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Thin films from functionalized carbon nanotubes using the layer-by-layer technique

Timo Bohnenberger [a,*], Lidija D. Rafailovic [b], Christian Weilach [c], David Hubmayr [a], Ulrich Schmid [a]

[a] Institute of Sensor and Actuator Systems, Vienna University of Technology, Floragasse 7, A-1040 Vienna, Austria
[b] CEST Centre of Electrochemical Surface Technology, Viktor Kaplan Strasse 2, 2700 Wiener Neustadt, Austria
[c] Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria

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ABSTRACT

In this study the surface of carbon nanotubes is functionalized to generate thin films with a highly porous network structure, as it is desired for electrode materials in electrochemical energy storages. To do so, the nanotubes are carefully treated in acids and analyzed to determine optimum deposition parameters.

1. Introduction

In the recent years, many fundamental as well as application oriented research activities have been done in the field of CNTs. Apart from having superior mechanical properties CNTs are especially attractive as a high surface area material when they are targeted via a porous network structure. These specific properties can be most beneficially used in a wide range of applications such as in filtration [1–3] and in electrochemical devices [4–7]. Especially in the latter case, electrodes can be formed with superior properties for an efficient device operation compared to activated carbon mostly used nowadays. In detail, CNT networks promise to provide enhanced electrical conductivity and to be tunable in pore size distribution. This specific property is of utmost importance in supercapacitor technology, as mesoporous structures with a pore size around 7 nm are most efficient in providing surface area for double layer capacitance [8–11]. In general, there are two standard approaches reported in literature to form thin films of carbon nanotubes. In many studies various vapor deposition techniques were applied to form forests of vertically aligned nanotubes on metallic substrates [12–14] which have in fact good ion accessibility to the network, but there proved to be a limit of the number of nanotubes per square restricting the density of such structures. Secondly, electrophoretic deposition [15,16] has fast kinetics and allows good control over the generated CNT films, but it requires substrates with good electrical conductivity. In contrast, the LbL assembly can be performed in principal on every substrate which provides sufficient surface charges. This charge can be measured as Zeta (ζ)-potential and should reside in the range of $\pm$ (40–60) mV for stable film morphology [17]. Mainly nanocomposites of CNTs and weak polyelectrolytes were realized by LbL technique and evaluated so far [18–20]. To ensure, however, the enhanced electrical conductivity provided by the pristine CNTs, the focus of this study is on the realization of networks made only of pure nanotubes [21] instead of composite structures. To reach this goal it is essential to investigate in detail the characteristics of the pH dependant surface charges.

CNT-based films are made by alternately dipping a cellulose nitrate substrate into dispersions of complementary functionalized CNTs. These dispersions have to be carefully prepared to adjust their ζ-potential at a level high enough to result in good film stability. In addition, the preparation procedure includes an efficient purification by a treatment in concentrated acids. Also, the ζ-potential of functionalized CNTs is compared to common surfactants such as SDS and CTAB, which are often used to implement charges on colloids. In case of the CNTs, the negative surface charges are provided by carboxylic acid groups [22] attached to the tubes' side walls and positive charges that originate from amine groups [23].

2. Experimental details

MWNTs were purchased from Nanocyl. They were functionalized and sonicated with a concentration of 0.1 $mg \cdot ml^{-1}$ either in pure DI-water or as pristine MWNTs in the presence of a surfactant. For this purpose, a Hielscher Sonicator UP400S with external cooling

Abbreviations: CNT, carbon nanotubes; MWNT, multiwalled carbon nanotubes; LbL, layer-by-layer; SDS, sodiumdodecylsulfate; CTAB, cetyl trimethylammonium bromide; DI, deionized; EDC, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide; Sulfo-NHS, N-hydroxysulfosuccinimide; XPS, X-ray photoelectron spectroscopy; PAH, poly(allylamine hydrochloride); PSS, poly-styrenesulfonic acid; PAA, polyacrylic acid; AFS, atomic sensitivity factor; SEM, scanning electron microscopy; BE, binding energy.

* Corresponding author. Fax: +43 1 58801 36698.
E-mail address: timo.bohnenberger@tuwien.ac.at (T. Bohnenberger).

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circuit was used. The cooling prevented an excessive formation of gas bubbles due to the increase in temperature during operation. Otherwise, this would lead to a substantial drop of ultrasonic energy transfer from the sonotrode into the dispersion. For the preparation of a stable dispersion without the addition of any surfactants, the –COOH groups were created by refluxing the CNTs at 75 °C in a mixture of concentrated H_2SO_4/HNO_3 (98%/70%) with a ratio 3:1 for 2 h and 4 h, respectively. The CNTs were cleaned thoroughly by filtering them through a membrane and excessive rinsing in deionized water. Afterwards, they were dried under nitrogen flow at 50 °C. To create amine functionalized nanotubes, the originally oxidized ones were treated in a bath of $SOCl_2$ at 75 °C for 6 h to chlorinate the –CO groups. Next, toluene was added to the bath and the temperature was increased to 120 °C so that the toluene evaporated and drove the acid out of the distilling flask. To free the tubes from any acidic residues, they were cleaned again as described. This step was followed by refluxing them for 24 h in a solution of ethylenediamine in dehydrated toluene (ratio: 1:1), which replaces the Cl-atoms by a molecule with a NH_2-tail. Finally, the nanotubes were cleaned and dried again. Additional dispersions were made, using pristine MWNTs in DI-water, but with addition of 0.01 $mg \cdot ml^{-1}$ SDS or 0.03 $mg \cdot ml^{-1}$ CTAB, respectively. Also, a combination of both approaches was made, dispersing MWNT-COOH with addition of SDS and MWNT-NH_2 with CTAB.

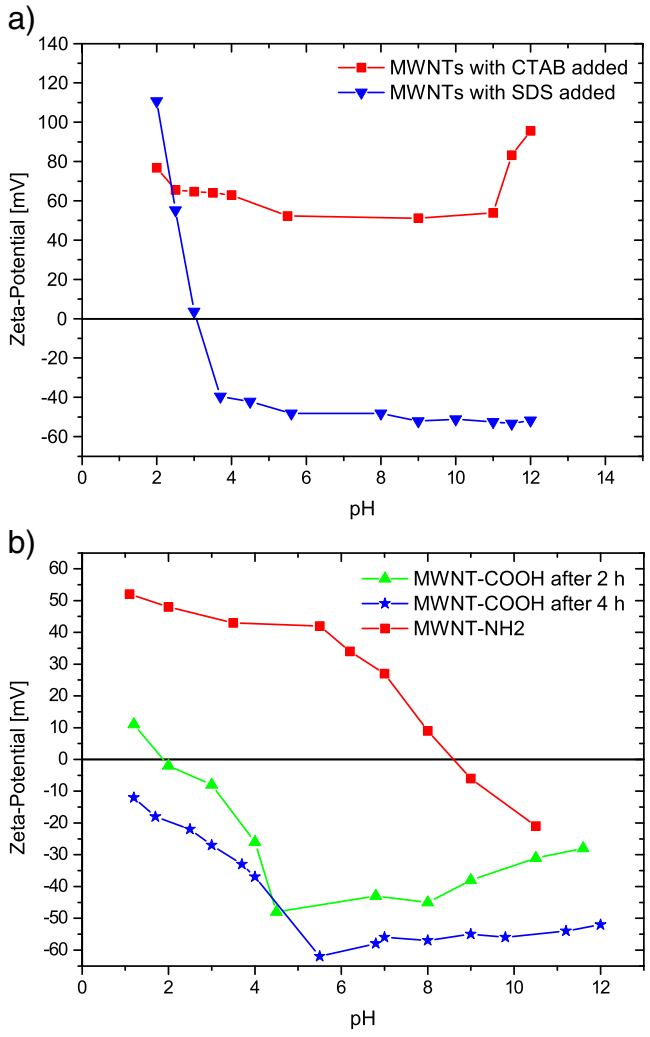

Fig. 1. ζ-Potential measurements for a) pristine and functionalized CNTs dispersed with SDS or CTAB and b) dispersions of modified CNTs without any surfactants.

Thin films of carbon nanotubes were made by alternately dipping a membrane of cellulose nitrate in dispersions with positive and negative ζ-potential for at least 15 min. Between the single steps, the sample was washed in deionized water three times for 3 min each to get rid of any weakly attached nanotubes.

To finish the pure nanotube thin film, it was dipped for 1 min into a crosslinking agent so that the single tubes become covalently bonded to make the film more durable. As agent 0.1 mol of EDC in water was used. To improve the efficiency of the reaction, 0.1 mol Sulfo-NHS was added to stabilize the carbodiimide in an aqueous solution.

The characterization of the functionalized CNTs was done by XPS with a non-monochromatic Al/Mg dual anode and a PHOIBOS EA 150 hemispherical analyzer. To determine the condition of highest Zeta (ζ)-potential of the dispersions an Acoustic Spectrometer DT-1200 was used, scanning the amount of surface charges depending on the pH value.

The membranes were weighed before and after the dipping process in a Sartorius analytical balance to monitor the progress of nanotube adsorption per cycle. The surface characteristics of the CNT-based thin films after the dipping process were analyzed using a Hitachi SU8030 scanning electron microscope. Electrical measurements have been done by van-der-Pauw method.

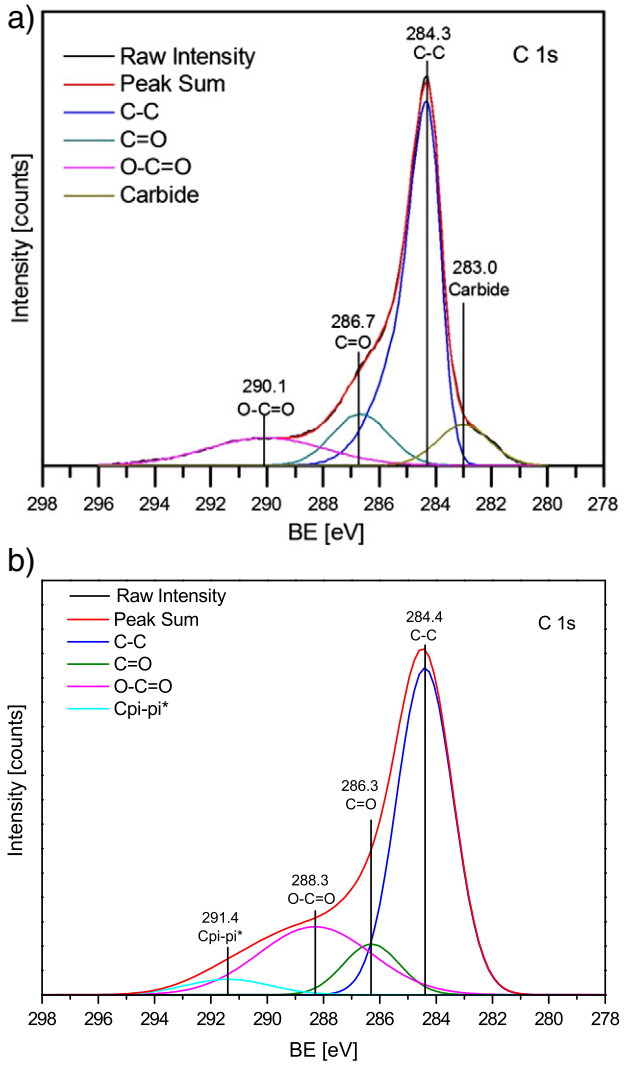

Fig. 2. XPS characteristics representing the different species in the C1s region after a) 2 h and b) 4 h treatment with acids by plotting measured intensity vs. binding energy. It is evident that the amount of carboxylic groups is increased by acid treatment while this is also a good method to remove any carbide.