

A new hybrid architecture consisting of highly mesoporous CNT/carbon nanofibers from starch†

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Received 26th April 2012, Accepted 10th August 2012

DOI: 10.1039/c2jm32631k

Currently used activated carbon electrodes from commercial products contain mostly micropores (<2 nm), which are not easily accessible to electrolyte ions. Therefore, mesoporous carbons, with their more accessible porous infrastructure, are promising materials to maximize the capacitance in electrochemical capacitors. This paper reports a new hybrid carbon nanofiber architecture having mesopores with a narrow distribution, highly accessible surface area, low resistivity, and high stability by electrospinning of starch without using the template method for the first time. By using the natural ability of the starch lamellar structure and controlling the carbonization temperature, we successfully fabricated a new hybrid carbon architecture consisting of CNT reinforced-carbon nanofibers with a pore diameter of 4.76 nm and pore volume of 0.31 cm³ g⁻¹. It shows a higher specific capacitance (170 F g⁻¹) and electrical conductivity (2.1 S cm⁻¹) than other carbon materials derived from synthetic polymers and free-standing CNT papers.

1. Introduction

Over the past several decades, porous carbon has been most promising due to its low density, good electrical conductivity, mechanical stability, high surface area and chemical inertness.^{1,2} Moreover, its benefit of inexpensiveness makes it a more attractive material. For example, porous carbon can be prepared inexpensively from a wide variety of low-cost precursors which are typically biocompatible and chemically stable as well as, being a high specific surface area material, it can be used as an effective sorbent, catalyst support, filter, and electrode in a range of applications. Until now, porous carbons have usually been prepared from organic precursors of natural or synthetic origin, which were carbonized and then activated through a mild gasification. However, these activated carbons consist of complex, intricate assemblies of distorted graphite-like nanocrystallites, with the consequent disadvantage that uniformity in pore size and shape is typically difficult to control in such carbons.³

Recently, the template method has been known as the best method for synthesizing porous carbons with a designed pore architecture that achieves control over pore-size distribution.^{4,5} The resultant activated carbons produced by the template method possess well-ordered mesoporous structures with a large specific volume,⁶⁻⁸ whereas highly aggressive chemicals involved limit this approach in producing stable graphitic carbons.^{9,10}

Current research related to porous carbons mainly focuses on the surface area of electrochemical capacitors, in which charge is stored within the double layers at the interfaces between the carbon electrodes and the electrolyte.¹¹⁻¹⁵ For an ideal electrochemical capacitor electrode material, it is necessary to have both a large surface area for charge accumulation and an interconnected porous network with sufficiently open pores for electrolyte wetting and rapid ionic transport. Unfortunately, currently used activated carbon electrodes from commercial products contain only micropores (<2 nm), which are not easily accessible to electrolyte ions.¹⁶ C. Kim *et al.*¹⁷ fabricated carbon nanofiber webs *via* electrospinning of polyacrylonitrile for electrochemical capacitors. Carbon nanofiber webs with 5 wt% zinc chloride exhibited large specific surface area and good specific capacitance. Y. Yang *et al.*¹⁸ reported porous poly(vinylidene fluoride)-based carbon fibers fabricated by electrospinning from solutions in dimethylformamide, poly(ethylene oxide) and water. The poly(vinylidene fluoride) fiber mats were then converted into electrospun carbon fiber paper using a low temperature chemical stabilization treatment followed by carbonization. The resulting self-supporting carbon fiber paper exhibits high surface area and performs well as an electrode. However, both these approaches have limitations in controlling the pore size and distribution of carbon nanofibers and poor electrolyte accessibility to intrapore

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† Electronic supplementary information (ESI) available: Microstructure of the stabilized CNT/starch nanofiber web, elemental analysis table, schematic of a method of cell test, CV curve of CNT/porous carbon nanofibers heat-treated at 1400 °C. See DOI: 10.1039/c2jm32631k

surface area because the average pore size of carbon nanofibers ranges from 0.5 to 0.6 nm and most of them consist of lots of micropores. Mesoporous carbons, with their more accessible porous infrastructure, are promising materials as it is known that pore sizes in the range of 3–5 nm are required to maximize the capacitance in the electric double-layer capacitors.^{19,20} Recently, researchers have focused on the design and fabrication of hybrid materials based on CNTs. By the combination of CNTs in the carbon matrix, hybrid composite fibers expected to deriving structural and multifunctional benefits from CNTs.

Here, we report a new hybrid carbon nanofiber architecture having mesopores with a narrow distribution, highly accessible surface area, low resistivity, and high stability by electrospinning of starch without the template method for the first time. By using the natural ability of the starch lamellar structure and controlling the carbonization temperature, we successfully fabricated a new hybrid carbon architecture consisting of CNT reinforced-carbon nanofibers with a pore diameter of 4.76 nm and pore volume of 0.31 cm³ g⁻¹. It shows a higher specific capacitance (170 F g⁻¹) and electrical conductivity (2.1 S cm⁻¹) than other carbon materials derived from synthetic polymers and free-standing CNT papers.

2. Experimental

2.1. Materials

The MWCNTs used in this study were the CVD-grown material produced by Iljin Co. The diameters of MWCNTs were about 20 nm with a typical length of a few μm . This sample was refluxed in 3 M nitric acid and stirred at 110 °C for 5 h to attach the functional groups of carboxyl and hydroxyl groups. MWCNTs were then dried after rinsing with distilled water. Corn starch was used as the carbon fiber precursor. Polyvinyl alcohol (PVA) was purchased from Aldrich Chemical.

2.2. Synthesis of CNT/carbon nanofibers

The prepared MWCNT of 0.02 g was immersed in 20 ml of distilled water and sodium dodecyl sulfate (SDS) was also added for MWCNT to disperse homogeneously. The MWCNT solution was sonicated for 3 h in a bath-type sonicator (Hwashin Technology Co. 520 W). MWCNTs were homogeneously dispersed and stable with a dark ink-like appearance without being precipitated for several hours. 0.67 g of PVA was dissolved in 10 ml of distilled water and stirred vigorously at 80 °C and the MWCNT solution was added to the PVA solution. PVA was used as the spinning agent because starch by itself cannot be electrospun into a fibrous structure. 2 g of starch was then dissolved in 30 ml of distilled water and stirred vigorously at 50 °C. The starch solution was boiled at 120 °C for an hour and cooled to room temperature. Finally, the MWCNT–PVA solution and starch solution were mixed and kept for a day. After that 1 M of *para*-toluenesulfonic acid was added to the starch solution to enable fast carbonization and fix the porous structure. Finally, the MWCNT–PVA solution and starch solution were mixed and kept for a day.

This MWCNT–starch–PVA solution was used for electrospinning. A power supply (CPS-60K02VIT, CHUNGPA, Korea) with variable high voltage (maximum voltage of 60 kV)

was used for the electrospinning process. The electrospun fiber was collected by attaching it to the aluminium foil wrapped on a metal drum with a diameter of 15 cm rotating at 1000 rpm. The bias voltage was fixed at 18 kV. The carbonization of the MWCNT–starch–PVA nanofiber web was performed in a vacuum furnace. The electrospun fiber web was stabilized at 250 °C with a ramping rate of 1 °C min⁻¹ for 1 h in air and then carbonization was performed at 500, 700, 1000, 1300, and 1400 °C with a ramping rate of 2 °C min⁻¹ for 1 h under vacuum. After carbonization, CNT/C nanofibers were heat treated at 250 °C for 1 h in air environment to functionalize their surfaces.

2.3. Characterization

The nanofiber morphology was analysed by using a scanning electron micrograph (SEM: XL-30S, Philips) and transmission electron microscope (TEM: Tecnai 20F). The carbon content was analysed by elemental analysis (EA). The transition from amorphous carbon to graphitic was characterized by XRD (D/MAX-IIIC. 3 kW). The functional groups of CNT/carbon nanofibers were studied by FT-IR analysis (FT-Raman, Bruker, Germany). The specific surface and pore size distribution of our samples were characterized by using the Brunauer–Emmett–Teller equation (Tristar3000, Micromeritics, USA). The cyclic voltammetry of CNT/carbon nanofiber electrode without binders or conductive materials was performed in a 1 M H₂SO₄ solution to evaluate the capacitance at the conditions of potential range 0–0.5 V and scan rate 10 mV s⁻¹.

3. Results and discussion

3.1. Morphology of CNT–starch–PVA nanofibers

Accordingly, our strategy to obtain mesoporous carbon materials without using the template method uses natural polymer, starch. Starch^{21–23} has a natural ability to assemble into a nanoscale lamellar structure consisting of crystalline and amorphous regions (Fig. 1a). J. H. Clark *et al.*²⁴ revealed that starch can be converted into a mesoporous carbonaceous material with an average pore carbon nanofiber web providing high surface area, easy access to ions, and a binder-free electrode due to its free-standing shape.

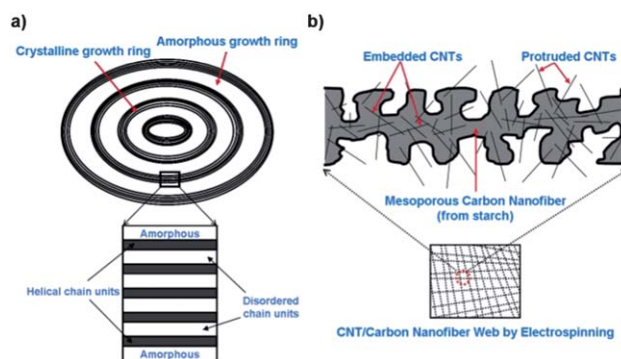


Fig. 1 (a) A schematic of the lamellar structure of starch granule and (b) CNT/carbon nanofiber web consisting of mesoporous carbon nanofibers reinforced with CNTs.

Embedded or protruded CNTs act as a strong reinforcement and high conductive path to enhance the mechanical and electrical properties of mesoporous carbon nanofibers.

Electrospinning is a powerful tool for fabricating thin and flexible organic nanofiber webs through an electrically charged jet of polymer solution or polymer melt. One of the important features of electrospinning is that a suitable solvent should be available for dissolving the polymer.²⁵ When native starch granules are exposed to water vapor or liquid water, they adsorb water and undergo limited, reversible swelling. Heating starch containing limited water results in melting of the starch crystallites and the melting temperature depends on the moisture content. With excess water, melting over 100 °C is accompanied by hydration and profound irreversible swelling, the collective process is known as gelatinization.²¹ This process is necessary for preparing gelatinized starch which produces mesoporous materials when it is carbonized. However, gelatinized starch cannot be electrospun within water solvent. Thus, polyvinyl alcohol (PVA) as a spinning agent was introduced into the fabrication process. With the aid of spinning agent, gelatinized starch was firstly electrospun in water solvent into a web with a large area ($10 \times 10 \text{ cm}^2$), as shown in Fig. 2a. The colour of fabricated web was light grey due to adding small amounts of CNTs. The electrospun starch nanofibers had straight shape with a smooth surface morphology and no defects or beads were found in all areas of the web as shown in Fig. 2b. Individual starch nanofibers showed a cylindrical shape with a diameter of *ca.* 150 nm. CNTs were successfully implanted within a starch nanofiber forming a candlewick-like shape as shown by the scanning electron microscopy image in Fig. 2c. The networking of CNTs within a starch nanofiber shown by the transmission electron microscopy image in Fig. 2d demonstrates that CNTs embedded within starch nanofibers can act as a conductive path and contribute to enhancement of the electrical conductivity of the final mesoporous carbon nanofibers as we expected.

Before the organic fibers are carbonized, chemical alteration is necessary to convert their linear atomic bonding to a more

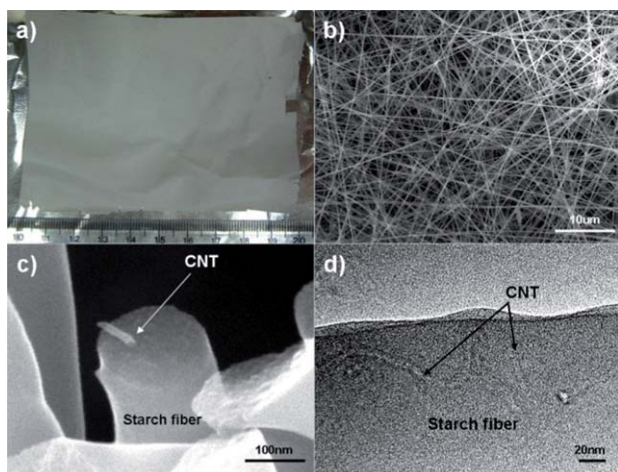


Fig. 2 (a) A light-grey coloured web consisting of starch nanofibers, PVA as the spinning agent, and CNTs, (b) SEM image of electrospun starch nanofibers, (c) SEM image of an individual starch nanofiber with a diameter of *ca.* 150 nm and implanted with CNT and (d) TEM image exhibiting CNTs networking within a starch nanofiber.

thermally stable ladder bonding that does not collapse their fiber morphology. In general, this is accomplished by heating the fibers in air to about 200–300 °C. This causes the fibers to pick up the oxygen molecules from air and rearrange their atomic bonding pattern. Therefore, the electrospun starch nanofibers were stabilized at 250 °C for 1 h in air environment to maintain their fibrous morphology during the high-temperature thermal treatment. After oxidative stabilization, the light-grey-coloured web changed into a brown-coloured one. In addition, the stabilized web was downsized and the starch nanofibers became curlier and more corrugated owing to shrinkage of the porous web during the heat treatment without collapsing their fibrous morphology (see Fig. S1†).

3.2. Effect of thermal treatment on CNT/carbon nanofibers

Once the nanofibers are stabilized, they were heated to a temperature of 700, 1300, and 1400 °C in vacuum (10^{-6} torr). The carbon content of starch nanofibers carbonized at each temperature was over 90% above 700 °C thermal treatment (Table S1†). From the result, we can notice that starch nanofibers were successfully converted into carbon nanofibers over 700 °C thermal treatment. Carbonization can also be verified by the Raman spectroscopy of the nanofiber. Fig. 3 shows the Raman spectrum of CNT/C nanofibers before and after the thermal treatment. Before the carbonization process, only broad and rough peaks were observed showing the presence of CNTs in amorphous carbon fiber. After the thermal treatment performed at 700 °C, two significant peaks were observed at D-band (near 1340 cm^{-1}) and G-band (near 1590 cm^{-1}), which represent disordered and graphitic carbon. At carbonization temperatures as high as 1400 °C, the surface of nanofiber becomes porous due to decomposition of the carbon structure, and the amount of amorphous carbons is increased. Therefore, 1400 °C heat treated CNT/C nanofiber showed a higher I_D/I_G ratio, 1.39, compared to that, 0.97, of 700 °C heat treated nanofiber in the Raman spectrum. Interestingly, the surface of carbon nanofibers heat-treated at 700 and 1300 °C was very smooth as shown by the scanning electron microscopy images in Fig. 4a and b, compared to the carbon nanofibers heat-treated at 1400 °C, which had a highly porous surface as shown by the scanning electron microscopy



Fig. 3 The Raman spectrum of CNT/carbon nanofibers (a) after being electro-spun and air-stabilized at 250 °C, (b) heat-treated at 700 °C and (c) 1400 °C for carbonization.

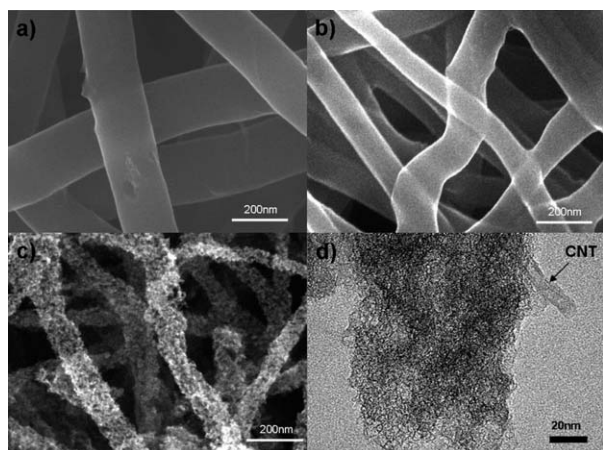


Fig. 4 The scanning electron microscopy images of microporous carbon nanofibers with smooth surface heat-treated at (a) 700 and (b) 1300 °C; (c) scanning electron microscopy (SEM) and (d) transmission electron microscopy (TEM) images of highly mesoporous carbon nanofibers with rough surface heat treated at 1400 °C.

and transmission electron microscopy images in Fig. 4c and d. This highly porous structure is caused by the natural ability of starch. Starch consists of two types of molecules: the linear and helical amylose and the branched amylopectin. In the native form of starch, amylose and amylopectin molecules are organized in granules as alternating semi-crystalline and amorphous layers that form growth rings as illustrated in Fig. 1a. The semi-crystalline layer consists of ordered regions composed of double helices formed by short amylopectin branches, most of which are further ordered into crystalline structures known as the crystalline lamellae. The amorphous regions of the semi-crystalline layers and the amorphous layers are composed of amylose and non-ordered amylopectin branches.²¹ This peculiar nanoscale lamellar structure of starch alternating between amorphous amylose and crystalline amylopectin makes it possible to form a porous carbon structure by converting into an ordered porous structure after it is heat-treated over 1400 °C.

This highly porous carbon nanofiber structure is the first report besides the template method. Generally, in the case of coal, pitch, wood, coconut shells, or polymers such as polyacrylonitrile, micrographitization can occur and some surface or edge functional groups are dissociatively distilled or pyrolyzed in the pre-treatment of activation procedures at 2000–2800 °C and consequently they have most of micropores on their surfaces. In the case of starch, graphitization starts from 1400 °C as shown by XRD analysis (Fig. S2†) and we can notice that the peak of all functional groups of porous carbon nanofibers heat-treated at 1400 °C decreases or disappears as shown in Fig. 5a. From these results, we can infer that carbon nanofibers heat-treated at 1400 °C originated by starch adapt a highly porous structure due to the dissociation and pyrolysis of functional groups by graphitization. However, because these highly porous CNT/carbon nanofibers have no functional groups on their surface as we mentioned before and are hydrophobic, they showed abnormal electrochemical properties (Fig. S3†). Therefore, we activated these highly porous CNT/carbon nanofibers at 250 °C in air environment to functionalize their surfaces. As a result,

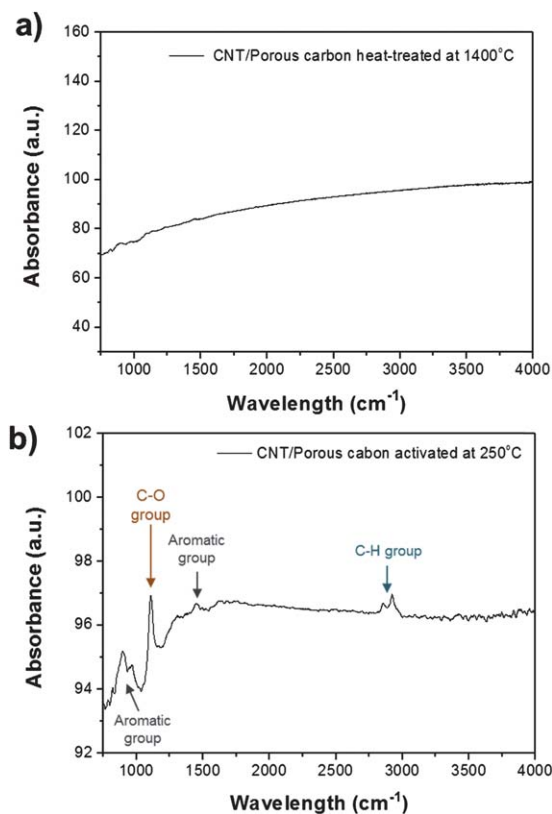


Fig. 5 (a) Porous CNT/carbon nanofibers heat-treated at 1400 °C exhibiting the dissociation and pyrolysis of functional groups and (b) functional groups observed at porous CNT/carbon nanofibers activated at 250 °C by FT-IR analysis.

CNT/porous carbon nanofibers were activated by the ether C–O group (1100 cm^{-1}) and C–H alkyl groups (2850, 2920 cm^{-1}) as shown in Fig. 5b.

3.3. Electrochemical characterization of CNT/carbon nanofibers

The specific surface area (SSA) and pore size distribution of the CNT/carbon nanofibers heat-treated at 700 °C and porous CNT/carbon nanofibers activated at 250 °C were characterized by the analysis of nitrogen adsorption–desorption isotherms at 77 K using the density functional theory. Each sample covered as high as 490 and 350 $\text{m}^2 \text{g}^{-1}$ of the BET surface area. The pore size distribution of CNT/carbon nanofibers heat-treated at 700 °C indicates that they consist of most of micropores with a pore volume of 0.33 $\text{cm}^3 \text{g}^{-1}$, whereas one of porous CNT/carbon nanofibers activated at 250 °C indicates a predominance of mesopores (4.76 nm) with a pore volume of 0.31 $\text{cm}^3 \text{g}^{-1}$ and the porous distribution exhibits a predominantly bimodal nature of the mesopore region as shown in Fig. 6a. From the above analysis, we can notice that the highly porous CNT/carbon nanofibers have mesopores with a diameter of 4.76 nm on their surface as expected in a schematic of our final goal structure.

The final black-coloured web was cut into a rectangular shape ($1 \times 1 \text{ cm}^2$) and its specific capacitance was characterized without mixing any binder using 1 M H_2SO_4 as the electrolyte (Fig. S4†). The electrical conductivity was calculated by the following equation:

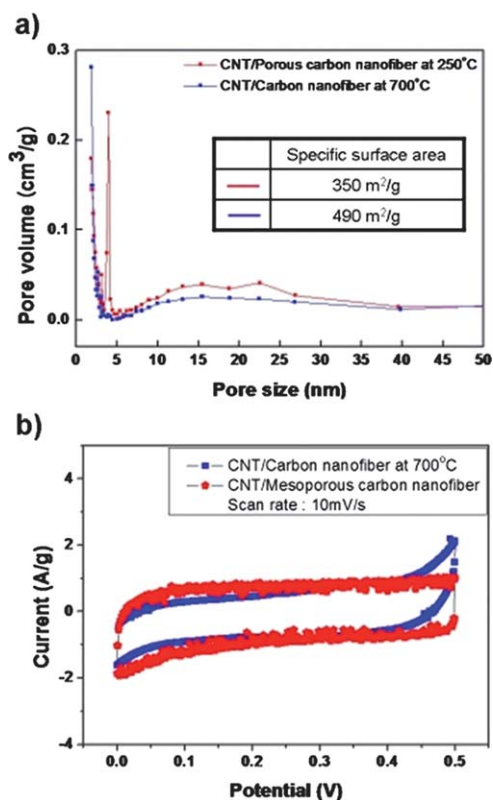


Fig. 6 (a) Specific surface area and pore size distribution of the CNT/carbon nanofibers heat-treated at 700 °C and porous CNT/carbon nanofibers activated at 250 °C and (b) CV curves at 10 mV s⁻¹ of CNT/carbon nanofibers heat-treated at 700 °C and porous CNT/carbon nanofibers activated at 250 °C.

$$\sigma = L/(AR) \quad (1)$$

where R is the electrical resistance in Ω , A is the cross-sectional area in cm^2 , and L is the distance between electrodes in cm. The electrical conductivity of CNT/carbon nanofiber electrode heat-treated at 700 °C and porous CNT/carbon nanofiber electrode activated at 250 °C was as high as 1.068 S cm^{-1} and 2.137 S cm^{-1} , respectively. About 2 times increase in the electrical conductivity of the latter is due to the transition of amorphous to a graphitic structure as shown by the XRD analysis mentioned before.

The electrochemical properties of the CNT/carbon nanofiber electrode heat-treated at 700 °C and porous CNT/carbon nanofiber electrode activated at 250 °C are shown in Fig. 6b. The cyclic voltammetry (CV) tests were recorded in the potential range between 0 and 0.5 V. The CV curve at 10 mV s⁻¹ of the former shows a little deviation from the ideal rectangular shape, but has a high specific capacitance of 132 F due to the high specific surface area of $490 \text{ m}^2 \text{ g}^{-1}$ and high electrical conductivity. This deviation can come from the side reaction of its functional groups such as hydrogen and oxygen as shown in Fig. 4a. On the other hand, the CV curve of the latter shows very small fluctuation due to its functional groups which interact with ions in the electrolyte, but it has a good rectangular shape owing to its mesoporous structure which has good ion accessibility and abundant pore distributions at effective pore sizes of 4.76 nm and a higher specific capacitance of 170 F g^{-1} than the former. This

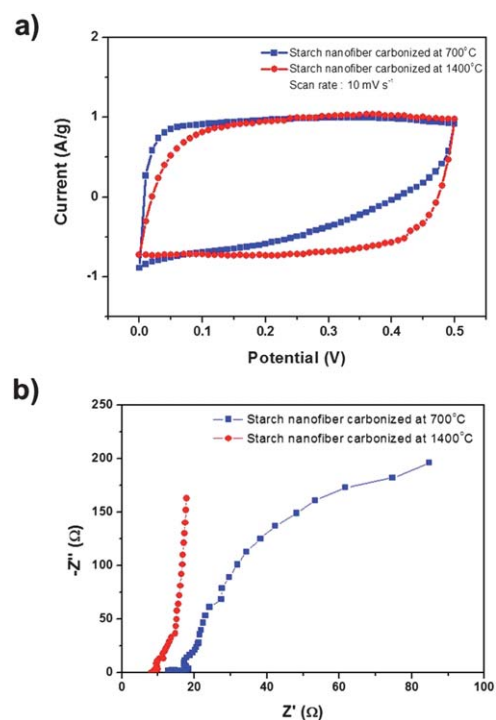


Fig. 7 (a) Cyclic voltammograms of starch nanofibers carbonized at 700 °C and 1400 °C in 1 M H₂SO₄ electrolyte at a scan rate of 10 mV s⁻¹ and (b) impedance plots of starch nanofibers carbonized at 700 °C and 1400 °C.

specific capacitance indicates a highly capacitive nature with good ion accessibility with higher value than other carbon fibers derived from polyacrylonitrile (140 F g^{-1})¹⁷ and CNT/carbon fibers derived from polyacrylonitrile (100 F g^{-1}).²⁶

3.4. Effect of carbon nanotubes in CNT/carbon nanofibers

To identify the role of CNTs in nanofibers, electrochemical properties of starch nanofibers were studied for the comparison between samples with and without CNTs. Starch nanofibers were prepared by the same method as that of CNT/carbon nanofibers and the CV tests were recorded in the potential range between 0 and 0.5 V. Fig. 7 shows cyclic voltammograms obtained from starch nanofibers carbonized at 700 °C and 1400 °C. The voltammogram of nanofibers carbonized at 700 °C shows little deviation from the ideally rectangular profile, indicating a high equivalent series resistance (ESR) of 39 Ω . The voltammetric response of nanofibers carbonized at 1400 °C is also close to the ideal rectangular shape, but exhibited a lower ESR of 14.8 Ω . The most noticeable thing is that the specific capacitance of this mesoporous starch nanofiber was extremely high, $105 \mu\text{F cm}^{-2}$. In general, the specific capacitance of activated carbon using EDLC is $10\text{--}30 \mu\text{F cm}^{-2}$. The observed specific capacitance of the mesoporous starch nanofibers originates not only from the moderate surface area and pore size distributions, as discussed above, but also from the low internal resistance. An ideal polarizable capacitance yields a straight line along the imaginary axis (Z'') in Nyquist plots of impedance. In real capacitors with a series resistance and a low-frequency spike show inclination at an angle of about 45°, representing the diffuse resistivity of the electrolyte

within the pore of the electrode. In Fig. 7b, starch nanofibers that had been carbonized at 700 °C exhibited precisely this phenomenon at low frequency, while those carbonized at 1400 °C showed a response more closely resembling the ideal straight line. Mesopore formation may also increase the diffusivity of hydrated ions in the pore, which would in turn reduce the charge transfer resistance and these electrochemical systems are kinetically fast.

Carbon nanotubes were added to this highly mesoporous starch nanofibers to enhance the mechanical strength and electrical conductivity as well as to provide effective surface area and to prevent dimensional changes or shrinkage due to their superior physical and chemical properties. Fig. 2 and 4 show that CNTs embedded within and protruded out of starch nanofibers can not only act as a conductive path and contribute to enhancement of the mechanical strength but also provide effective surface area of the final mesoporous carbon nanofibers. By adding 1 wt% carbon nanotubes to mesoporous carbon nanofibers, the tensile strength is increased from 50 kPa to 100 kPa (see Fig. S5†). This enhancement of mechanical strength made it possible to fabricate a binder-free electrochemical electrode by the electrospinning method.

The electrochemical properties of porous CNT/carbon nanofiber electrodes with various CNT contents are shown in Fig. 8a. In the case of the CNT/carbon nanofibers which were

heat treated at 1400 °C, the CV curves maintain ideally a rectangular shape and the gravimetric capacitances are increased from 144 to 193 F g⁻¹ as the content of CNTs is increased. In order to understand the resistance associated with the starch nanofiber carbonized at 1400 °C and the CNT/starch nanofiber carbonized at 1400 °C, electrochemical impedance spectroscopy studies were also performed. The Nyquist plots recorded for the starch nanofibers carbonized at 1400 °C, 1 wt% CNT/starch nanofibers carbonized at 1400 °C and 3 wt% CNT/starch nanofibers carbonized at 1400 °C are shown in Fig. 8b. When the CNT content increases, the angle of inclination of the low frequency also increases and 3 wt% CNT/starch nanofibers carbonized at 1400 °C have a very low ESR of 5.1 Ω and low frequency spike at exactly 90° to the x-axis. These data support the hypothesis that the presence of CNTs in the composite decreases the overall resistance of the electrode.

4. Conclusion

In summary, starch was firstly electrospun into the starch nanofibers with diameters ranging from 150 to 200 nm with the aid of a spinning agent (PVA) and used as a carbon source material for the electrochemical capacitor electrode. By using the natural ability of the starch lamellar structure and controlling the carbonization temperature, we successfully fabricated a binder-free electrochemical capacitor electrode material consisting of highly mesoporous carbon nanofibers reinforced with CNTs with a higher specific capacitance (170 F g⁻¹) and electrical conductivity (2.1 S cm⁻¹) than other carbon electrodes derived from synthetic polymers and free-standing CNT electrodes. The high specific capacitance of highly mesoporous carbon nanofiber electrode reinforced with CNTs comes from the high specific surface area and the sufficient pore distributions at effective mesoporous sizes of 3–5 nm. In addition, transitions between amorphous and graphitic structures occurred at a high temperature (1400 °C) and CNT networking within the carbon nanofibers lead to the increase of electrical conductivity of our newly developed electrode material.

Thereby, the research reveals that starch which has advantages in aspects of low cost and environmentally friendly material is an ideal material as the carbon source of electrochemical capacitor electrode and can provide a simple and cheap approach for the fabrication of a binder-free electrochemical capacitor electrode. In the future, we may also see further incorporation of designed mesoporous carbon nanofibers web into fuel cell electrodes, catalysis, and hydrogen storage.

Acknowledgements

This research was supported by a grant (KFR-2007-313-D00362) from the Korea Research Foundation.

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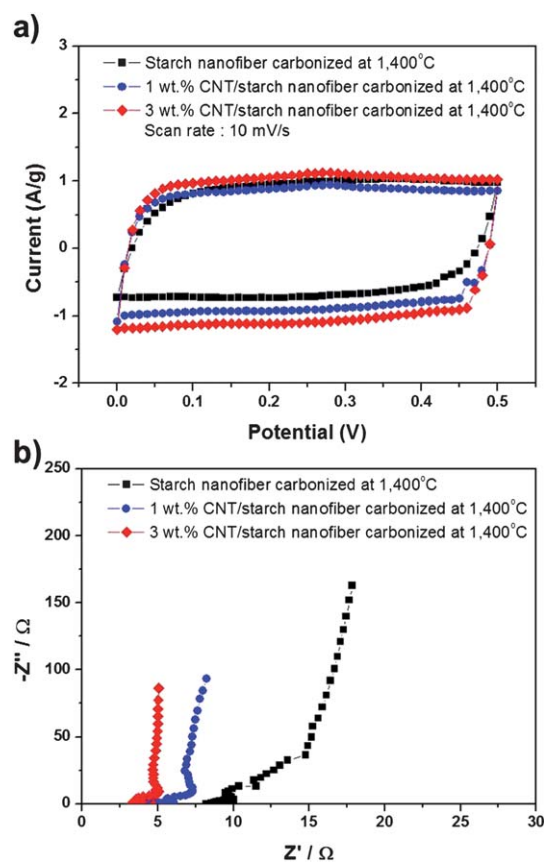


Fig. 8 (a) CV curves of starch nanofibers carbonized at 1400 °C reinforced with 0, 1, 3 wt% carbon nanotubes in 1 M H₂SO₄ at a sweep rate of 10 mV s⁻¹ and (b) the impedance plot of starch nanofibers carbonized at 1400 °C reinforced with 0, 1, 3 wt% carbon nanotubes.

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