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Chemically Modified Carbon Nanotubes: Synthesis and Implementation*

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Carbon nanotubes (CNTs) are an allotropic form of carbon, in which all carbon atoms have sp^2 hybridization. They exist in two forms: as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs can be described as hexagonal networks of carbon atoms that have been rolled into seamless cylinders with diameters close to 1 nm. MWCNTs can be considered as coaxial assemblies of SWCNT cylinders; one within another, with the distance between tubes being approximately equal to the distance between layers in natural graphite. The length of the carbon nanotubes is about four orders of magnitude higher than their diameter, therefore they are called one-dimensional structures.

CNTs possess unique electrical and mechanical properties, but many of their potential applications require chemical modification. Synthetic routes for noncovalent and covalent modifications already exist. As for the latter, two main approaches for functionalizing CNTs have been implemented: (*i*) end/defect-site derivatization and (*ii*) sidewall derivatization. However, examples of covalent sidewall derivatization are limited and generally require highly reactive carbenes, free radicals, or azomethine ylides [1].

We report here on CNT derivatization with chemical moieties possessing specific recognition sites or electroactive (redox) groups. Both end/defect-site and sidewall derivatization were performed on SWCNTs, as well as on MWCNTs (Figs. 1 and 2).

Centrifugation was found to be a very convenient method for isolation and purification of modified carbon nanotubes.

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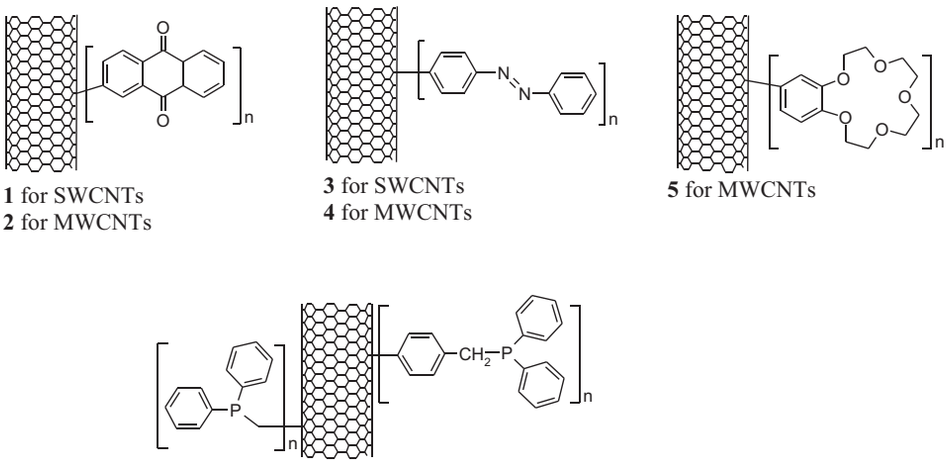


1 for SWCNTs
2 for MWCNTs

3 for SWCNTs
4 for MWCNTs

5 for MWCNTs

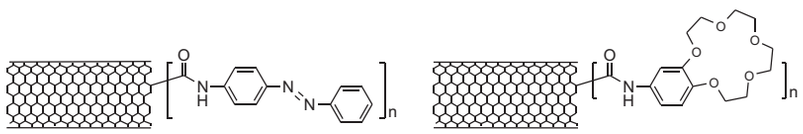
6 for MWCNTs

Figure 1. Covalent sidewall derivatization of SWCNTs and MWCNTs.

Chemical functionalization of nanotubes leading to **1**–**5** was performed analogously as described in [2]. 50 mg (~4 mmol of carbon) of SWCNTs or MWCNTs were mixed with 4 equiv/mol of carbon of an adequate amine, *i.e.* 2-aminoanthraquinone (MW. 223 g/mol), or *p*-aminoazobenzene (MW. 197 g/mol), or 2-aminobenzo-15-crown-5 (MW. 283 g/mol). After the mixture was placed in a round-bottom flask equipped with a magnetic stirring bar, isoamyl nitrite (4.8 equiv/mol of carbon; MW. 117 g/mol), prepared as described in [3], was added. The resultant paste was heated to 75°C and stirred under argon for 24 h. Then, the reaction mixture was diluted with DMF and centrifuged. The collected solid was washed until the supernatant became colorless and dried under reduced pressure obtained with water pump.

Derivative **6**: Following the description in [4] 100 mg of MWCNTs was sonicated in 50 ml of benzene for 30 minutes to form a suspension. Then, benzoyl peroxide (3 equiv per mol of carbon) was added and the mixture was heated to 75°C and stirred under argon for 24 h. After that time, the reaction mixture was centrifuged and nanotubes with phenyl groups attached to their side-walls were washed with chloroform.

The material was subjected to 3 ml of hydrogen bromide (45% w/v HBr) in glacial acetic acid and 0.6 g of paraform(aldehyde) within 72 h. In the reaction, bromomethyl groups are introduced onto phenyl moieties, but under such conditions the end/defect-site derivatization may also occur. After washing with THF, the centrifuged modified nanotubes were taken to the last step of the reaction, *i.e.* with lithium diphenylphosphide. Lithium diphenylphosphide and nanotubes were stirred for 96 h, washed with THF and methanol and centrifuged, giving derivative **6**.



7 for MWCNTs **8** for MWCNTs

Figure 2. Covalent end/defect-site derivatization of MWCNTs.

Derivatives **7** and **8**. MWCNTs were sonicated in a mixture 3:1 *v*/*v* of conc. H_2SO_4 (98% *wt*) and HNO_3 (16 M) for 4 h and left overnight [5]. The resultant suspension was diluted with deionized water and centrifuged. Carefully washed nanotubes were treated with $SOCl_2$ at 70°C for 24 h. An excess of thionyl chloride was removed by evaporation with toluene. A subsequent reaction with *p*-aminoazobenzene or 2-aminobenzo-15-crown-5 in pyridine was performed, giving **7** and **8**, respectively.

Modified carbon nanotubes were characterized by UV-Vis spectroscopy, confocal Raman spectroscopy, X-ray photoelectron spectroscopy and electrochemically.

Functionalized with azobenzene moieties, carbon nanotubes **3**, **4** and **7** were found to form stable Langmuir and Langmuir-Blodgett monolayers. Surface pressure – mean molecular area and surface potential – mean molecular area isotherms were recorded to show the formation of monolayers and their characteristics (Fig. 3).

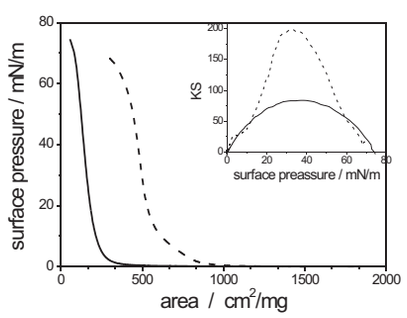


Figure 3. Surface pressure – mean molecular area isotherms for MWCNT-**4** (solid line) and mixture of **4** and $C_{18}OH$ (10:1 mass ratio) (broken line). Inset: Monolayer compressibility coefficient *vs*. surface pressure. Subphase: water.

Layers of modified nanotubes were spread on the water surface and compressed to the surface pressures 40 mN/m before the collapse of the organized layer takes place. They were transferred onto the solid substrates using the Langmuir-Blodgett approach [6]. The transfer was performed by withdrawing in the indium-tin oxide substrate (ITO) through the monolayer covered air-water interface with the speed of 7 mm/min. Next, the substrates are dried in air and placed in the electrolytic cell. Since azocompounds are electroactive, the amount of the compound present on the conducting support can be evaluated based on the charge of the voltammetric reduction peak (Fig. 4).

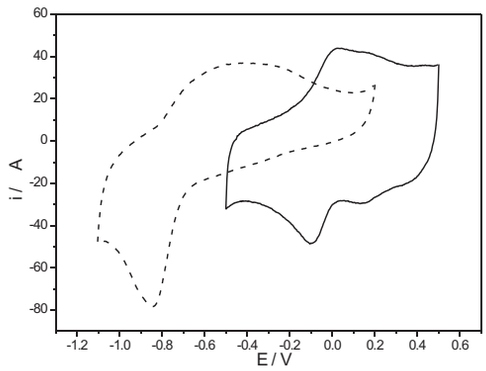


Figure 4. Cyclic voltammograms for MWCNT-**7** transferred onto ITO by the Langmuir-Blodgett method. Supporting electrolyte: Citrate buffer with 0.1 M $LiClO_4$ (solid line) pH 3, (dashed line) pH 12.

The changes in the electroactivity of the layer upon light induced isomerization were also monitored. The Langmuir-Blodgett technique was found to be a convenient method for the preparation of reproducible nanotube layers at the electrode surfaces.

Derivatives **5** and **8** are also expected to form monolayers [7] and now are under investigation.

Glassy-carbon electrodes (GCE), modified with derivatives **1** and **2,** were used in the process of catalytic reduction of oxygen in the presence of laccase (Fig. 5). GCE electrodes covered with nanotubes were prepared by dropping the mixture of nanotubes SWCNT-AQ or MWCNT-AQ in methanol and allowed to dry. For preparation of CNTs electrode, appropriate amount of CNTs was mixed firstly with 0.5 ml methanol with ultrasonic agitation over 2 min. Next, 5 µl of this mixture was pipetted onto the electrode and allowed to dry (Fig. 5).

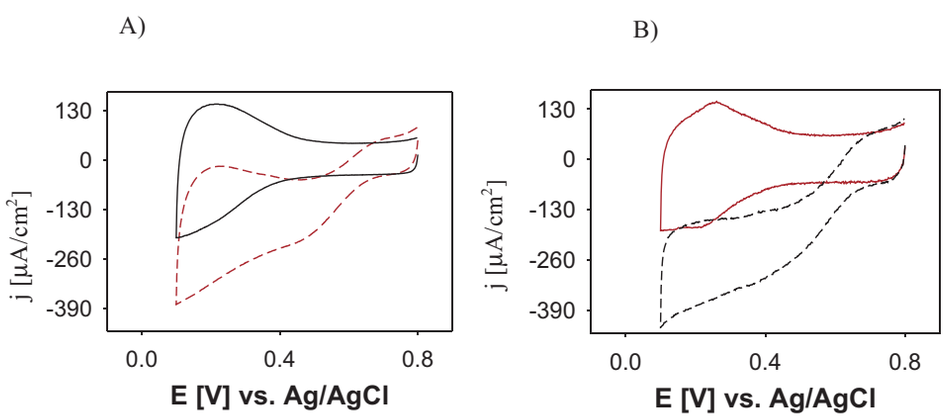


Figure 5. Cyclic voltammograms recorded for catalyzed dioxygen reduction using electrodes modified with nanotubes A) MWCNT-**2** and B) SWCNT-**1** in McIlvaine buffer solution (pH 5.2) containing 0.047 mg/ml laccase: (—) deoxygenated and (– –) saturated with oxygen, scan rate 5 mV/s.

At unmodified GCE, reduction of oxygen proceeds with a large overpotential (at potentials *ca*. –0.6 V) both in the absence and in the presence of laccase in the solution [8,9,10]. However, in case of electrodes modified with nanotubes the overpotential of the reduction of dioxygen catalyzed by laccase is negligible. This fact, together with the remarkable stability of such electrodes makes the GCE/CNT-laccase system very interesting for the applications in electrochemical sensing and biofuel cells.

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