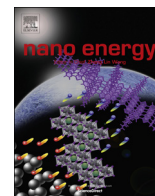




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# Carbonized nanocellulose sustainably boosts the performance of activated carbon in ionic liquid supercapacitors

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## ABSTRACT

Carbonized cellulose nanofibrils (CNF) have been employed to improve the rate performance of activated carbon (AC) traditionally used in supercapacitors. Because of the large amount of surface functionalities, CNF form strongly interconnected composite with AC, which turns into a free-standing carbon nanofibers/AC film after carbonization. In the film, the carbon nanofibers are 'welded' on AC particles and integrate them into one piece of carbon. The interaction between AC and carbon nanofibers, originating from the strong AC-nanocellulose affinity, is much stronger than the traditional physically mixed AC/nanocarbon composite and also significantly reduces the contact resistance in the composite. Conductive atomic force microscope (C-AFM) analysis reveals that the network of carbonized CNF possesses markedly better electron transport efficiency than the AC particles. When tested as supercapacitor electrode at commercial level mass loading, the composite film exhibits 2 times slower capacitance fading at high current and 3 times higher maximum power density than the bare AC. In addition, using the nanocellulose, which is derived from renewable resources, increases the total electrode cost only by a small margin, thereby making the composite a competitive electrode material for electricity storage on a large scale.

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## 1. Introduction

The increasing need for energy storage devices for transportation electrification and smart grids has stimulated active research on electrochemical energy storage technologies. Depending on the balance between energy and power density, electrochemical energy storage solutions can be roughly categorized into two groups: batteries and supercapacitors. When compared to batteries, supercapacitors store about 5–10% of energy, but can work at 10–100 times higher power density, making them excellent energy storage devices to handle pulse energy [1–3]. The most popular supercapacitors on the market are electric double-layer capacitors (EDLC), which use high surface area activated carbons as both electrodes and organic electrolytes with operational potential window of 1.8–2.7 V [4,5].

For supercapacitors, the electrochemical potential window of electrolytes ( $V$ ) is critical in achieving high energy density and power density since both are proportional to  $V^2$ . Therefore, ionic liquids (IL) with potential windows in the range of 3–5 V have

been extensively investigated in recent years as alternative electrolytes [6–9]. However, ionic liquids often suffer from sluggish ion diffusion as a result of their large ion sizes and high viscosity, compared with organic or aqueous electrolytes [6]. To improve the ion diffusion efficiency and achieve high power performance, significant efforts have been made to optimize the structures of carbon electrodes either by tuning the pore size to accommodate larger IL ions [10,11] or employing low-dimensional nanocarbons to decrease the ion diffusion length [12]. Significant improvements in both energy density and power density have been achieved from carbide-derived carbons [13,14], mesoporous carbons [15], carbon aerogels, carbon nanotubes (CNTs) [16], activated graphene [17,18], graphene aerogel [19–21] and many other 1D or 2D carbon materials [22].

In spite of performance achievements obtained using nanocarbons, high production costs may hinder large-scale application. In the foreseeable future, the dominant electrode materials for EDLCs will most likely still be based on low-cost activated carbons (AC), typically derived from petroleum coke and dead trees [23,24]. In the recent past, there has been an increasing interest in tailoring the structures of activated carbon, aiming to improve performance without dramatic increase in cost [25–27]. One such effort has been to composite activated carbons with small amount of nanocarbons, such as CNTs [28–32], carbon nanofibers [33] and

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graphene [34–36]. The role of nanocarbons is to enhance the overall electron transport efficiency in the electrode. However, two carbon materials do not often form strong composite because of the lack of affinity, resulting a poor distribution of nanocarbons in AC.

Recently sustainability and environmental responsibility have been receiving increasing attentions in the energy storage technologies [37–42]. Renewable feedstock, green synthesis route and environmental friendly components have been finding more applications in the battery and supercapacitor technologies [43–48]. Nanocellulose is one of the most promising sustainable nanomaterials [49]. Because of its impressive mechanical strength, excellent flexibility, and large specific surface area [50], nanocellulose has been successfully used as additive to form flexible electrode materials [51,52]. However, being an insulating material, nanocellulose may reduce the conductivity of the electrodes, and may pose challenges when used for high power applications. In order to boost its conductivity, researchers have converted nanocellulose into carbon nanofibers and used them in supercapacitors and batteries [53–56]. Although these carbon fibers show excellent rate performance in supercapacitors, their specific capacitances are limited because of their relatively low specific surface area. Therefore, additional activation is often required [56].

Compared to traditional nanocarbons (e.g. CNTs), nanocellulose have much stronger affinity to guest materials due to the large amount of surface functionalities (–OH). In this work we have taken advantage this property in fabricating better interconnected AC/nanocarbon composites. Mechanically delaminated nanocellulose fibrils (CNF) composited with traditional AC to create a paper-like film. When heated to 800 °C, the insulating CNF were converted into highly conductive carbon nanofibers that wrap around AC particles, serving as electron transport highways in the electrode. Even at very high mass loading of  $\sim 10 \text{ mg cm}^{-2}$ , the carbon film still exhibits significantly higher capacitance than bare activated carbon, especially at high current densities.

## 2. Material and methods

### 2.1. Materials

The high surface area activated carbon (NORIT<sup>®</sup> A SUPRA) was obtained from Sigma Aldrich. The BMPY TFSI ionic liquid electrolyte (> 98%) was obtained from Ionic Liquids Technologies Inc. USA. Mechanically delaminated cellulose nanofibrils (CNF) were purchased from the Nanocellulose Process Development Center at Maine University.

### 2.2. Synthesis of NCAC

The received cellulose fibrils (2.9% suspension in water) were first diluted into a 0.4% suspension. Activated carbon (200 mg) was added to the diluted CNF suspension (250 ml,  $\sim 100 \text{ mg CNF}$ ) under vigorous stirring. After an additional 5 min of stirring, the mixture was sonicated for 10 min with a probe sonicator (100 W). The sonication process generates a significant amount of heat in the dispersion process. To avoid overheating the suspension, a 4-min rest followed each minute of sonication to allow the system to cool down. A damp filter cake ( $\sim 10 \text{ cm}^2$ ) was obtained by vacuum filtrating the well-dispersed AC–CNF suspension (50 ml). After freeze drying, a flexible paper-like AC–CNF film was achieved and noted as AC–CNF. The AC–CNF composite was further heated to 800 °C in argon for 2 h (heating rate:  $5 \text{ °C min}^{-1}$ ), during which the CNF was converted into carbon fibers and yielded a free-standing film composed of nanocellulose derived carbon nanofibers and activated carbon (noted as NCAC).

### 2.3. Structure characterizations

Scanning helium ion microscopy (SHIM) analysis was performed using a Zeiss Orion NanoFAB equipped with Ga FIB. Transmission electron microscopy (TEM) analysis was performed using a JEOL 2100 Lab6 TEM at a 200 kV accelerating voltage. The topography and current maps were acquired using Bruker Dimension FastScan, operated under Peak Force TUNA mode with a Platinum-Iridium coated tip (SCM-PIT tip from Bruker). The NCAC composite was dispersed in ethanol after 5 min sonication. The diluted suspension was casted on Pt coated Si wafer and then dried in vacuum oven at 110 °C before analysis. For the best conductivity and flatness, the coating on Si wafer consists 3 layers, which are thermally grown 500 nm  $\text{SO}_2$ , sputtered 10 nm Ti and 100 nm Pt. A piece of copper tape was used to bridge the Pt coated Si surface and AFM stage. The microphotographs were captured with Nikon H550L microscope. One drop of aqueous dispersion was placed on a glass slide for imaging. Thermal gravimetric analysis (TGA) was performed using a SDT Q600, TA Instruments DSC–TGA, in Ar with a heating rate of  $5 \text{ °C min}^{-1}$ .

### 2.4. Electrochemical measurements

The obtained NCAC film was punched into disks with diameter of 1.4 cm (15 mg for each disc) and used as an electrode. In the test using activated carbon as a reference, electrodes were prepared by mixing the AC with 10 wt% carbon black and 10 wt% PVDF (binder) in N-methylpyrrolidone (NMP) to form a homogeneous slurry. The well-mixed slurry was then spread onto stainless steel spacers with a diameter of 1.4 cm and dried at 110 °C overnight in a vacuum oven. Two symmetrical electrodes separated by a porous polymeric separator were sealed in a 2032 stainless steel coin cell filled with BMPY TFSI. The cyclic voltammetry, impedance analysis and galvanostatic charge–discharge cycling were performed on a Solartron 1470E Multichannel Potentiostat/Cell Test System. The specific capacitance of material, energy density and power density were calculated in 2-electrode setup as  $2 \text{ It/mV}$ ,  $1/8 \text{ CV}^2$  and  $1/2 \text{ IV}$ , respectively; where  $I$  is the change/discharge current,  $t$  is the discharging time,  $m$  is the mass of total electrode materials on single electrode (including carbon black and binder if used),  $V$  is the potential window (after deduction of  $IR$  drop) and  $C$  is the specific capacitance of the active materials.

## 3. Results

### 3.1. Strategy of fabricating carbonized nanocellulose enhanced activated carbons

Fig. 1 shows the concept for developing sustainable energy storage solutions using two renewable materials derived from biomass – cellulose nanofibrils (CNF) and activated carbons (AC). Although AC may not be considered as a typical sustainable material, most of them are produced from renewable biowaste, such as dead trees, bamboo, and coconut shells. The CNF slurry (2.9 wt%) used in this study is received as semitransparent viscous gel (obtained from Nanocellulose Process Development Center at Maine University). The petri dish in upper right corner of Fig. 1 shows a thin layer ( $\sim 2 \text{ mm}$ ) of ultrasonically dispersed aqueous slurry of (0.04 wt%) and a commercially purchased AC (0.08 wt%). The slurry appears to be a cloudy mixture when observed with the naked eye. The photomicrograph of the slurry (bottom right corner) reveals the AC particles are firmly trapped in the loose network of CNF and form a flocculent structure. No AC particles are found in the area void of CNF (also see the full sized microphotograph showing a larger area in Fig. S1). The AC–CNF aqueous

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