



Layer-by-layer approach for deposition of pure carbon nanotubes and composite films for use as electrodes in electrochemical devices



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ABSTRACT

A series of thin films of carbon nanotubes (CNT) was made using the layer-by-layer technique. Experiments were conducted to investigate the need for polymer incorporation since pure CNT films are considered too brittle for application. However, the transition to a CNT–polymer composite material limits its suitability for many applications such as electrode material in electrochemical devices. This is due to the high electrical resistance of more common polymers. This study will explore the mechanisms of film growth and analyze the resulting material in terms of porosity and electrical conductivity for a pure CNT and a composite approach.

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1. Introduction

Since the discovery of carbon nanotubes (CNT) in 1991 [1] and the beginning of the investigation of their outstanding mechanical and electrical material parameters, much research has been invested to make the most beneficial use of their properties in macroscopic structures. While single CNTs are unchallenged in their features considering the high Young's modulus or the ballistic transport of electrical charges [2], many technical challenges hinder the applicability of CNT films. The contact resistance between the tubes and the limited amount of pathways dramatically reduce the overall sheet conductivity compared to the conductivity of a single tube [3]. In addition, mechanical stability is a common problem, as network structures held together only by van der Waals forces are prone to erosive influences [4]. To overcome these drawbacks, composite materials made from CNTs and polymers were developed to combine the advantages of both materials [5–10]. Typically, CNTs are embedded in a polymer matrix that provides mechanical ductility to the film. Much research focuses on the optimum polymer content to increase the film's mechanical toughness without inhibiting the current flow via the inter-CNT contacts [11,12].

When thin films made by self-assembly of nanoparticles are considered, the specific properties of the resulting films strongly depend on the molecular structure of the used colloids. To allow a more independent engineering of the film's properties, a template assisted approach has to be used, trapping the particles in the non-equilibrium state of the desired configuration. One of these methods is the so-called layer-

by-layer (LbL) technique, in which an electrically charged substrate is dipped alternately in dispersions of oppositely charged colloids. This method allows very good control of the film thickness, density, and porosity. In addition, it is also well suited for creating films with multiple functionalities by changing layer materials in between.

In this study, the LbL method is used to make films consisting of either pure CNT or a polymer–CNT composite for application as electrode material in electrochemical energy storages [13,14]. This application requires good electrical conductivity, high porosity, and a high resistance to corrosive influences [15]. Since the LbL approach allows such good control of the film properties, it is perfect to compare a pure CNT and a composite approach with respect to this application.

2. Experimental Details

Multi-walled carbon nanotubes (MWNT) were purchased from Nanocyl and COOH-functionalized in a bath of concentrated sulfuric and nitric acid (3:1) for 4 hours at 75 °C. X-ray photoelectron spectroscopy (XPS) measurements confirmed that the share of carboxylic acid groups lies at 12.1% after this treatment. To generate amine groups on the MWNT shells, the previously carboxylated tubes were chlorinated in thionyl chloride for 6 hours at 75 °C. This converted the carboxylic acid groups into acylchloride groups. The acid was removed by distillation and replaced by a mixture of anhydrous toluene and ethylene diamine (1:1) before being refluxed for 24 hours at 75 °C. This process leads to the formation of amine groups that are bound to the MWNTs via amide bonds. The following XPS measurements confirmed an amine content of 2%, along with a reduction of COOH groups to 6.8%. To prepare the pure CNT dispersions for the deposition process, the functionalized tubes

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were sonicated in pure deionized (DI) water using a Hielscher UP400S tip sonicator.

The dispersions for the composite films were made in the same manner but with an additional 0.2 wt.% poly(ethylenimine) (PEI) to the aminated dispersion. This weak cationic polyelectrolyte can be charged over a wide pH range. In this special case, the dispersion was adjusted to a pH of 7. As a method of deposition, an LbL approach was used with a substrate of polished silicon. The silicon was cleaned in piranha solution (98% H₂SO₄/70% H₂O₂ 1:3) for 20 min at 70 °C. Thin films were made by dipping the substrate alternately into the MWNT-COOH and -NH₂ dispersions with extensive rinsing in DI water three times for 3 min each between the single steps. The silicon was masked at one side by an adhesive tape to form a sharp edge for measurement of thickness.

To establish covalent bonding between the single layers of nanotubes, the sample was either annealed under nitrogen atmosphere for 2 hours at 150 °C or dipped into a 0.1 mol solution of a cross-linking agent 1-ethyl-3-(3-dimethylaminopropyl)carbo-diimid (EDC).

Surface analysis of the samples was made in an FRT MicroProf 100 chromatic white light sensor, which offers the possibility of measuring the film thickness contact-free over a large area. In order to investigate the corresponding microstructure of the CNT network, a Hitachi SU8030 scanning electron microscope (SEM) was applied. Additional information regarding surface roughness was extracted from an Asylum Research MFP-3D-SA atomic force microscope (AFM) using a silicon cantilever. Electrical characterization was done in a Van der Pauw measurement set-up at room temperature.

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. Electrochemical cyclovoltammetry was done using a potentiostat PGU 10 V-1A-IMP-S.

3. Results and discussion

The most basic requirement for materials suitable for use as electrodes is good electric conductivity. CNTs fulfill this requirement well, which is why the CNT content within the films should be as high as possible. By adding carboxylic groups to the exterior shell of the CNTs, they become negatively charged and can be used in an LbL approach to make thin CNT films. Thus far, the positive charges come from a polymer solution [5,16–18]. The addition of charged polymers to the composition of the deposited films resulted in a decrease in the film's electric conductivity, which made them useless as electrodes. This study provides two possible solutions for this problem and compares the two. First, surface-modified MWNTs were used as raw material for the deposition steps resulting in a pure CNT thin film, with amine MWNT-NH₂ as the positively charged part. Second, a CNT-polymer compound was made, with PEI added to the dispersion of the positively charged amine MWNTs. In this way, the repulsive forces between the like charged polymer molecules and the CNTs give better stability to the dispersion. However, most importantly, the two materials compete against each other during the adsorption process to a negatively charged sublayer. This ensures a high CNT content within each layer of the film. The combinations of charged particles used for multilayer formation are given in Table 1.

When the treated silicon wafer is dipped into an aqueous solution, highly polarized silanol groups dissociate and add negative charges to the surface of the substrate. The degree of ionization depends on the pH value of the surrounding solution and can be measured as zeta-

potential. The corresponding electrostatic forces allow the adsorption of opposite charged particles, like amine functionalized CNTs and PEI molecules (if added), that move toward the substrate. Since the electrostatic interactions strongly depend on the distance, and since CNTs are very stiff, many positive charges are not bound to the substrate after adsorption but extend into the bulk dispersion. This mechanism is called overcompensation and is a key element to the formation of multilayers. To get rid of weakly adsorbed material, the sample is extensively washed in DI water. Afterward, the sample is dipped into a dispersion of CNT-COO⁻ and adsorb to the now positively charged sample, thus overcompensating it. After an additional washing step, one cycle is completed and a so-called bilayer (BL) is formed on the silicon. In this way, limitless numbers of bilayers can be made.

Since the amount of charge at the CNTs depends on the degree of ionization or protonation of their functional groups, zeta-potential measurements were made to correlate the charge density with the pH of the dispersion (Fig. 1).

According to the standard given by the American Society for Testing and Materials [19], good film stability requires a zeta-potential of at least ± 30 mV. For the carboxylated MWNTs, this is achieved for pH > 3.8. NH₂ functionalized MWNTs meet this requirement for pH < 7. Dispersions with PEI added fulfill the requirement within an even broader pH region. Hence, a deposition condition of pH = 7 was chosen to charge the functional groups, allowing for the formation of multilayers via electrostatic bonding.

To allow a deposition procedure as quick as possible, experiments were made considering the dipping time. When dipped into a dispersion of charged particles, their adsorption to the substrate surface will stop, when the substrate's original charge is overcompensated and the further approach of particles from the bulk dispersion is prevented by coulomb repulsion. Therefore, measurements of film thickness vs. dipping time, given in Fig. 2, reveal a saturation effect for film growth.

As shown, the rate of adsorption is linear with time until at around 15 min, when the predicted saturation comes into its own. Derived from these results, the dipping time was fixed at 15 min for all further experiments.

Fig. 3 shows the result of the measurements regarding the growth rate of films made from pure CNT as well as the CNT-PEI composite. As expected, the film growth of the pure CNT film is linear with the number of dipping cycles. This confirms the high reproducibility claimed by the LbL technique. As can be seen, the films made from the composite are slightly thicker than the corresponding pure CNT films and show a deviation of linear growth for high numbers of BL. There are many reports in the literature of exponential film growth via LbL

Table 1
Combinations of dispersions used for multilayer formation.

	Negatively charged	Positively charged
Pure CNT	MWNT-COOH	MWNT-NH ₂
Composite	MWNT-COOH	MWNT-NH ₂ + PEI

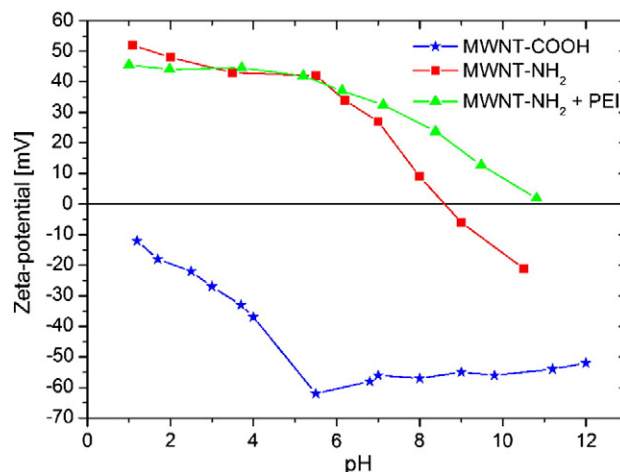


Fig. 1. Zeta potential measurements of the used dispersions according to Table 1.

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