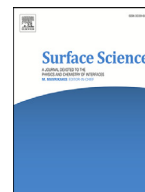




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# Chemical *in situ* modulation of doping interactions between oligoanilines and nanocarbon films<sup>☆</sup>

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## ARTICLE INFO

### Keywords:

Interfacial doping  
Oligoaniline  
Polyaniline  
Carbon nanotubes  
Raman  
Chemiresistive Sensors

## ABSTRACT

The electronic properties of carbon nanotubes are commonly customized through doping with various moieties, however, the modification is permanent as long as the dopant is present. Here we present a family of dopants that can be switched on and off while in place via environmental stimuli, in particular redox conditions and exposure to acids and bases. Aniline oligomers are firmly attached to the carbon nanotubes and are not easily displaced by other dopants or through rinsing with solvent in either oxidation state. As opposed to the reduced form of the aniline oligomers, their oxidized form causes p-doping of the carbon nanotubes. Similarly, the free base and chloride salt form of the aniline oligomers can be distinguished by their doping impact on the carbon nanotubes. The switching of the doping state can be followed by X-ray photoelectron spectroscopy, Raman spectroscopy and especially also electrically (film resistance), opening up applications as switches and sensors.

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## 1. Introduction

Many applications of single-walled carbon nanotubes (SWCNTs) rely on our ability to customize their electronic properties [1–3]. Carbon nanotubes can be used as circuit elements, solar cells, switches or sensors [4–9]. Particularly in sensing applications, for carbon nanotubes to work as transducers they have to vary their electronic properties in response to environmental stimuli, e. g. of mechanical, thermal, electromagnetic or chemical nature. Most chemical sensors require amplification due to the marginal change in electronic properties as a function of a small change in the magnitude of a stimulus that is nevertheless desirable to detect. Amplification strategies include sophisticated control electronics, nanostructured percolation conductivity networks [10,11], as well as chemical field effect transistors (ChemFETs) [12]. SWCNT-based sensors have the potential to circumvent the need for additional amplification, because certain select analytes (e.g. ammonia [8]) cause a strong change in the SWCNT electronic structure (“doping”) and can be detected very sensitively by simple resistance measurement of a SWCNT film [13].

The process of modifying the electronic structure of SWCNTs by removing or adding charge is known as ‘doping’. Permanent doping of carbon nanotubes can be achieved either by substitutional or by chemical doping. Substitutional doping involves replacing some carbon atoms in the SWCNT structure with atoms that have a different number of valence electrons, such as boron (p-doping) or nitrogen (n-doping) [14],

and is not of concern to us here. The electronic structure of SWCNTs can also be modulated via chemical doping, i.e. the covalent or non-covalent attachment of functional groups or molecules that withdraw (p-doping) or donate (n-doping) charge to the SWCNT host [15,16]. Numerous molecules have been identified which induce charge transfer from (e.g. molecular oxygen [17], FeCl<sub>3</sub> [18], TCNQ [19,20], TCNQF<sub>4</sub> [19–21]) or to (e.g. ammonia [8], alkylamines [22,23], alkali metals [24], TTF [19,20], TDAE [19,20]) SWCNTs. Furthermore, the charge carrier density can also be modulated by applied external electric fields (e.g. in field effect transistors) [7], which has the benefit that the doping state of the SWCNTs can be changed over time, unlike in the case of traditional chemical dopants. It would be desirable to modulate the effect of chemical dopants directly by environmental stimuli, such as light [25] or chemical environment [26–28].

Aniline oligomers and polyanilines (PANI) are an interesting class of molecules that have been reported to interact with carbon nanotubes electronically [29,30]. Carbon nanotubes have been reported to act as dopants for PANI films [13,31]. PANI and its oligomers are also known for being able to assume different oxidation states [32–34]. The impact of a change in oxidation state of PANI or one of its oligomers on its ability to dope SWCNTs has never been documented or utilized, however. Only on one occasion it has been mentioned that PANI can be used to control doping in carbon nanotube devices [7].

Here we introduce aniline oligomers as a class of switchable dopants for carbon nanotubes. We are elucidating the interactions of the

<sup>☆</sup> This paper is dedicated to Professor P.R. Norton on the occasion of his 75th birthday, in honor of his profound contributions to Surface Science.

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<https://doi.org/10.1016/j.susc.2018.01.003>

Received 1 December 2017; Received in revised form 5 January 2018; Accepted 5 January 2018

Available online xxx

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phenyl-capped aniline dimer (diphenyl *p*-phenylenediamine, DPPD) and phenyl-capped aniline tetramer (PCAT) with SWCNTs using UV–visible spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and electrical resistance measurements. In the oxidized state(s), the oligomers strongly *p*-dope SWCNTs, while the fully reduced state does not result in any detectable doping effect. Hence films of aniline oligomer doped carbon nanotubes are suitable candidates for redox-sensors, since their electrical resistivity strongly depends on their doping state and hence the redox state of the aniline oligomers, which in turn depends sensitively on the chemical environment of the films.

## 2. Experimental

SWCNTs (Unidym, formerly Carbon Nanotechnologies Inc., HiPco process, batch# PO343) were annealed at 800 °C under vacuum for 1 h (after ramping up at 1 °C/min) to remove any residual contaminants [35,36]. Phenyl-capped aniline dimer (diphenyl *p*-phenylenediamine, DPPD) was purchased from Sigma Aldrich. Phenyl-capped aniline tetramer (PCAT) was synthesized and purified according to published procedures [34,37]. Both oligomers were converted into the desired oxidation states before use as described below. Ammonium persulphate (98.0% pure, Sigma Aldrich), L-ascorbic acid (99.0% pure, Caledon), hydrochloric acid (LabChem, Inc.), potassium hydroxide (Fisher Scientific) and methanol (anhydrous, Comalco) were used as received. PTFE 0.2 μm filter membrane was purchased from Pall Life Science.

SWCNTs were mixed with the dopant molecules (DPPD or PCAT) while maintaining the SWCNT to dopant mass ratios constant throughout the study. Methanol was used as a solvent for all experiments. SWCNTs were also suspended in methanol as a reference sample. The weight to volume ratio for SWCNT samples suspended in methanol was maintained throughout the study. Batches of DPPD and PCAT were dissolved in methanol and combined with either ammonium persulfate as an oxidizing reagent or ascorbic acid as a reducing agent in slight stoichiometric excess in order to obtain their fully oxidized or reduced forms respectively [32]. The half-oxidized form of PCAT was obtained from the fully reduced form by mixing it with the appropriate stoichiometric amount of the oxidizing reagent. Sonication of all samples prepared with SWCNTs and oligomers was performed under ambient conditions for 1 h in a Branson 1510 bath sonicator (42 kHz, 70 W). The respective samples of oligomers mixed with oxidizing agent, reducing agent, acid or base were sonicated for 5–10 min. The suspensions were dropped on glass slides and dried in air, or filtered through PTFE membranes to prepare bucky-paper-style samples for Raman spectroscopy. Flakes of the bucky paper obtained from filtered samples were collected on glass slides for Raman spectroscopy.

Raman spectra were recorded with a Renishaw 2000 Raman microscope over a range of 100–3600 cm<sup>-1</sup>, with a spectral resolution of 2 cm<sup>-1</sup>, using a 50× objective in backscattering configuration. Data were collected on several spots on the samples having a size of about 1.2 μm and recorded with a fully focused 514 nm laser at 1% power, corresponding to a power density of ~ 10 μW/μm<sup>2</sup> in order to avoid laser damage to the sample [38]. Where explicitly mentioned, some Raman spectra were collected using a 785 nm solid state laser. The spectra were scaled with respect to the maximum intensity of the D\* mode (2570–2730 cm<sup>-1</sup>) to visually aid the comparison within and amongst the samples [39]. The D\* peaks have been de-convoluted by Lorentzian peak fitting. UV–vis spectra were recorded on an Ultraspec™ 100 *pro* Visible Spectrophotometer with a wavelength range of 330–830 nm, a spectral band width of 8 nm and a wavelength accuracy of ±2 nm. Before recording each UV–vis spectrum of an oligomer, the spectrometer was calibrated with methanol. Powder samples of reduced PCAT, oxidized PCAT, half-oxidized PCAT, reduced PCAT mixed with SWCNTs, oxidized PCAT mixed with SWCNTs, and half-oxidized PCAT mixed with SWCNTs were pressed into double-sided adhesive tape and analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra X-ray

photoelectron spectrometer. High resolution analyses were carried out with an analysis area of 300 × 700 μm<sup>2</sup> and a pass energy of 20 eV.

For electrical characterization, a SWCNT film was drop-casted from a methanolic suspension between two gold electrodes on a substrate, and then covered by a microfluidic channel such that any liquid flown through the channel could not contact the gold electrodes directly. A methanolic solution of DPPD was then flown over the SWCNT film, followed by a pure methanol rinse and methanolic solutions of the oxidizing and reducing reagents respectively. Resistance of the film was measured by applying a 0.1 mV potential and measuring the current response in a simple two electrode configuration. Several devices were tested to assure reproducibility.

## 3. Results and discussion

### 3.1. Oxidized aniline oligomers *p*-dope SWCNTs

Different oxidation states of DPPD and PCAT were produced, and their effect on SWCNTs was studied using Raman spectroscopy. (Fig. 1) DPPD is an aniline dimer that is terminated with an additional phenyl ring, whereas PCAT is an aniline tetramer that is also terminated with an additional phenyl ring. Even-numbered aniline oligomers have the special property that pairs of neighboring amine groups can lose their attached hydrogen atoms, in effect oxidizing the molecule [32]. These oxidized versions of the aniline oligomers can then add pairs of hydrogen atoms to neighboring imine groups to regenerate the amine groups of the reduced molecules. Raman spectra of predominantly semiconducting SWCNTs interacting with reduced (amine, Fig. 1a) and oxidized (imine, Fig. 1b) PCAT molecules were taken with a 514 nm green laser [40], and contrasted with spectra taken on the same sample with a 785 nm red laser that preferentially excites metallic SWCNTs (Fig. 1c and d). All typical Raman features of SWCNTs are present: radial breathing modes between 100 and 300 cm<sup>-1</sup>, the G-band around 1590 cm<sup>-1</sup>, and the D\*-band around 2660 cm<sup>-1</sup> [35,36,38]. Since the Raman spectral features of carbon nanotubes are resonantly enhanced, the PCAT molecular features in a mixed sample are not normally visible. For the purpose of Fig. 1 only, a large excess of PCAT was used, so that some features of the molecules are also visible in the spectra, namely the bands at 1179, 1221 and 1621 cm<sup>-1</sup> typical of reduced PCAT in Fig. 1a and the bands at 1166, 1218 and 1498 cm<sup>-1</sup> typical of oxidized PCAT in Fig. 1b [41,42]. Some molecular features overlap with the G band of the SWCNTs, but for the interaction with oxidized molecules a blue shift of 10 cm<sup>-1</sup> is seen in the location of the D\*-band of the semiconducting nanotubes. The 785 nm laser is not well-suited for detection of the molecular features, but it can be seen that the oxidized PCAT molecules had a significant impact on the metallic nanotubes, as witnessed by the rise of a very large D peak at 1370 cm<sup>-1</sup> (Fig. 1d) while the D\* feature has almost vanished.

For the remainder of the work, Raman spectra of molecule - SWCNT complexes were taken with a 514 nm laser over a range from 100 to 3600 cm<sup>-1</sup>, but for clarity only the D\* feature at around 2660 cm<sup>-1</sup> is presented in the following figures, since a shift in the location of this peak is sufficiently indicative of the SWCNT doping state [35,43]. When Raman spectra of freshly annealed SWCNT networks were taken after 30 min sonication in pure methanol, the main peak of the D\* feature is located at 2656 cm<sup>-1</sup>. (Fig. 2a, also see Fig. S1 in Supporting Materials for a full spectrum) This position is typical for un-doped SWCNT films [35,36]. Methanol - as a radical quencher - was used in this study instead of water in order to avoid doping effects due to O<sub>2</sub> species from water sonication [36]. It is also a reasonably good solvent for our dopant molecules, thus providing for homogeneous samples of strongly attached molecules rather than non-interacting mixtures of molecules and SWCNTs.

When the reduced form of DPPD was added to SWCNT samples in methanol, the position of the main peak of the D\* feature essentially remains the same as for the pure SWCNT sample. (not shown) While

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