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Ambient effects on the electrical conductivity of carbon nanotubes

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A B S T R A C T

We show that the electrical conductivity of single walled carbon nanotubes (SWCNT) networks is affected by oxygen and air humidity under ambient conditions by more than a magnitude. Later, we intentionally modified the electrical conductivity by functionalization with iodine and investigated the changes in the band structure by optical absorption spectroscopy.

Measuring in parallel the tubes electrical conductivity and optical absorption spectra, we found that conduction mechanism in SWCNT is comparable to that of intrinsically conducting polymers. We identified, in analogy to conducting polymers, in the infrared spectra a new absorption band which is responsible for the increased conductivity, leading to a closing gap in semiconducting SWCNT.

We could show that by different functionalizations of the same SWCNT starting material the properties like conductivity can be dramatically changed, leading to different imaginable applications. We investigated here, an ultraviolet sensor with weakly modified SWCNT.

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1. Introduction

Quantum wells and wires like graphene or single walled carbon nanotubes (SWCNT) were of great interest in the last years. Especially the extraordinary electrical properties of these materials offer different potential applications. The very high electron mobility in semiconducting carbon nanotubes ($10^5$ cm$^2$/V$\cdot$s) and graphene ($1.25 \times 10^5$–$2.75 \times 10^5$ cm$^2$/V$\cdot$s) [1–3] as well as the high current density in metallic SWCNT $10^9$ A/cm$^2$ [4] are relevant for transistor developments, micro or nanoelectronics or electrical cables [5–9]. The reason for the outstanding electrical performance is the low dimensionality of the electronic structure in these materials. The ballistic conduction in 1D or 2D structures was studied by different groups theoretically and experimentally [10,11].

The electrical current is in 1D or 2D structures directly proportional to the voltage and independent of the conductor length. If the band structure allows the free movement of charges, the relation between current $I$ and voltage $U$ for the 1D case is e.g. given as:

$$I = \frac{2e^2}{h} U$$

Thus, the resistance of a single 1D conducting channel is given in analogy to Ohms law, in the so called von Klitzing resistance $h/e^2$.

Several experiments have shown results, which are fitting quite nicely to that theory and ballistic electron movement was found in multi-walled carbon nanotubes (MWCNT), SWCNT or single graphene flakes as well as in silver nanowires [10–13]. Although the conduction mechanism of nanomaterials is well known and the theory is experimentally proofed, there is less success in practically working with such materials or finding applications in the macro scale.

The maybe most well-known application of carbon nanotubes is their integration as additive in battery or capacitor materials in order to improve the conductivity of the electrodes and performance of the storage devices [5,14,15]. But the step to wider electrical applications fields is not done, yet [14].

In this paper we investigate the conduction mechanism in SWCNT networks under ambient conditions and analyze the consequently appearing changes of the electrical conductivity. Our
investigation is targeted to support the understanding of this extraordinary material and should help to find electrical application for SWCNT.

Especially low dimensional material made of a single atomic layer shows a strong susceptibility to external influences. Thus, also graphene, an atomic layer of carbon, reduces its charge carrier mobility by the interaction with the substrate where it is placed [3]. Due to the fact that SWCNT, consist of one atomic layer, the electronic properties are directly influenced by adsorbents and the surrounding conditions, too [16].

If there is an adsorption process on the surface, the CNTs pi-electrons change their energy state to energetically more favored new binding energies. This has a strong influence on the electrical band structure, OAS, charge carrier density, and the properties of SWCNT like dispersibility in solutions by changing the Zeta-potential/surface energy [17,18].

Therefore, by processing the same SWCNT material by different purification techniques, the performance and properties of the SWCNT material can differ, the reproducibility might be unsatisfying or the electrical properties are not stable.

In this paper it is analyzed experimentally what is going on in SWCNT-networks and why the effect of functionalization on the electrical conductivity is so strong.

We have investigated the electrical properties of SWCNT by 4-terminal sensing after functionalization of SWCNT with different adsorbents. In parallel we investigated the band structure of the SWCNT by optical absorption spectroscopy (OAS).

The 1D structure of the SWCNT leads to van Hove singularities (vHs) in the density of states (DOS) [19,20]. These vHs are responsible for the characteristic S11, S22 and M11 absorption bands of SWCNT. These absorption bands are directly affected by the adsorbed adsorbates [19,21,22]. Therefore we measured by OAS the absorption in order to find a relation between band structure and changing electrical conductivity.

Additionally we depict that it is indispensable to control the degree of functionalization of such materials especially when looking for electronic applications. We used our results to find applications for SWCNT as UV-sensor.

2. Experimental

We used for the experiments homemade SWCNT produced by the pulsed arc technique. The as-produced material contains −35 wt.% SWCNT, 20 wt.% catalyst particles and −45 wt.% amorphous carbon [20]. The used SWCNT material consists of a mixture of individual SWCNT with different characteristics like chirality or band gaps $E_g$ [20]. The amount of semiconducting SWCNT (sc-SWCNT) is about 55% and of metallic SWCNT (m-SWCNT) 45% with diameters of between 1.0 and 1.8 nm. The produced SWCNT material was analyzed in previous publications [20,23–25].

The raw SWCNT material was purified by wet chemical treatment with $\text{H}_2\text{O}_2$ and HCl (SWCNT-C) or $\text{H}_2\text{O}_2$ and HNO$_3$ (SWCNT-N). This treatment removes about 100% amorphous carbon and about 50% of the metal catalyst particles. Later on, the SWCNT were dispersed by an ultra-sonication bath in isopropanol. For the film preparation, the SWCNT material was deposited by spray coating techniques. In parallel we investigated the band structure of SWCNT already by oxygen and air humidity. We deposited SWCNT-C material, which is relatively unaffected by functionalization during the purification, on a quartz glass substrate by spray coating and heated it up under N$_2$ – atmosphere to 1173 K. This should remove all absorbents which are maybe attached to the SWCNT-surface by handling the material.

After heating we deposited the sample in the lab under ambient condition for 90 days. From time to time, the conductivity and OAS of the SWCNT-C were measured (5. Table 1). As a surprising result, we found that the conductivity increases significantly with longer deposition time. In parallel the S11, S22 and M11 absorption bands became larger. Fig. 2a shows the spectra of one sample after different deposition times.

When the samples were heated up to $T$ = 1173 K after 30 days the absorbents were removed and the absorbance bands became larger and the resistance increased, too (Fig. 2b).

Thus, we could show that ambient and storage conditions of SWCNT material needs to be taken into account for subsequent use in electrical applications. Physical adsorption and chemical adsorption (C–O) seems to affect the electrical conductivity dramatically. Comparable results are discussed in literature and are confirmed here [16]. The effect that the higher energetically S22 band is affected thought the lower energetically S11 band is still visible can be attributed to inhomogeneous doping. The disregard of dispersing film preparation should avoid side effects by tensids in the OAS spectra. Without dispersing however SWCNT have a strong inclination for forming bundles. This can
hinder the homogeneously functionalization of all tubes. Furthermore the reactivity of the tubes can differ depended on the diameter/chirality. Therefore we believe the S_{22} band can change though the S_{11} is still visible.

In order to increase the conductivity further on by functionalization we used iodine as strong oxidative agent in order to reinforce the oxidizing effect. The doping effect of iodine on SWCNT is already mentioned in different publications\cite{9,22,31}. Usually, it is assumed that the functionalization increases the concentration of positive charge carriers (holes)\cite{31}. Therefore we prepared another SWCNT-C sample and heated it up to 1173 K in order to detach all unintended adsorbents. Thus we can assume that iodine can interact with SWCNT on the surfaces effectively without other disturbing artifacts. Iodine was dissolved in isopropanol and sprayed on the “cleaned” SWCNT-C samples. The samples were heated up to ~80 °C during the iodine deposition in order to evaporate the solvent immediately. In Fig. 3 is shown that after the treatment with iodine the S_{11} band is completely suppressed and even the M_{11} absorption band is suppressed.

The suppression of the M_{11} band shows that iodine can strongly

<table>
<thead>
<tr>
<th>Deposition time, days</th>
<th>Resistance Ohm/sq.</th>
<th>Adsorbates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>534</td>
<td>None</td>
</tr>
<tr>
<td>10</td>
<td>210</td>
<td>O_{2}/H_{2}O</td>
</tr>
<tr>
<td>30</td>
<td>188</td>
<td>O_{2}/H_{2}O</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
<td>O_{2}/H_{2}O</td>
</tr>
</tbody>
</table>

hinder the homogeneously functionalization of all tubes. Furthermore the reactivity of the tubes can differ depended on the diameter/chirality. Therefore we believe the S_{22} band can change though the S_{11} is still visible.

In order to increase the conductivity further on by

![Figure 1](image1.png)  
**Fig. 1.** a) TEM image of SWCNT purified with H_{2}O_{2} and HNO_{3} from amorphous carbon and ~50% catalyst metal particles (SWCNT-N). b) SWCNT purified with H_{2}O_{2} and HCl treatment from amorphous carbon and also ~50% of the catalyst metal particles (SWCNT-C). c) Optical absorption spectra of SWCNT-N- and SWCNT-C- material sprayed on a quartz glass. d) Far infrared spectroscopy of pristine SWCNT-, SWCNT-N- and SWCNT-C-material prepared with KBr-SWCNT pellets.

![Figure 2](image2.png)  
**Table 1**  
Sheet resistance of a sprayed SWCNT-C film on a quartz glass substrate. The sample was placed under ambient conditions in the lab.

![Figure 3](image3.png)  
**Fig. 2.** a) Optical absorption spectra of one SWCNT-C sample during deposition time under ambient conditions. The small extract shows the background subtracted spectra. b) Optical absorption bands of one SWCNT-C sample after 30 days under ambient condition. Afterwards it were heating up to 1173 K in order to evaporate the solvent immediately. In Fig. 3 is shown that after the treatment with iodine the S_{11} band is completely suppressed and even the M_{11} absorption band is suppressed.

The suppression of the M_{11} band shows that iodine can strongly
functionalize even metallic SWCNT. The conductivity of the SWCNT network was increased through iodine by more than one magnitude. The sheet resistance changed from 1830 Ω/sq. to 114 Ω/sq.

By measuring the Seebeck coefficient $\alpha$ of SWCNT after the heating process and before functionalization we found a Seebeck coefficient $-65 \mu V/K$. Thus the majority charge carriers are p-type in the SWCNT network. The explanation might be the higher content of sc-SWCNT in the initial material ($-55\%$).

By measuring the Seebeck coefficient $\alpha$ of the iodized SWCNT-C-network we found that after doping the whole network remains p-type but $\alpha$ reduces from $-65 \mu V/K$ to $+30 \mu V/K$ which supports the assumption of increased charge carrier density $n$ by the oxidation with iodine ($\alpha \approx 1/n$ [33]).

In order to explain why the effect of iodine is so strong we measured the OAS up to the infrared region in order to get a better overview of the band structure.

By careful analysis of the spectra, a shift of $-50$ meV of the $S_{11}$ band up to higher energies ($S_{11}$) can be observed and a significant, new absorption band below 0.5 eV appears ($A^*$) (Fig. 4). Comparable results were shown by measuring the absorption of purified SWCNT up to $-0.004$ eV [27]. The increasing absorption in the infrared region was proposed to be emerged by defects or impurities induced states in the band gap of semiconducting SWCNT [27] or by small band gaps of around 10 meV in some SWCNT [34].

From our point of view, this interpretation did not sufficiently consider the strong effect on the conductivity of SWCNT by oxidation. On the one hand we believe an appearing energy gap in metallic SWCNT ($-45\%$ m-SWCNT exists in our material) would reduce the conductivity of the SWCNT network. On the other hand, taking into account the appearing new absorption bands and the parallel vanishing of $S_{11}$- and $M_{11}$-bands further the strong increase of the conductivity, we believe that positive polaron-/soliton bands are generated in carbon nanotubes by the functionalization. We consider them to be responsible for the new absorption bands in the infrared region ($A^*$-band) and the increased conductivity by closing the energy gap in semiconducting SWCNT. This assumption cannot be proven completely with the available adsorbents are removed. Three cycles of irradiation, each 1 h, were performed. At the beginning of the irradiation a strong increase of
the resistivity was measured. After some minutes of irradiation the slope flattens and the resistance increases more slowly. The resorption of adsorbents is a time dependent process and even after 22 h the initial resistance is not reached. It took the films 72 h to recover its initial values. The same experiment does not work with pristine (un-purified) SWCNT which are covered with e.g. amorphous carbon or other chemical groups, which avoid the adsorption/desorption of oxygen or air humidity so effectively.

For comparison similar experiments were made in a glove box with 5 ppm O₂ and 10 ppm H₂O. The results are shown in Fig. 7.

Comparing the experiments in the glove box with experiments under ambient conditions it becomes obvious that ambient conditions have a strong influence on the electrical properties of the SWCNT-C.

In order to explore more carefully the effect of oxygen and air humidity we heated a SWCNT sample up to 175 °C on a heat plate...
under ambient conditions and measured the change in the resistance of two printed lines. These results are shown in Fig. 8. It could be demonstrated that up to 100 °C the resistance increases and after it, it decreases (Fig. 8a).

For the explanation of this effect it is helpful to take into account TGA measurements of the same material under dry air. From the TGA measurement in Fig. 8b it becomes obvious that temperatures up to 100 °C result in a mass reduction of 4% related to the loss of moisture [25]. This is followed by a small mass gain of ~1% for temperatures of up to ~300 °C. The mass gain can be considered as an effect of oxygen adsorption on the carbon surfaces [47].

Since the resistance increases during the moisture evaporation we show that even the moisture has an effect on the electrical performance of the tubes. Therefore under ambient conditions with e.g. changing air humidity it is often difficult to measure reproducible electrical performance of SWCNT material.

Nevertheless the effect of oxygen adsorption on the conductivity is higher than that of moisture. The adsorption of oxygen between 100 and 175 °C reduces the resistance again and much further as it was at the beginning. At 175 °C the resistance was reduced by around 50% with respect to the initial value. We suppose that such a heating accelerated the effects shown in Fig. 2, which were measured over 90 days.

4. Conclusion

We investigated the environmental influence on the electrical conductivity of SWCNT. We have shown that the conductivity is dramatically depended on oxidative agents which lead to an increased p-type conductivity. Already ambient influences are sufficient for changing the conductivity of SWCNT about more than a magnitude. Oxygen and moisture have an influence on the conductivity of the SWCNT networks. Additionally the Seebeck coefficient could be reduced from +65 to +30 μV/K by oxidizing SWCNT with iodine. This indicated a charge carrier increase by oxidation.

We assume that oxidative agents create polarons and solitons in SWCNT which are dominant for the electrical transport in conducting polymers and can also exist in SWCNT. This assumption need to be verified by further investigations.

We show in this paper that an appropriate functionalization of SWCNT is an essential precondition for a successful application. Finally, we show the potential for using SWCNT as UV-sensor.

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