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Published in:
Carbon

Link to article, DOI:
10.1016/j.carbon.2015.08.045

Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

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Ambient effects on the electrical conductivity of carbon nanotubes

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ARTICLE INFO

ABSTRACT

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.

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) and graphene ($1.25 \cdot 10^5$–$2.75 \cdot 10^5$ cm^2/V) [1–3] as well as the high current density in metallic SWCNT 109 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:

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

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

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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 S_{11}, S_{22} and M_{11} absorption bands of SWCNT. These absorption bands are directly affected by the attached 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 Eg_n [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 H_2O_2 and HCl (SWCNT-C) or H_2O_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 on quartz glass substrates in order to measure both the OAS and the electric conductivity of the SWCNT network. We used for the experiments quite thin SWCNT films in the range of 100 nm thickness in order to enable the covering of the whole SWCNT surfaces by adsorbents. The transparency was between 20 and 60%. The thin film should avoid inhomogeneous functionalization within the film thickness as good as possible. The optical absorption spectra of the SWCNT-films were measured between 0.25 and 3.0 eV (with *Varian, Cary 5000*, range 0.5–3 eV and *Perkin Elmer,*

Spectrum 2000, range 0.25–1 eV).

We used a homemade measurement setup for the determination of the Seeback coefficient α. The Seeback coefficient allows a conclusion about the type of majority charge carriers (p-type or n-type). A positive Seeback coefficient α identify p-type material in our setup.

For the investigation of electrical application for the SWCNT we used an aerosol printer for printing the SWCNT dispersion.

3. Results and discussion

After having purified the SWCNT, the TEM images of the SWCNT-C and SWCNT-N samples look very similar. Both purification procedures have removed the amorphous carbon completely and the metal particles were reduced by ~50%. The main difference between the materials is the electrical conductivity which is about 3 times higher in the SWCNT-N material (measured by preparing buckypapers with 20 mg SWCNT-material).

After comparing the OAS of the SWCNT-C and SWCNT-N, we found that the SWCNT-N material shows smaller van Hove singularities signal (S_{11}, S_{22}, and M_{11}). This might be explained either by a higher content of impurities like amorphous carbon in the SWCNT-N material or by a functionalization of the SWCNT-N [26,27]. Since we could show by FTIR-spectroscopy covalent C—O bindings in the SWCNT-N samples (Fig. 1) and we do not find any amorphous carbon by TEM images, we assume a covalent functionalization of the SWCNT by forming a quinoid systems or carboxyl acids which is discussed as functionalization by strong oxidative agents like HNO_3 or H_2SO_4 [19]. There are different papers which discuss the effect of wet chemical oxidation of carbon nanotubes [28–30]. The effect on the electrical conductivity however is not discussed in detail despite its extreme importance for electrical applications. Although there are publications which show the effect of doping on the conductivity [22,31,32] and the absorbance bands [19,22,32], the physical context is still worthy of discussion. Especially for electrical applications it is crucial to understand the property changes during processing the material in order to avoid confusing results.

Therefore we investigate if there is an environmental influence on 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 substrates 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 (s. Table 1). As a surprising result, we found that the conductivity increases significantly with longer deposition time. In parallel the S_{11}, S_{22} and M_{11} absorption bands became smaller. 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 adsorbents 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 S_{22} band is affected thought the lower energetically S_{11} band is still visible can be attributed to inhomogeneous doping. The disregarding of dispersing by 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
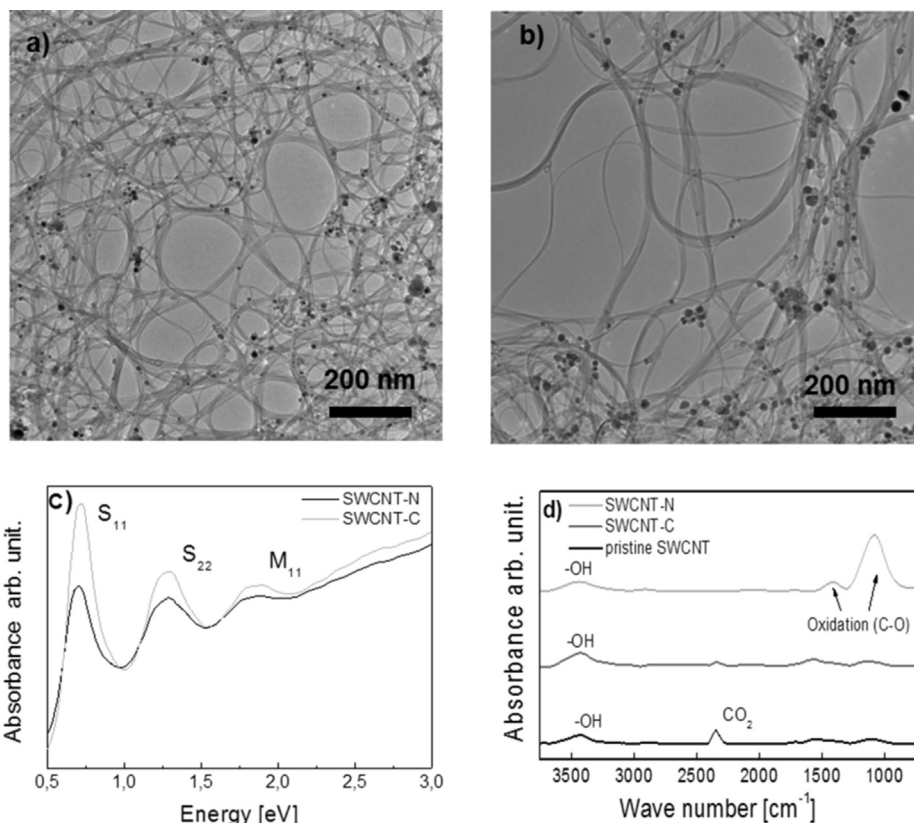
Fig. 1. a) TEM image of SWCNT purified with H_2O_2 and HNO_3 from amorphous carbon and ~50% catalyst metal particles (SWCNT-N). b) SWCNT purified with H_2O_2 and HCl treatment from amorphous carbon and also ~50% of the catalyst metal particles (SWCNT-C). c) Optical absorption spectra of SWCNT-N- and 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.

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.

Deposition time, days	Resistance Ohm/sq.	Adsorbates
1	534	None
10	210	O_2/H_2O
30	188	O_2/H_2O
90	60	O_2/H_2O

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 [9,22,31]. Usually, it is assumed that the functionalization increases the concentration of positive charge carriers (holes) [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
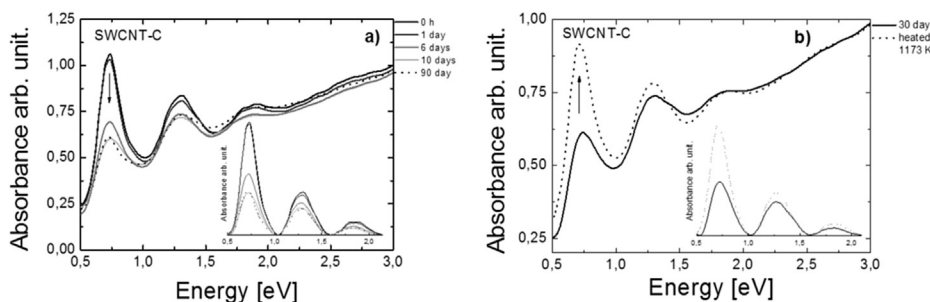
Fig. 2. a) Optical absorption spectra of one SWCNT-C sample during deposition time under ambient conditions. The small extract shows the background subtracted spectra. b) Optical absorption bands of one SWCNT-C sample after 30 days under ambient condition. Afterwards it were heating up to 1173 K under N_2 atmosphere. The small extract shows the background subtracted spectra.

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 α of SWCNT after the heating process and before functionalization we found a Seeback coefficient +65 μV/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 α of the iodized SWCNT-C-network we found that after doping the whole network remains p-type but α reduces from +65 μV/K to +30 μV/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 and 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 results and remains our suspicion based on the observations. The existence of polarons as well as solitons is however shown theoretically in carbon nanotubes in previous publications [35–37].

Both quasi particles polarons as well as solitons are known to be able to increase the conductivity of organic materials by several orders of magnitude. Especially iodine is known as a strong oxidative agent for intrinsic conductive polymers e.g. for polyacetylen (PA), which is oxidized strongly creating solitons [38]. But also polarons as wells as bi-polarons can arise by oxidative agents in conjugated carbon systems [39,40].
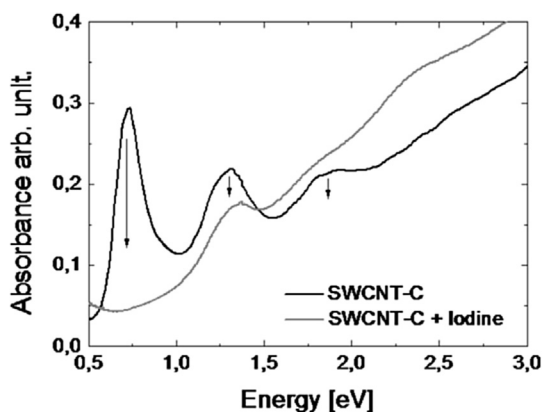
The OAS of doped polymers show amazing parallels to the OAS of functionalized SWCNT. In both spectra a dominant transition (S_{11}-band for SWCNT) vanishes by functionalization and further a lower energetically bands appear which have been interpreted in the case of polymers as polaron bands [39,41] and which are also detectable in SWCNT (A*-band). Thus, in our point of view similar effects compared to intrinsic conducting polymers might appear in SWCNT by functionalization. This presumption need to be confirmed by further investigations. The effect of polarons and solitons is especially relevant for semiconducting SWCNT with a band gap. For metallic (armchair) SWCNT it should be less relevant.

A general attempt at an explanation for polaron or soliton generation in SWCNT is given below. If the binding energy of two p_z electrons in the aromatic chain is overcome, the aromaticity is lost and at least one p_z-electron forms the bond between the adsorbents and SWCNT-surface. These bonds can be covalent as shown for the SWCNT-N material above. The second, now unbound p_z electron, has its energetic position in the middle of the energy gap between the π-valence and π*-conduction band. Without an adequate counterpart it does neither belong to the binding valence- nor to the non-binding conduction band and is placed energetically between both. The lost aromaticity can lead to a lattice distortion in the region and leads per definition to a polaron state. Polarons are detectable by OAS in conducting organic materials [42–44]. After removing more and more electrons, the number of unoccupied states in the gap of SWCNT increases which might be in our opinion responsible for the appearing absorption band (A*) in the infrared region and the increased conductivity by reducing the gap energy E_g. The new absorption band is most likely attributed to transitions from π-valence band to the new absorption bands and from transitions to the π*-conduction band (s. Fig. 4).
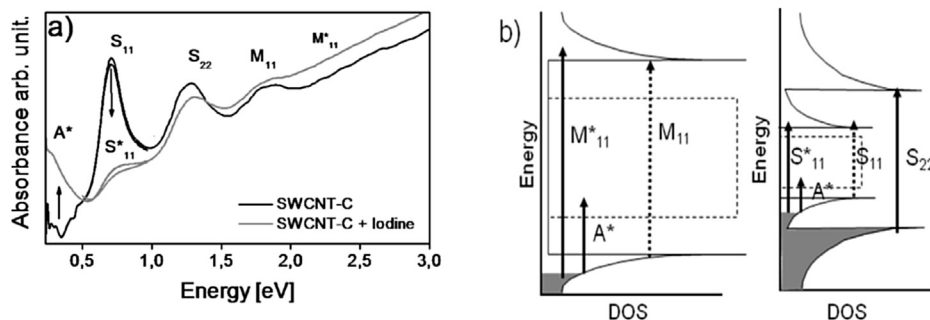
In order to use the strong affinity of SWCNT to interact with oxidative agents for applications, we investigated the idea of SWCNT-based UV sensors. In different publications it is mentioned that the ambient condition can affect the electrical behavior of carbon nanotubes and that they can be used e.g. for gas sensors [45,46]. The upper discussion confirms the reported gas sensitivity of carbon nanotubes at least regarding oxygen and air humidity.

We investigated therefore SWCNT-films as light sensor by removing oxygen and air humidity due to light absorption. In order to remove the adsorbents we used UV irradiation for "cleaning" the SWCNT surfaces from adsorbents. By measuring the resistance of SWCNT network during UV irradiation it should be detectable if adsorbents are removed. Based on this assumption, we below investigated the idea to use the unmodified SWCNT-C material, which is more reactive than already functionalized SWCNT, as UV sensor.

First, we deposited by physical vapor deposition, 20 nm TiN contacts on a glass substrate (microscope slides). Using an aerosol printer, we printed SWCNT-C on the substrate. The SWCNT-C were dispersed in pure isopropanol and directly printed on the substrate. A sample is shown in Fig. 5. The TiN contacts were connected with a data acquisition unit (DAQ) in order to control the electrical resistance during the UV radiation very precisely.

On the left side of Fig. 5 the sample holder is shown, where the sample is put in, clamped with contact pins connected to the DAQ and irradiated. On the left side in Fig. 5 the measurement setup is shown, which was used for connecting the measuring card with the sample. In Fig. 6 are shown the results during the measurement of the SWCNT lines treated with two different UV lamps (366 nm and 254 nm).

Obviously the higher the photon energy is, the more effectively adsorbents are removed. Three cycles of irradiation, each 1 h, were performed. At the beginning of the irradiation a strong increase of

Fig. 3. Optical absorption spectra of one SWCNT-C sample after heated up to 1173 K. Later the sample was functionalized with iodine suppressing the S_{11}- and M_{11}-bands.

Fig. 4. a) The optical absorption spectra of SWCNT-C were measured (after heating up until 1173 K in N_2 atmosphere) from 400 nm until 5000 nm (3.0−0.25 eV). Later on the SWCNT-C were functionalized with iodine and the optical absorption was recorded again. Observing the spectra some significant differences show up. New absorption bands A* below 0.5 eV appear, the S_{11}- and M_{11}-bands are suppressed and the S_{11}-band shows a shift to higher energies (S_{11}^*). Furthermore, a broad absorption above the M_{11}-band appears called M_{11}^*- transition (compare also Fig. 3). The spectra were measured with the Varian Cary 5000 for 0.5−3.0 eV and with Perkin Elmer, Spectrum 2000 for 0.25−1.0 eV. In the spectra are overlapping in the range between 0.5 and 1 eV. b) Schematic drawing of the relation between energy and DOS to explain the new transitions and changes of the band structure. The functionalization reduces the electron density of the π-band. This leads to band shifting to higher energies of the vHs and finally it suppresses the M_{11}-and S_{11}- band. By breaking up the π-binding the unbounded quasi free electrons are located in the band gap forming new energy bands. This leads to the absorption bands A* in the infrared region.
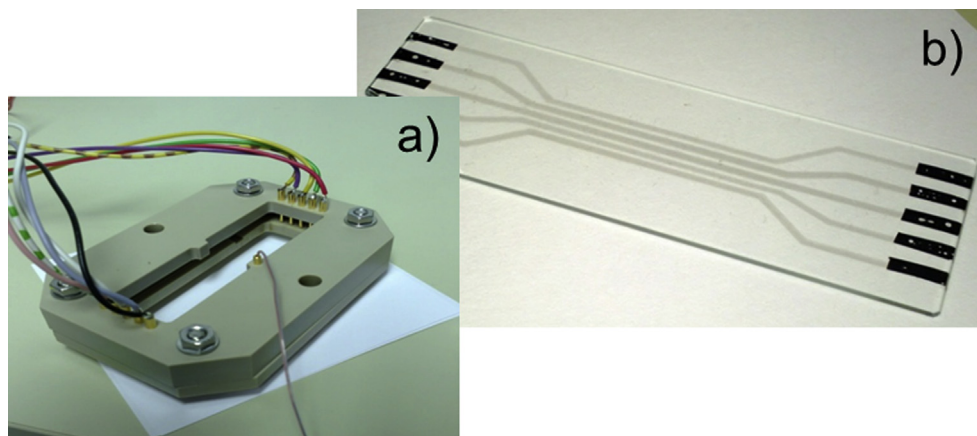
Fig. 5. a) Sample holder for UV sensor tests. b) 5 printed SWCNT-C lines on a glass substrate with sputter TiN contacts at the ends. (A colour version of this figure can be viewed online.)
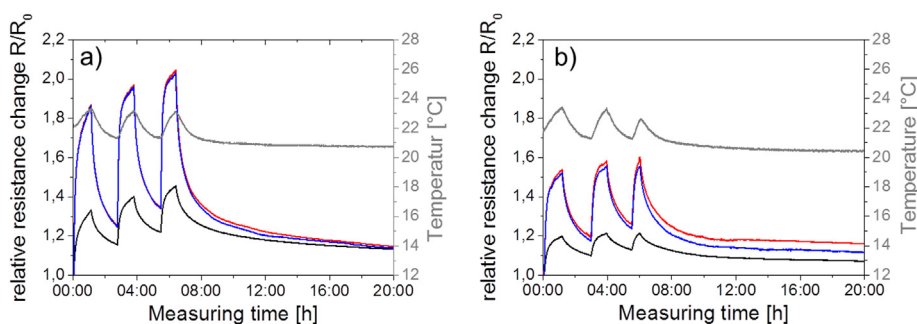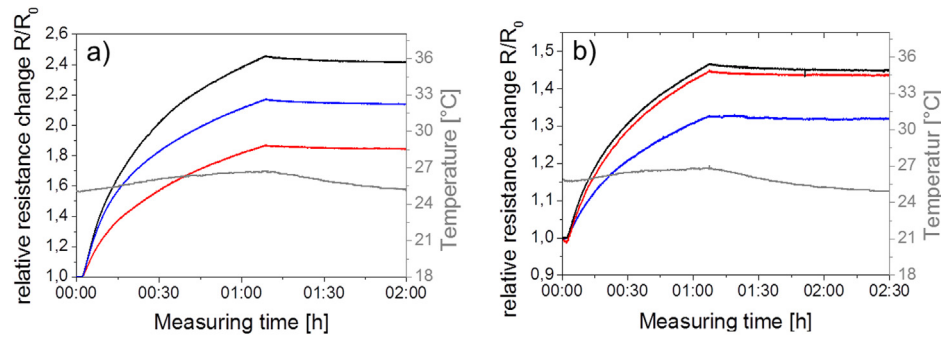

Fig. 6. Evaluation of relative change in the resistivity of three printed SWCNT-C lines under ambient condition during UV irradiation. The substrate temperature was measured during the irradiation a) irradiation with a 256 nm lamp, b) irradiation with 366 nm lamp. (A colour version of this figure can be viewed online.)

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 O_2 and 10 ppm H_2O. 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

Fig. 7. Evaluation of relative change in the resistivity of three printed SWCNT-C lines in a glove box under N$_2$ atmosphere. The substrate temperature was measured during the irradiation a) irradiation with a 256 nm lamp, b) irradiation with 366 nm lamp. (A colour version of this figure can be viewed online.)
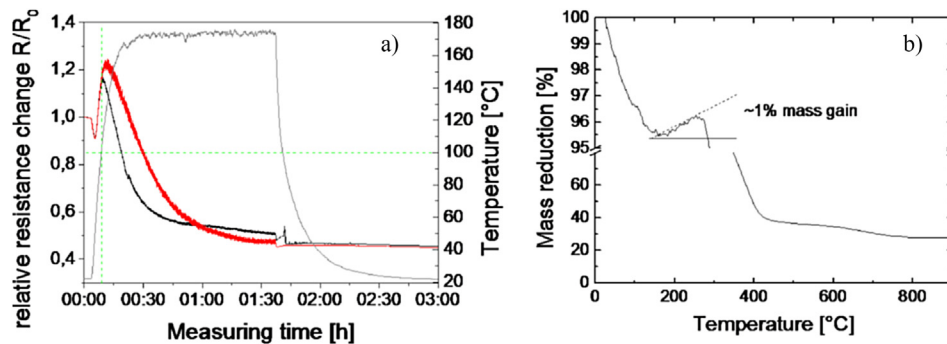
Fig. 8. a) Relative change of the resistance of two printed SWCNT lines during the heating on a hotplate under ambient conditions. The temperature of the substrate was measured parallel. b) TGA analysis of SWCNT-C material under dry air. Especially the temperatures range from 150 to 260 °C show a mass gain which is related to the adsorption of oxygen. (A colour version of this figure can be viewed online.)

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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