32 Integration of Carbon Nanotubes in Microelectrode Arrays by Microcontact Printing and Electropolymerization for Neurostimulation and Biosensing Applications

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32.1 Background

Electrical recording and stimulation of brain tissue in vitro and in vivo is widely used to gain an understanding of the central nervous system (CNS) and in the development of neuroimplants for the treatment of disorders like parkinson or epilepsy. Another important tool for the investigation of CNS disorders is the analysis of neurotransmitters such as dopamine.

The interface between the electrical device and the brain tissue in vitro or in vivo typically consists of a metal electrode \[1, 2\]. In order to improve signal to noise ratio and cell viability, efforts have been made in electrode surface modification using carbon nanotubes (CNT).

Neuronal cells have shown exceptional viability and efficient integration with layers comprised of CNT \[3, 4\]. CNT are biocompatible and biostable and form layers that exhibit a large effective porosity and surface area. This results in very favorable charge transfer capability \[5\]. Moreover, it has been shown that CNT modified electrodes exhibit increased sensitivity towards dopamine \[6\].

CNT layers are therefore considered an attractive candidate for the fabrication of electrodes in neuroprostheses as well as in vitro and in vivo diagnostics. The ultimate goal of this research consists in robust technologies to fabricate mechanically stable, micropatterned layers of CNT and to integrate them into neuroprostheses and biosensors.

32.2 Concept

Two methods are proposed to further the aim of developing multipurpose CNT-electrodes: Microcontact printing (\(\mu\)CP) \[7\] can be used to directly deposit CNT onto any surface while, by electropolymerization, CNT are embedded in a matrix of conductive polymer like polypyrrole or poly(3,4-ethylenedioxythiophene) (PEDOT) \[5\].
32.3 Materials and methods

32.3.1 Microcontact printing (µCP)

For µCP, micromoulds were fabricated from glass, patterned using photolithography and etching in buffered hydrofluoric acid. Stamps were cast in these moulds from polydimethylsiloxane (PDMS). Carboxylized multi-walled CNT were suspended in deionized water and filtered to obtain a homogeneous film (see Fig. 1a). CNT were then transferred from the filter to the PDMS stamps and printed onto multielectrode arrays (MEA). A fine placer (Finetech, Berlin, Germany) was used to align the stamp with respect to the electrode array.

32.3.2 Electropolymerization

Electropolymerization was carried out using suspensions of ethylenedioxythiophene (EDOT, 0.02 M), Poly(sodium-p-styrenesulfonate) (Mₜ ≈ 70,000 g/mol; 1%) and carbon nanotubes (0.03%). Poly(styrenesulfonate) (PSS) fulfills 3 different functions: it serves (i) as a conducting salt for electrodeposition, (ii) as dispersant for CNT by polymer wrapping [8] and (iii) as counterion for the positively charged PEDOT chains (see Fig. 1b).

The deposition was performed under ambient conditions in a three electrode system under galvanostatic control with current densities between 35 and 140 pA/µm² or potentiostatic control at U = 1 V vs. Ag/AgCl. The counter electrode is integrated in the MEA and either Au or TiN micro-electrodes served as working electrodes.

Fig. 1: (a) Procedure employed for microcontact printing of CNT onto MEA: CNT are dispersed, centrifuged and filtered. The CNT layer is transferred to the MEA using microstructured PDMS stamps. (b) Procedure used for electropolymerization of PEDOT and CNT on microelectrode: CNT are dispersed by wrapping in poly(styrenesulfonate) and EDOT is added to the aqueous solution. CNT are embedded during electropolymerization of PEDOT.
32.4 Results and discussion

32.4.1 Microcontact printed (µCP) CNT

In particular, µCP allows for the deposition of CNT layers on insulators and on materials with low temperature stability. The method yields well defined microstructures on electrodes as well as on insulators (Fig.2). Annealing at 330°C under N₂ during 30 minutes leads to a great improvement in conductivity and homogenization of the electronic characteristics.

Film thickness is controlled via the concentration of CNT in suspension. In order to determine the concentration of CNT, UV-VIS spectra are measured. The maximum absorption at 247 nm is proportional to the CNT concentration and film thickness of printed CNT (Fig.3).

![Micrographs of microcontact printed CNT on MEA](image1)

**Fig.2:** Micrographs of microcontact printed CNT on MEA: Optical microscope images (left and middle) confirm the well defined microstructure. SEM micrograph (right) shows the homogenous surface of the microelectrode.

![UV-VIS absorbance](image2)

**Fig.3:** UV-VIS absorbance of aqueous CNT-suspension before µCP. The absorbance (at 247 nm) of filtered volume (50 ml) is proportional to film thickness of printed CNT (n = 4, error bar: ± SD).
32.4.2 Electropolymerized PEDOT-CNT composites

Embedding CNT in conducting polymer creates a porous and highly crosslinked composite material (Fig. 4). The large surface area of the porous material in combination with the high conductivity of PEDOT and CNT result in very low impedance as shown in fig. 5. Here, three different PEDOT-CNT electrodes are compared to a bare Au microelectrode. The impedance is decreased over the whole frequency range. The higher the charge passed during deposition, the lower the impedance at lower frequencies and the higher the capacity of the electrode. Low impedance and high capacity of PEDOT-CNT electrodes make them good candidates for neuronal recording and stimulation.

![Image](image1.png)

**Fig.4:** SEM micrographs of porous and highly crosslinked PEDOT-CNT composite on microelectrode

![Image](image2.png)

**Fig.5:** Impedance spectra of PEDOT-CNT electrodes. Deposition was performed at 50 nA for 50, 100 and 200 s (2.5, 5, 10 µC, respectively).

32.4.3 Application: Measurement of Neurotransmitter Dopamine

Dopamine measurements were performed to prove the applicability of CNT electrodes in neurotransmitter sensing. Dopamine concentrations were detected at a minimum of 1 µM. Fig.6 shows cyclic voltammograms of a 100µM dopamine solution in PBS recorded at bare TiN, µCP and
PEDOT-CNT electrodes. CNT electrodes, especially those from µCP, show fast electron transfer as compared to TiN. The oxidation potential of dopamine is decreased significantly. The electron transfer at PEDOT-CNT electrodes is not as fast as at µCP electrodes but still faster than at bare TiN. However, the composite material can be advantageous concerning stability and electric properties.

![Graph showing I/V characteristics](image)

**Fig.6:** Measurement of dopamine (100µM in PBS) at bare TiN electrode, PEDOT-CNT electrode and CNT electrode from µCP. The oxidation potential of dopamine is lowered at CNT electrodes.

### 3.2.5 Conclusion and Outlook

µCP and electropolymerization have been used to generate well defined micropatterns of CNT on microelectrodes. Coatings display favourable electrical properties like low impedance and high capacity. Furthermore, CNT-modified electrodes show increased sensitivity for dopamine detection.

Current studies are focussing on improving mechanical stability as well as lowering the detection limit for dopamine sensing.

An extended account of the results of this work is in preparation and will be presented soon [9].
32.6 References


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