CARBON NANOTUBES/NANOFIBERS COMPOSITES FROM CELLULOSE FOR SUPERCAPACITORS

V. Kuzmenko[a,b*], A. M. Saleem[a,c], O. Naboka[a,b], H. Staaf[a], G. Göransson[d], M. Haque[a], V. Desmaris[c], P. Gatenholm[b,e], P. Enoksson[a,b]

[a]*Department of Microtechnology and Nanoscience, Chalmers University of Technology, Kemivägen 9, Gothenburg, SE-41296, Sweden*
[b]*Wallenberg Wood Science Center, Chalmers University of Technology, Kemivägen 4, Gothenburg, SE-41296, Sweden*
[c]*Smoltek AB, Regnbågsgatan 3, Gothenburg, SE-41755, Sweden*
[d]*Department of Chemistry and Molecular Biology, University of Gothenburg, Kemivägen 4, Gothenburg, SE-41296, Sweden*
[e]*Department of Chemical and Biological Engineering, Chalmers University of Technology, Kemivägen 4, Gothenburg, SE-41296, Sweden*
**kuzmenko@chalmers.se*

Keywords: carbon nanofibers, carbon nanotubes, supercapacitor.

Abstract
Cellulose-based carbon nanofibers (CNFs) with high mechanical strength and electrochemical stability were nitrogen-doped and functionalized with carbon nanotubes (CNTs) via two different methods. The diameter of incorporated CNTs was in the range of 1-20 nm. The doping with nitrogen atoms and incorporation of CNTs into the CNFs improved conductivity, while CNTs also increased surface area of the produced material. As a result, the composite materials with capacitance values up to 241 F/g were obtained.

1. Introduction

Flexible sheets made of carbon nanofibers (CNFs) with their well interconnected pores, high mechanical and electrochemical stability are prospective electrode materials for supercapacitors. The porosity is of great importance, as ions are able to diffuse into the cavities, enabling the required ion conductivity. CNFs sustain a considerable uptake of electrolyte solution and enable high ion conductivity; the freestanding nature allows using them without polymeric binder [1,2].

However, the main drawbacks of the CNF material are its relatively low specific surface area and electrical conductivity which leads to low values of specific capacitance. Pseudo-capacitive effect induced by doping and functionalization with carbon nanotubes (CNTs) should solve the mentioned problems and provide CNT/CNF composites suitable for supercapacitors with high power density and long life-cycle performance [3].

As demand on carbon nanostructures continues to grow, renewable resources should be accounted as an alternative to the currently most used CNF precursors: coal tar pitch and synthetic polymers. The biopolymer cellulose is a vast source that could be used for the synthesis of CNFs [4].

In this work, cellulose-based CNFs with high mechanical strength and electrochemical stability were nitrogen-doped and functionalized with carbon nanotubes (CNTs) via two different methods in order to get enhanced electrode materials for supercapacitors.

2. Experimental

2.1. Preparation of electrode materials

The sheets of carbon nanostructures were produced by three consecutive steps of cellulose acetate electrospinning, cellulose regeneration and carbonization. The 17 wt% CA solution in 2:1 solvent ratio of acetone and dimethylacetamide was electrospun at 21°C and 40-60% relative humidity. Regeneration of CA to cellulose without N-doping was made in 0.1 M water solution of NaOH, while doped cellulose samples were obtained by dipping the electrospun CA fibrous mats in 0.3 M solution of NH_4Cl in NH_4OH. The carbonization of all cellulose samples was carried out in a quartz tube furnace in N_2 flow by heating up to 800 °C with the heating rate of 5 °C/min [4].

Functionalization with double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs) was achieved by immersion of cellulose samples into dispersions of DWCNTs and MWCNTs with concentration of 2 mg/mL. Cetyltrimethylammonium bromide was used as a surfactant to prepare the dispersion via heating, stirring, and sonication followed by centrifugation to remove undispersed CNTs [5].

Another type of composite material was made by chemical vapor deposition of carbon nanotubes (cvdCNTs) on top of cellulose-based CNFs. cvdCNTs were grown by thermal chemical vapor deposition at 700 °C using iron as a catalyst, acetylene as a carbon source, and hydrogen as a carrier gas. The time of growth was 10 minutes.

2.2. Characterization

The morphology of samples was investigated with *Scanning Electron Microscopy* (SEM, Leo Ultra 55 FEG SEM, Zeiss) at the acceleration voltage of 3 kV. *X-ray Photoelectron Spectroscopy* (XPS) was performed with the Quantum 2000 scanning ESCA microprobe from Physical Electronics.

Capacitance measurements were carried out by a three electrode system with carbon nanostructures as working electrodes, Ag/AgCl (saturated KCl) as reference electrode, Pt net as counter electrode and 1 M KOH as electrolyte. Capacitive behavior of the composite electrodes was studied using a potentiostat (Gamry Reference600) controlled by a computer using a Gamry Echem Analyst. To explore the capacitive performance, all the cyclic voltammetry (CV) tests were done in the voltage range of -0.4 V to 0.4 V with different scan rates.

3. Results and discussion

3.1. Morphology and surface properties of the electrode materials

Carbonization of pure electrospun cellulose samples results in the formation of 25-40 μm thick carbon sheets consisting of fibers with 20-180 nm diameter (not shown here), and

electrical capacitance of 11 F/g. Impregnation with NH_4Cl before carbonization allows obtaining N-doped CNFs and electrical capacitance of 20 F/g. Thermogravimetric analysis also showed the increase in the carbon yield of the impregnated samples from 12% to 20%. According to x-ray photoelectron spectra carbon fibers synthesized in the presence of NH_4Cl contained nitrogen embedded into the carbon structures in the form of pyridine, aromatic amines or pyrrole and quaternary nitrogen in a form of pyridinium ion [4]. The diameter of fibers is 70-400 nm (Fig. 1A), larger than for the samples carbonized in the absence of NH_4Cl. In both cases the fibers look quite smooth.

The functionalization of CNFs with CNTs is clearly seen in Fig. 1 (B-D). For the composite material containing DWCNTs this effect is less visible, while for the other two, with MWCNTs and cvdCNTs, many CNTs with diameter 1-20 nm can be found attached to the surface. It proves both methods of CNT functionalization to be successful in this study. Surface area of all the samples should obviously be increased after functionalization with CNTs.

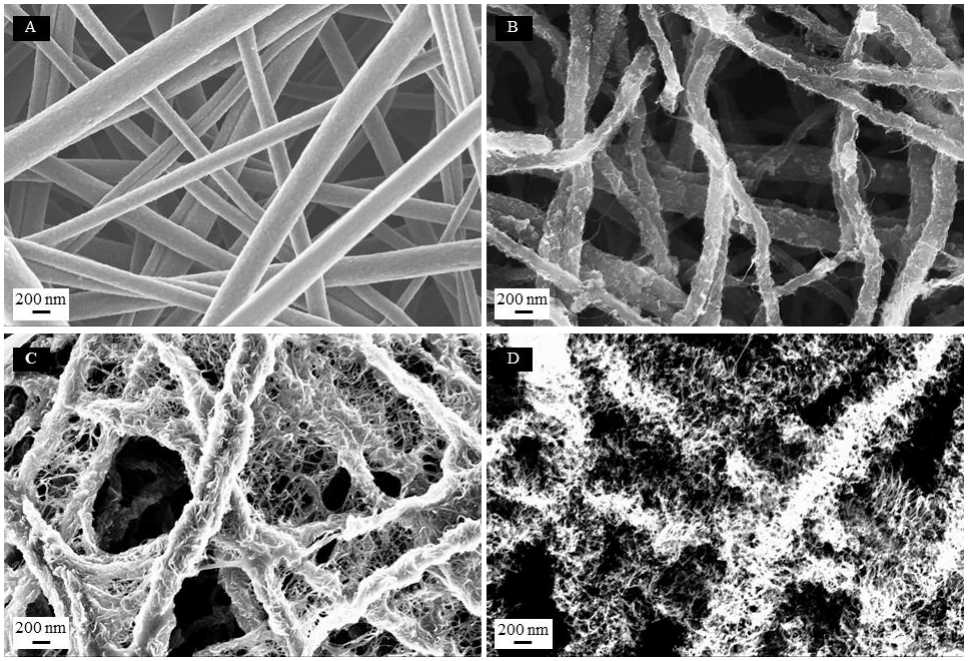

Figure 1. SEM images of N-doped CNFs: (A) without CNTs; (B) with DWCNTs; (C) with MWCNTs, (D) with cvdCNTs.

3.2. Electrochemical analysis

In Figure 2A typical variations of the capacitance of the synthesized electrode materials depending on different scan rates are shown. The comparison of the CV curves of different nanostructured materials is presented in Fig 2B.

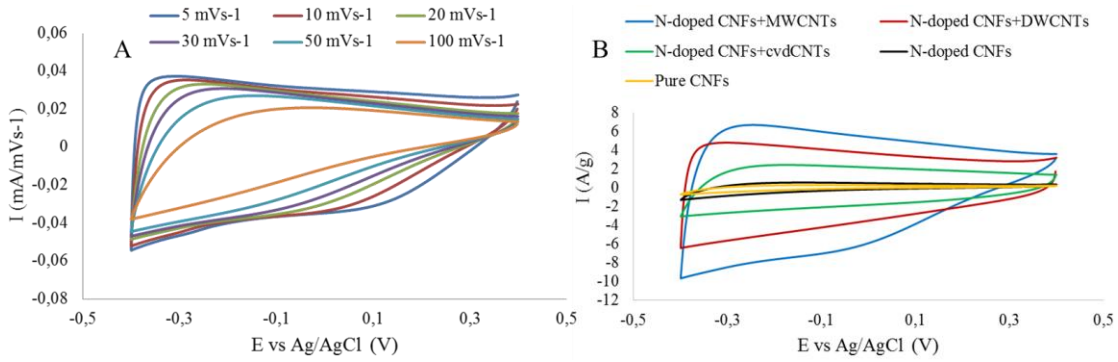

Figure 2. A. CV curves of the N-doped CNFs + MWCNTs at different scan rates. B. Comparison of CV curves at 20 mVs^{-1} for different electrode materials.

In general, N-doped CNFs functionalized with MWCNTs, DWCNTs and cvdCNTs revealed superior specific capacitance (241 F/g, 163 F/g and 89 F/g, respectively, at scan rate of 20 mVs^{-1} with the potential window ranging from -0.4 V to 0.4 V). It can be explained by the higher surface area and conductivity of these CNF/CNT composite materials compared to pure CNFs and N-doped CNFs.

4. Conclusions

As can be observed, functionalization of CNF led to the composite materials with higher capacitance values. This positive effect can be explained by few factors. First of all, doping with nitrogen atoms and incorporation of CNT into the CNF should improve conductivity (electrode's ability to transfer charges), while CNT also increase surface area (electrode's ability to uptake electrolyte and accumulate charges). Concluding all from above, carbon nanotubes/nanofibers composites from cellulose are prospective electrode materials for supercapacitors.

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