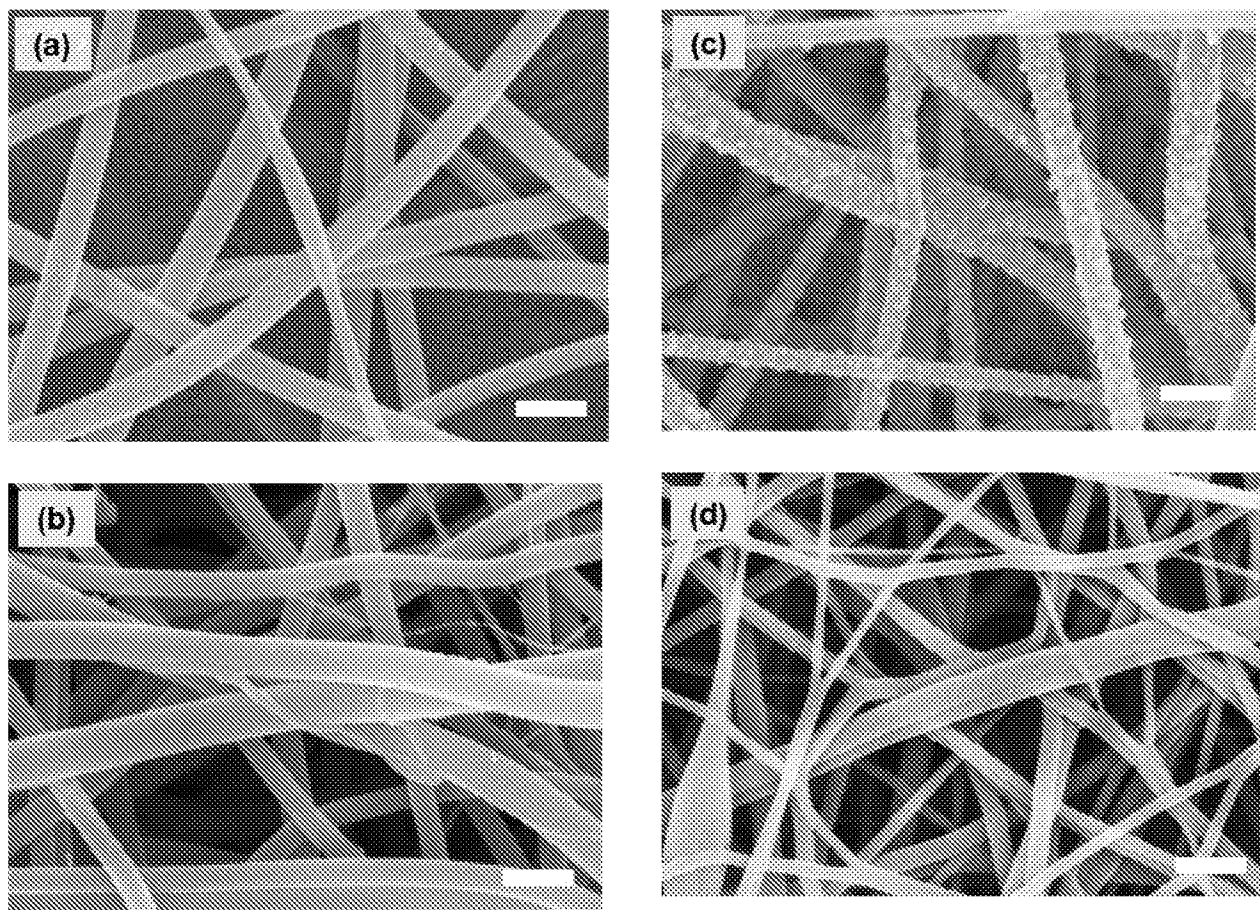


Figure 1

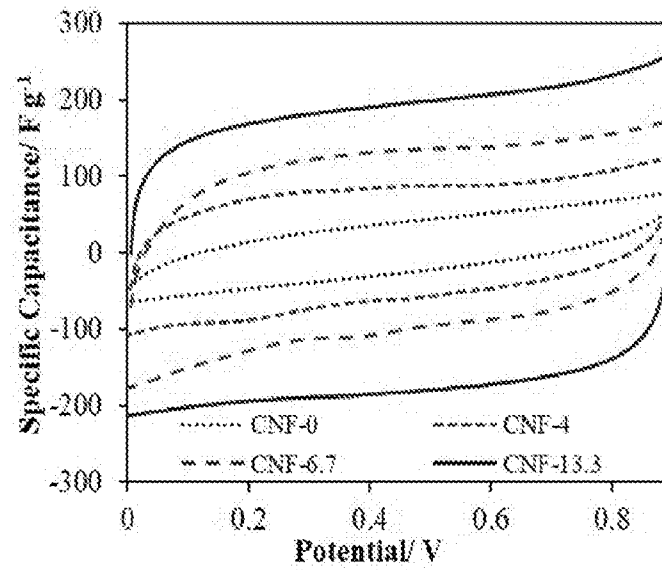


Figure 2

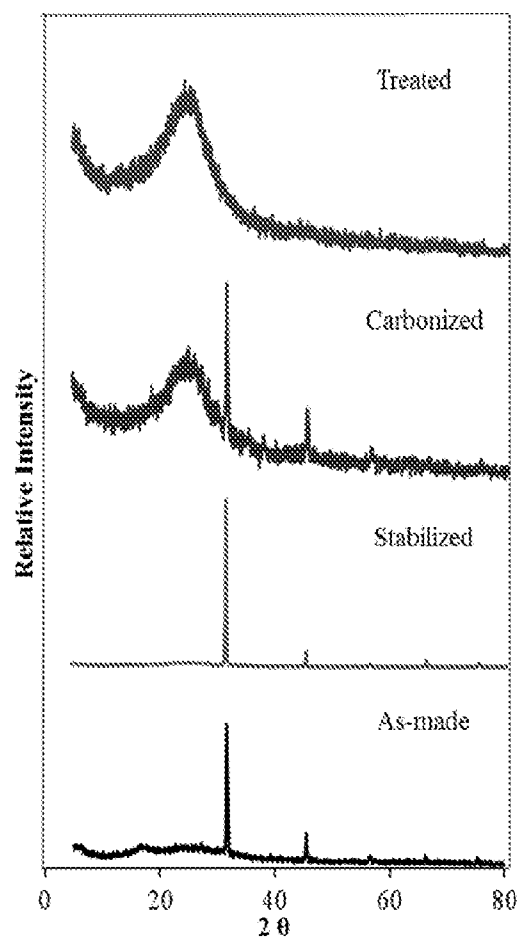


Figure 3

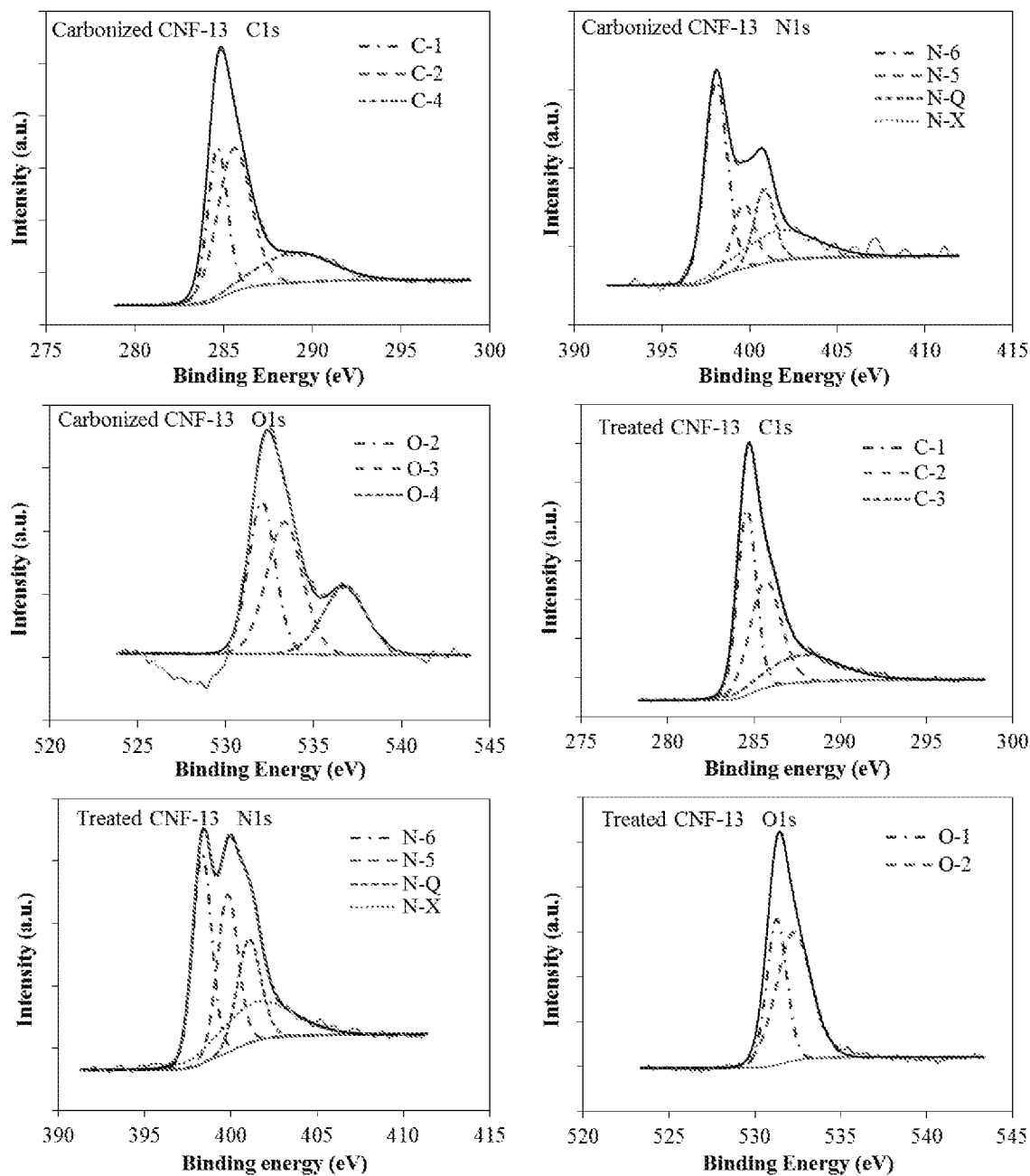


Figure 4

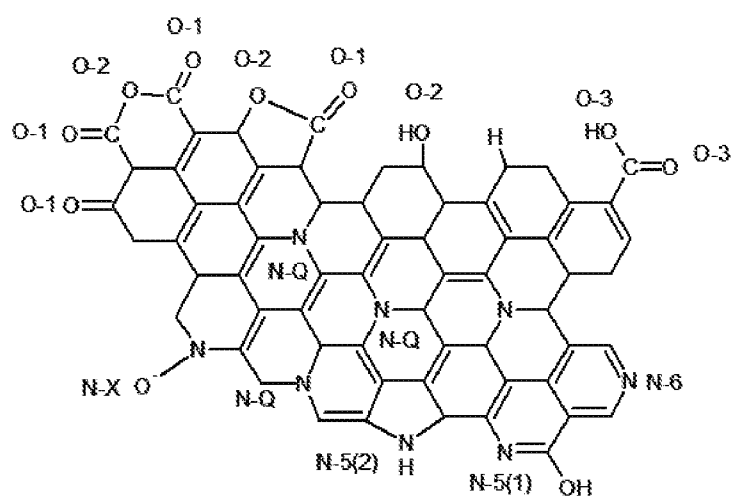


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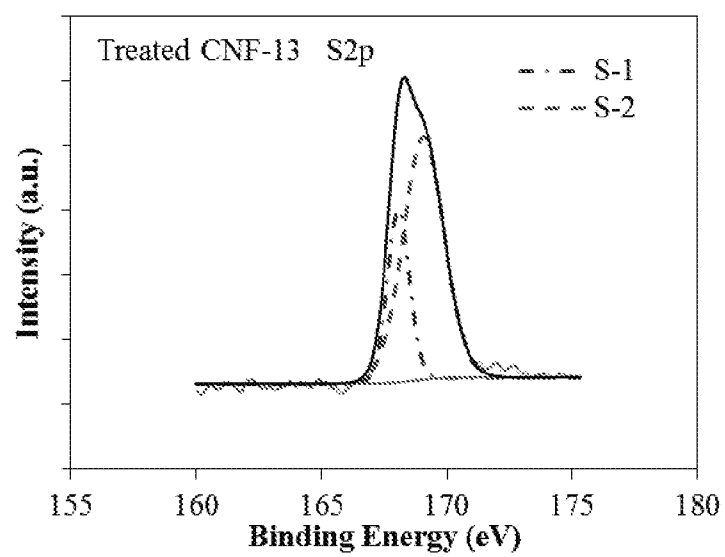


Figure 6

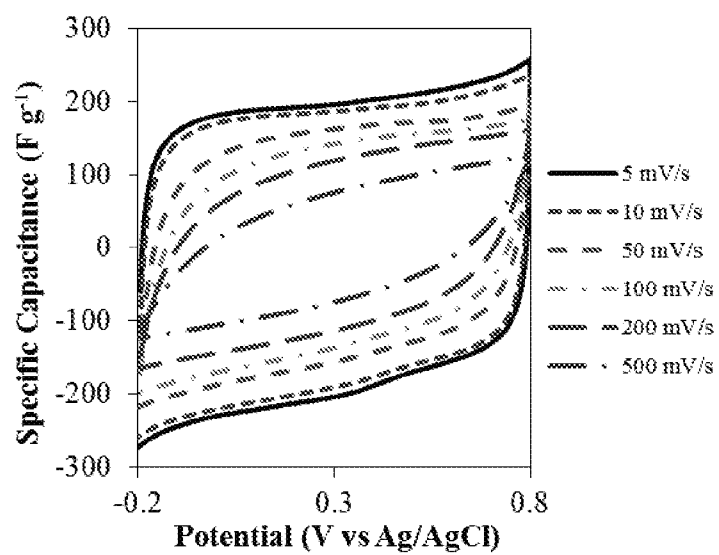


Figure 7

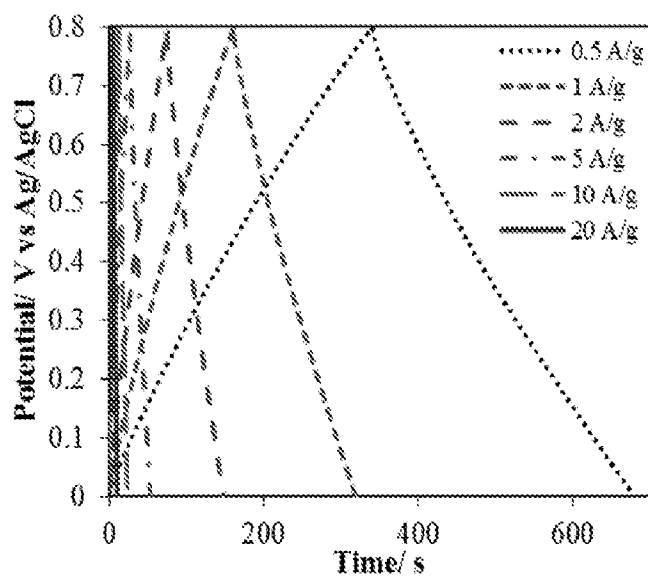


Figure 8

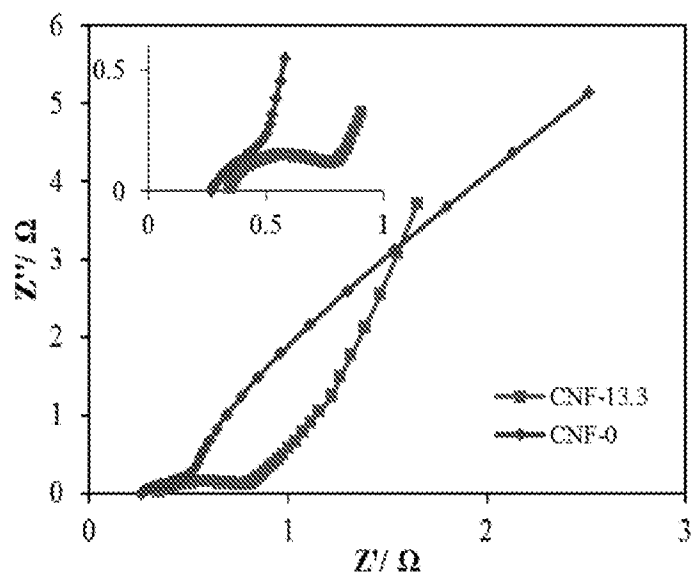


Figure 9

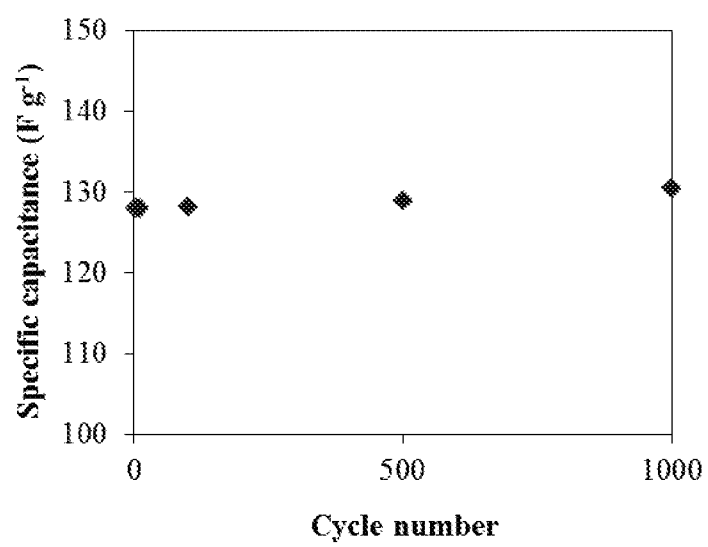


Figure 10

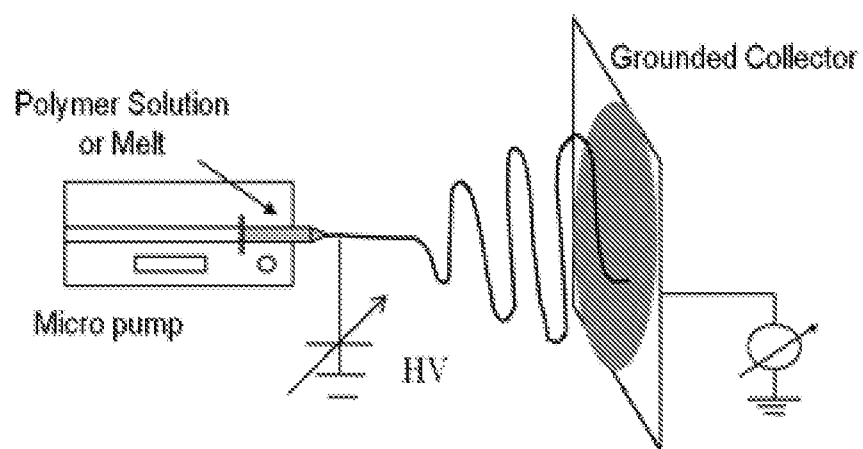


Figure 11

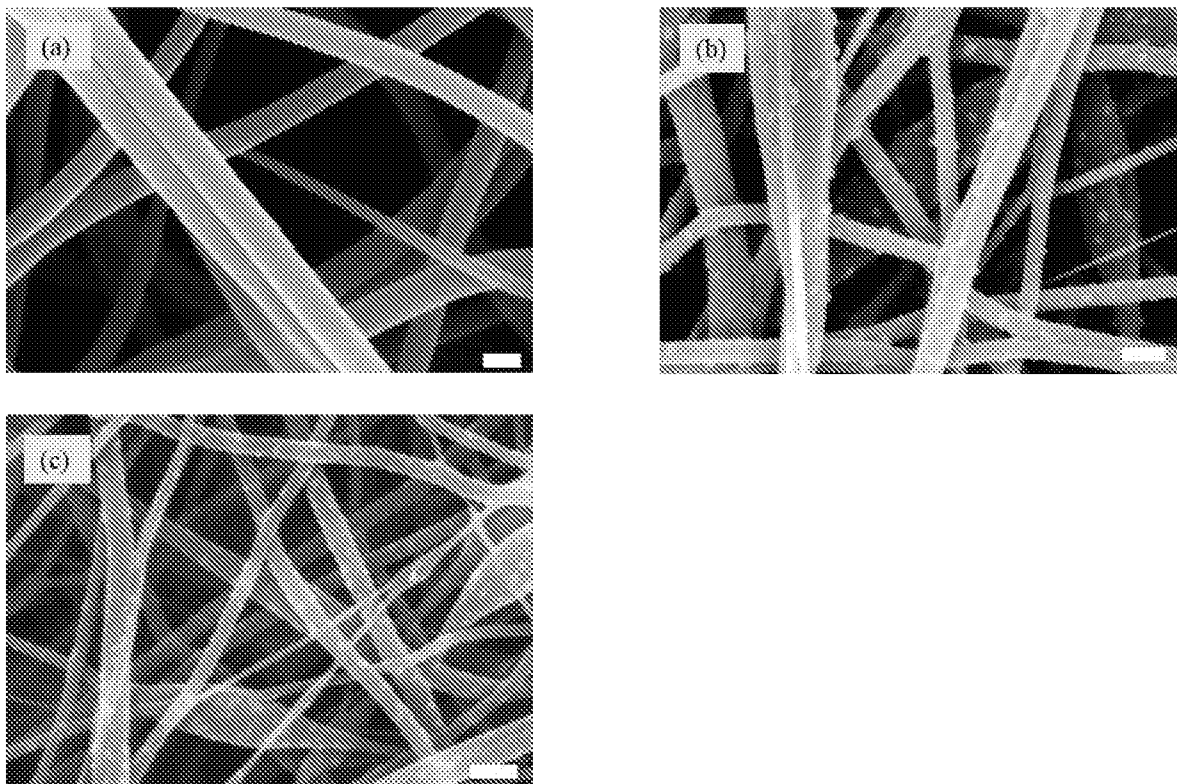
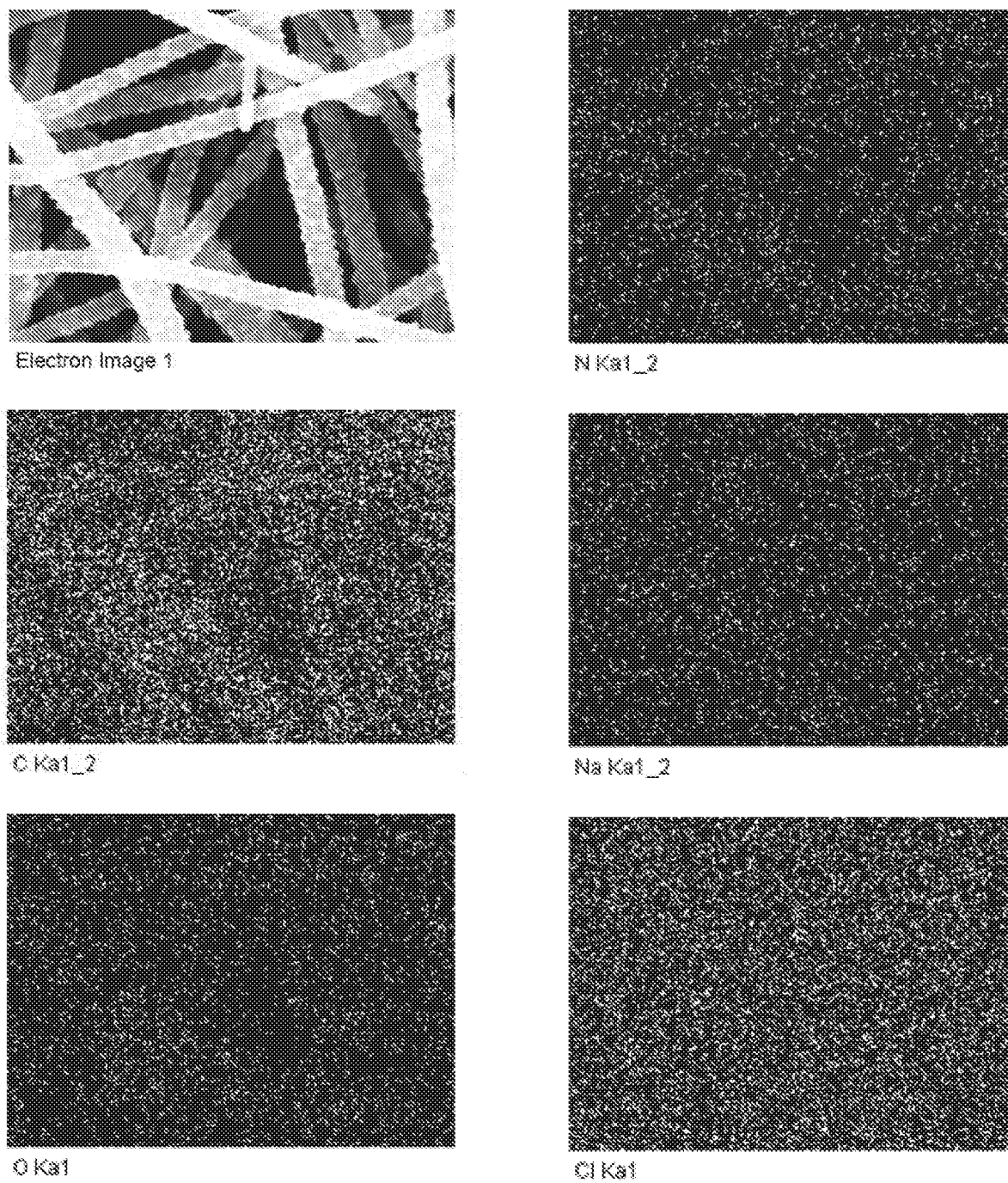


Figure 12

**Figure 13**

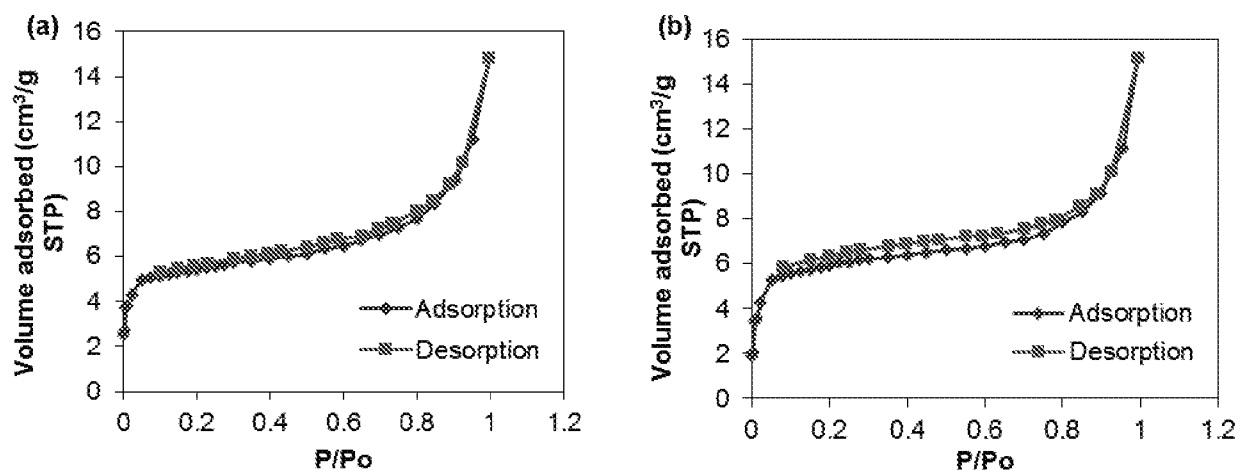


Figure 14

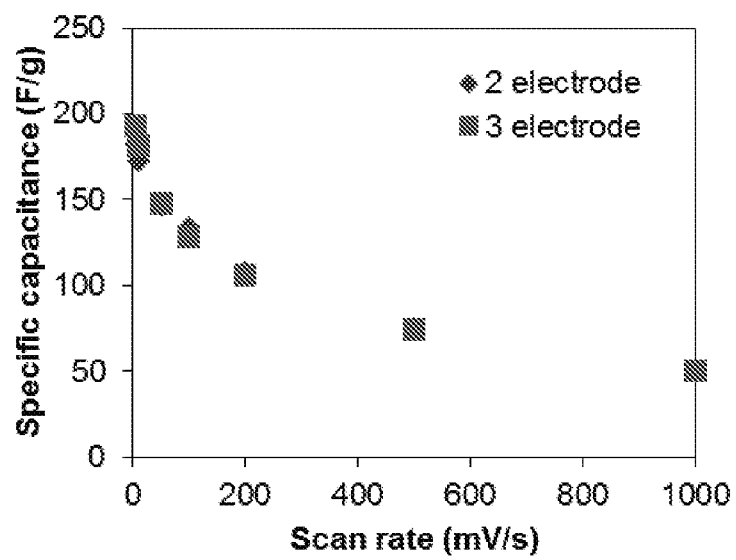
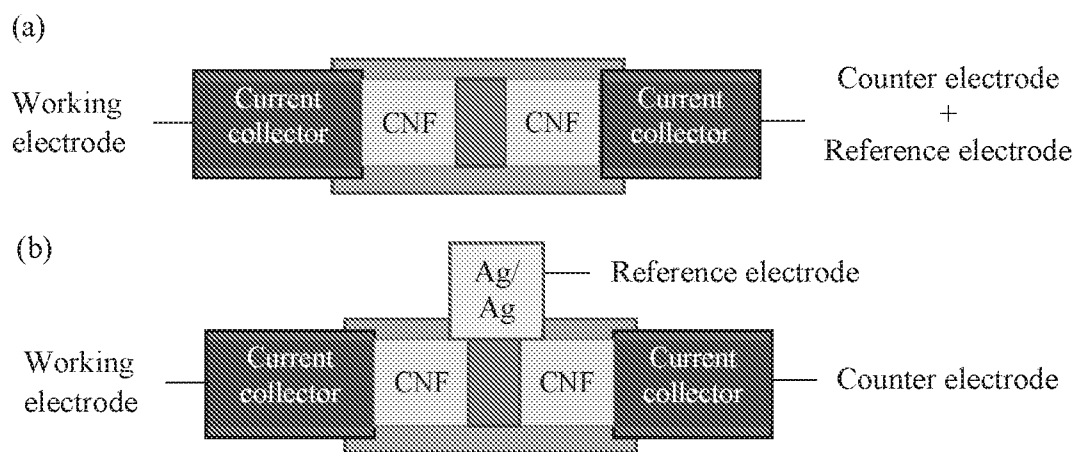


Figure 15

**Figure 16**

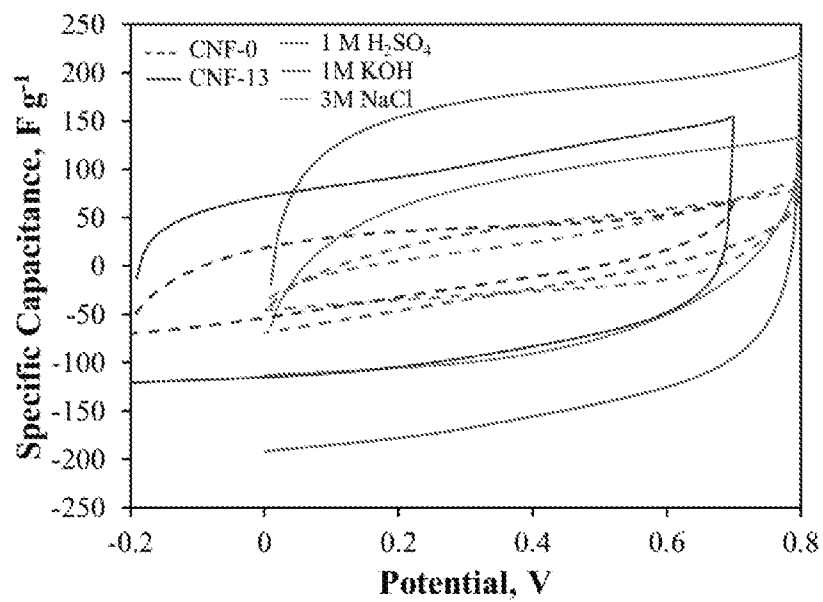


Figure 17

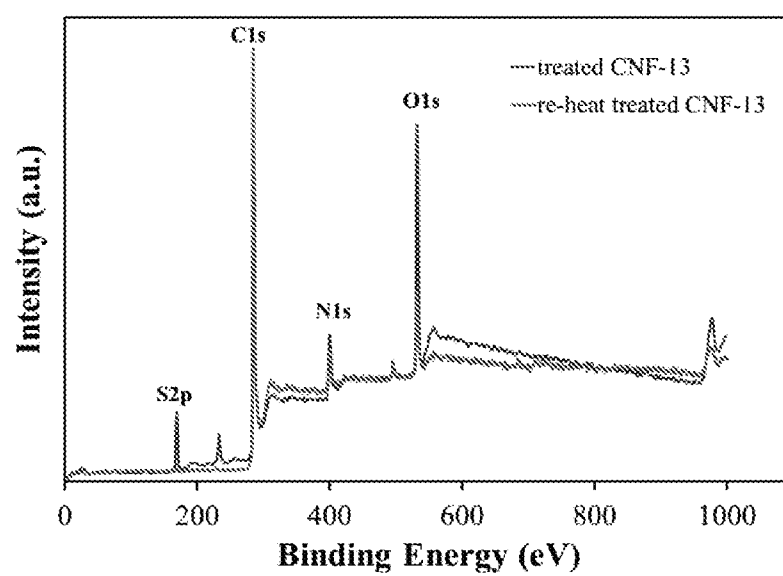


Figure 18

Table 1. BET surface area and total pore volume calculated from nitrogen adsorption/desorption isotherms.

Sample	BET SSA, $\text{m}^2 \text{g}^{-1}$	Total Pore volume, $\text{cm}^3 \text{g}^{-1}$
Carbonized CNF-13	21	0.017
Treated CNF-13	24	0.017
Carbonized CNF-0	14	0.011

Table 2. Elemental composition (at.%) of carbonized and treated CNF-0 and CNF-13 nanofibers determined from XPS.

	Carbonized CNF-0 (%)	Treated CNF-0 (%)	Carbonized CNF-13 (%)	Treated CNF-13 (%)
O	6.22	7.07	13.51	18.63
C	80.08	78.59	68.3	64.3
N	13.69	13.49	9.51	10.65
Na	-	-	4.93	0.31
Cl	-	-	3.75	-
S	-	0.84	-	6.11
O/C	7.8	9.0	19.8	29.0
N/C	17.1	17.2	13.9	16.6

Table 3. XPS core level peak analysis of C1s, N1s and O1s peaks for carbonized and treated CNF-0 and CNF-13.

Sample	C1s peaks				N1s peaks				O1s peaks			
	C-1 ^{a)}	C-2 ^{b)}	C-3 ^{c)}	C-4 ^{d)}	N-6 ^{e)}	N-5 ^{f)}	N-Q ^{g)}	N-X ^{h)}	O-1 ⁱ⁾	O-2 ^{j)}	O-3 ^{k)}	O-4 ^{l)}
Carbonized CNF-0	39.3	39.54	21.16	-	41.49	58.51	-	-	56.77	43.23	-	-
Treated CNF-0	39.96	38.77	21.27	-	34.66	50.39	-	14.95	40.4	59.6	-	-
Carbonized CNF-13	29.99	47.99	-	22.01	46.03	14.74	15.91	23.33	-	35.4	39.66	24.94
Treated CNF-13	39.46	38.01	22.53	-	31.5	26.32	19.59	22.59	38.63	61.37	-	-

^{a)} 284.6 eV; ^{b)} 285.6 ±0.12 eV; ^{c)} 287.7 ±0.1 eV; ^{d)} 288.9 eV; ^{e)} 398.1 ±0.2 eV; ^{f)} 399.9 ±0.3 eV; ^{g)} 400.9 ±0.17 eV; ^{h)} 402.5 ±1.64 eV; ⁱ⁾ 531.4 ±0.1 eV; ^{j)} 532.3 ±0.2 eV; ^{k)} 533.4 eV; ^{l)} 536.4 eV.

Table 4. Comparison of gravimetric capacitances of heteroatom-enriched carbons in the literature.

Carbon type	Surface area, $\text{m}^2 \text{g}^{-1}$	Electrolyte	Scan rate/Current density	Capacitance, F g^{-1}
(1) Carbonized carbon nanotube/PAN blend ⁴³	130	1 M H_2SO_4	5 mV s^{-1}	100
(2) Oxygen enriched seaweed biopolymer ¹³	270	1 M H_2SO_4 1 M	2 mV s^{-1}	198
(3) Nitrogen-enriched carbon from silk fibroins ⁴⁴	2600	TEABF ₄ /PC	1 mV s^{-1}	52
(4) Nitrogen-enriched carbons derived from melamine-mica composites ¹⁴	28	1 M H_2SO_4	0.05 A g^{-1}	115
(5) Nitrogen- and oxygen- containing microporous activated carbon ¹⁷	829	1 M H_2SO_4	0.05 A g^{-1}	~200
(6) Oxygen-containing electrochemically modified graphite electrode ⁴	6	2.3 M H_2SO_4	50 mV s^{-1}	179.7
(7) Nitrogen-doped carbon nanotubes ⁴⁵	200	1 M H_2SO_4	5 mV s^{-1}	190.8
(8) Nitrogen-doped carbon monolith ³³	679	6 M KOH	1 mV s^{-1}	246
(9) Nitrogen-doped porous carbon nanofibers ¹⁶	562.51	6 M KOH	1 A g^{-1}	202
(10) Sulfur-doped activated carbons ⁴²	3010	0.5 M H_2SO_4	1 mV s^{-1}	200
(11) Nitrogen- and oxygen- containing activated carbon nanotubes ¹⁵	706	1 M H_2SO_4	0.5 A g^{-1}	384.9
(12) Nitrogen-doped activated porous carbons ⁴⁶	1463	1 M H_2SO_4	0.1 A g^{-1}	363
Present work	24	1 M H_2SO_4	5 mV s^{-1} 0.5 A g^{-1}	193 204

Table 5. Values of fitting parameters of equivalent circuit (inset) to Nyquist plots.

Parameters	R_s (Ω)	CPE_1 (mF)	α_1	R_F (Ω)	CPE_2 (mF)	α_2
CNF-0	0.255	25.5	0.658	0.703	3.94	1
CNF-13	0.3639	4.09	0.803	0.466	357.5	0.73

Table 6. Summary of XPS data before and after re-heat treatment.

	Carbonized CNF-0 (%)	Treated CNF-13 (%)	Re-heat treated CNF- 0 (%)	Re-heat treated CNF- 13 (%)
O1s	6.22	18.63	6.36	7.84
C1s	80.08	64.3	84.76	84.4
N1s	13.69	10.65	8.88	7.38
S2p		6.11		0.38
O/C	7.8	29.0	7.5	9.3
N/C	17.1	16.6	10.5	8.7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/050899

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - D01F 9/22; B29C 47/00; D01F 9/14; H01M 4/86 (2016.01)

CPC - D01F 9/22; B29C 47/0076; D01F 9/14; H01M 4/86 (2016.08)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) *

IPC(8) - B29C 47/00; D01F 9/14; D01F 9/22; H01M 4/86 (2016.01)

CPC - B29C 47/0076; D01F 9/14; D01F 9/22; H01M 4/86 (2016.08)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC - 264/10; 361/502; 423/447.2; 428/367; 429/418; IPC(8) - B29C 47/00; D01F 9/14; D01F 9/22; H01M 4/86; CPC - B29C 47/0076; D01F 9/14; D01F 9/22; H01M 4/86 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Orbit, Google Patents, Google Scholar

Search terms used: electrode, sodium chloride, polyacrylonitrile

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SINGHAL et al., Using common salt to impart pseudocapacitive functionalities to carbon nanofibers, Journal of Materials Chemistry A, 20 October 2014, entire document	1-3, 20-22, 26
A	US 2006/0098389 A1 (LIU et al) 11 May 2006 (11.05.2006) entire document	1-3, 20-22, 26

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 October 2016

Date of mailing of the international search report

23 NOV 2016

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/050899

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-19, 23-25
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.