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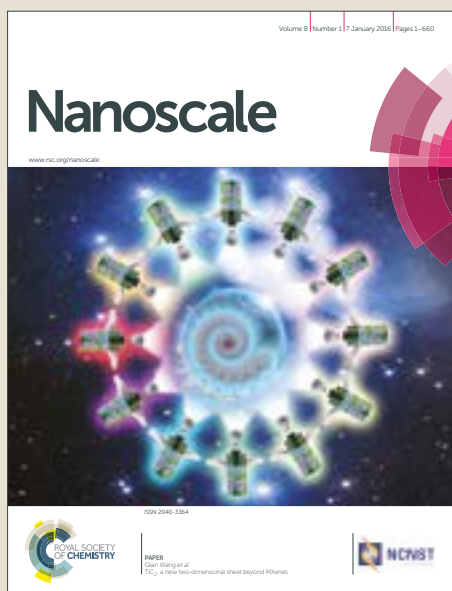
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Films of filled single-wall carbon nanotubes as a new material for high-performance air-sustainable transparent conductive electrodes operating in a wide spectral range

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In this paper we show the advantages of transparent high conductive films based on filled single-wall carbon nanotubes. The nanotubes with internal channels filled with acceptor molecules (copper chloride or iodine) form networks demonstrating significantly improved characteristics. Due to the charge transfer between the nanotubes and filler, the doped-nanotube films exhibit the electrical sheet resistance drop by an order of magnitude together with a noticeable rise of films transparency in the visible and near-infrared spectral range. The thermoelectric power measurements show a significant improvement of air-stability of nanotube network in course of the filling procedure. For the nanotube films with the initial transparency of 87% at 514 nm and the electrical sheet resistance of 862 Ohm/sq we observed the improvement of transparency up to 91% and the decrease of sheet resistance down to 98 Ohm/sq. The combinations of nanotube synthesis technique and molecules for encapsulation have been optimized for applications in optoelectronics.

Introduction

Single-wall carbon nanotubes (SWCNTs) show a unique set of physical and chemical properties such as high mobility of charge carriers¹, ballistic transport along the nanotube axis², chemical stability³, et al. However, these properties are inherent only to the individual SWCNTs. In general, for different applications, such as transparent conductive films (TCF) or light sensitive structures in electronic devices, the

SWCNTs are merged in macrostructures as films⁴, fibers⁵ and mats⁶. It is quite natural that nano-objects assembled in macrostructures lose or change their characteristics. For instance, the high conductivity (up to 30000 S cm⁻¹^{7,8}) and mobility (up to 100 000 cm² V⁻¹ s⁻¹) decrease by several orders of magnitude in assembled nanotubes^{9,10}.

This happens because the mixture of as-synthesized non-treated SWCNTs usually contains both metallic and semiconducting nanotubes¹¹, and the SWCNTs by themselves are not well-aligned and not perfectly straight^{12–16}. Moreover, there is a significantly high contact resistance between individual SWCNTs or between their bundles when they are collected in films, wires or mats^{17–20}. Because of these features, as-synthesized SWCNTs assembled in transparent conductive flexible (TCF) films concede the widely used materials such as indium-tin oxide (ITO), PEDOT:PSS, Ag-nanowires or FTO/ITO electrodes which have R_{sq} of 20-30 Ohm/sq under the same optical transmission T_{tr}^{21–23}.

There are several ways to enhance the conductivity of as-synthesized SWCNT films: a post-synthesis treatment of SWCNTs (like a chemical doping, an attachment of functional groups to the CNT walls, and etc.^{24–28}); a post-synthesis separation of SWCNT mixture into metallic and semiconductor fractions²⁹; an alignment and densification of SWCNTs in films to decrease the number of contacts and to shorten the electric current path³⁰; a selective growth of SWCNTs with a preferential conductivity type³¹. These approaches allow to increase the conductance of SWCNT films by an order on magnitude.

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Also, in addition to the conductive properties of TCF, the operating spectral range, the methods of deposition and formation are important. This is primarily due to utilizing of transparent conductive electrodes in solar cells (organic), transparent displays, LED, OLED and photosensitive detectors^{32–34}. In such, typically, layered structures, it is necessary to have a transparent top electrode. According to modern requirements and depending on specific application, the top electrode should have a high conductivity, transparency in the operating range, flexibility, stability, low toxicity, low cost, and embeddability in the manufacturing process³⁵. Unfortunately, there is no universal material for TCF. ITO, despite its high conductivity and transparency, is a fragile material, with a narrow window of transparency (visible range) and a high cost^{32,36}. Moreover, the methods of CVD growth and sputtering of ITO are not applicable to the formation of organic solar cells, light-sensitive elements, and OLEDs³⁷. PEDOT, PEDOT:PSS, Ag nanowires, acid-doped CNT, externally doped CNTs are superior to ITO in many ways, but the main problem is the formation and deposition of such electrodes^{32,33,35,38}. The formation process of organic electrodes involves the use of suspensions with surfactants, solvents, drop-casting deposition, doping on an already formed structure of LED or solar cells^{17,18,39}. Such treatments contaminate or destroy the layered structures.

In the present work we show the advantages of gas phase filling of the SWCNT interior channels by acceptor molecules (which is usually utilized for synthesis of unique 1D-structures^{25,40–42}) in the context of TCF production. This method is very promising due to the higher stability of such films in comparison with the films assembled from SWCNTs with functionalised outer walls^{27,43–45}. We have found efficient parameters for SWCNT conductivity improvement through encapsulation. For nanotube synthesis and film formation we used the aerosol-CVD synthesis where the SWCNT film is automatically formed at the bottom of the chamber⁴⁶. We used gas-phase filling of SWCNT by copper chloride or iodine^{24,47–49}. Our previous articles demonstrate a significant change of optical and electrical properties of single- and multiwall CNTs after encapsulation of copper chloride or iodine. In our approach we have selected these dopants due to a high encapsulation efficiency, an ability of filling from gaseous phase and a substantial dopant-nanotube charge transfer. From our point of view, this approach is the most versatile and satisfying all requirements for top electrode. The optimized filling technique and the method of nanotube synthesis make it possible to deposit films that are already doped. A high conductivity and a wide transparency range make this material promising as multipurpose transparent conductive films (TCF). In this paper, we investigated the conductivity and thermoelectric power (TEP) as a function of temperature for “pristine”, iodine- and copper chloride-doped SWCNT films to estimate the advantages and the features of TCF based on filled SWCNTs. Also, the optical transmission (T_{tr}) improvements of a unique set of aerosol-grown SWCNT films with T_{tr} = 60–90 % were discovered. The effect of different charge transfer on optical and electrical properties of films was

investigated. The most important practical results are the complex improvement of TCF based on filled SWCNTs. The rise of transparency within a very wide spectral range, the rise of conductivity by an order of magnitude and the presence of environmental insensitivity and flexibility were discovered for our samples.

Experimental

Preparation of SWCNT network and samples description

In this work the aerosol chemical vapor deposition (CVD) SWCNTs were used for formation of transparent conductive flexible electrodes. The aerosol-SWCNTs are synthesized in the vertical laminar flow reactors. The experimental setups for aerosol synthesis include a precursor feed system, a furnace with a metal or ceramic tube, sampling and analysis devices⁴⁶. The advantages of aerosol CVD synthesis are:

- formation of extended SWCNT films consisting of relatively long (more than 1 μm) nanotubes and their bundles;
- growth of SWCNTs with large diameters (up to 2 nm);
- possibility to assemble SWCNTs in transparent high conductive flexible buckypaper structures;
- possibility to tune gradually several parameters: the SWCNT diameters, buckypaper density and optical transparency.

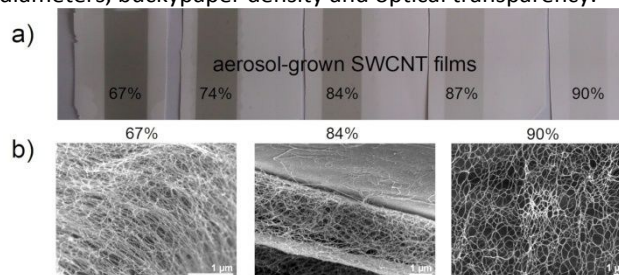


Fig. 1 (a) Photograph of a set of aerosol-grown SWCNT films with different optical transparency (transparency values are given for 514 nm); (b) SEM images of aerosol-grown SWCNT films with different optical densities.

These features make aerosol-SWCNTs the very promising for formation of transparent conductive flexible electrodes. The films synthesized by aerosol CVD are networks formed from long bundles of SWCNTs. The nanotubes have a mean diameter of 1.8 nm (Figure 1 b)). For our investigation the SWCNT films with transparency (T_{tr}), gradually changed in the range from 60 to 90 %, were prepared (Figure 1 a)). The nanotube network transparency was controlled by changing the time of accumulation of SWCNTs on filter (Millipore, pore size about 0.45 μm) during synthesis. Initial R_{sq} of prepared films was in the range from 150 Ohm/sq to 4800 Ohm/sq depending on T_{tr}, with higher resistance for higher transparency. For instance, the films with T_{tr} of 67 % and 87% showed R_{sq} of 150 and 860 Ohm/sq, respectively. As it was noted in introduction, the main disadvantages affecting the conductivity of films based on assembled nanotubes are high electrical resistance of contacts between the nanotube bundles and relatively low concentration of metallic (conductive) nanotubes in the SWCNT mixture. In this work we apply a new approach to increase the electrical conductivity of

semiconducting SWCNTs in films. It is based on gas-phase filling the nanotubes with copper chloride or iodine. From each sample shown in Figure 1 (a) (samples with transparency 60–90%) 3 strips have been cut for studies. A comparison of doping effects was performed with those strips of each sample.

The doping procedure of SWCNT network

A simple method of SWCNT doping was used. The SWCNT films were deposited on polished quartz plates and heated at 200°C in air during 2 hour to remove organics. At the main stage of treatment procedure a sealed tube with samples and doping crystals was heated up in an electric furnace. There were no direct contacts between the nanotube network and the crystals²⁴. The treatment temperature should be close to the sublimation temperature of dopant materials. The sublimation temperature value of crystalline iodine is 113.5°C. The iodine treatment was carried out in the temperature range 125 - 130°C⁴⁹ during 14 hours. About 20 mg of solid iodine (Sigma-Aldrich, 99.8 %) was used for the treatment process.

The second dopant used for the same SWCNT films was copper chloride. According to literature, Copper chloride demonstrated a higher, in comparison with iodine, charge transfer value, while the treatment procedure was also quite simple^{47,48}. A gas-phase treatment by copper chloride was carried out in the temperature range 210–230°C during 26 hours. We used 1 - 5 mg of solid copper (I) chloride (Alfa Aesar, metals basis, 99.999 %) for treatment.

A post-treatment procedure includes heating of treated films in un-sealed tube during 2 hours under the same treatment conditions but without dopant crystals. This step was performed to partly remove the outer-wall adsorbed dopant crystals. A doping effect due to nanotube filling and other changes of the nanotube film properties were compared in case of iodine and Copper chloride treatment.

Optical, microscopic and transport measurements of prepared materials

The Raman spectra of «pristine», iodine- or copper chloride-treated SWCNT films were registered with a Jobin Yvon S-3000 spectrometer and Ar-Kr laser (Spectra-Physics). The Raman spectra of SWNTs were recorded with 514 nm (2.41 eV) excitation wavelength in the spectral ranges of tangential G-mode (around 1600 cm⁻¹) and radial breathing modes (RBM) (50–500 cm⁻¹). The UV-vis-NIR optical absorption spectra were recorded within a spectral range 200 - 3000 nm with a spectrophotometer Lambda-950 (Perkin-Elmer).

The measurements of electrical resistance of aerosol-synthesized SWCNT films were made by an ordinary DC four-probe method, using the model Keithley 220 as the switchable current source, and the model Keithley 182 for measuring the potential drop. The measured current was 10⁻⁷ A. The films were fixed in a special holder. Contacts to the sample were manufactured from a 30 μm-diameter copper wire and attached with a self-solidifying silver paste. In our investigations we measured not only the value of the electrical

resistance at room temperature but also its temperature dependence in the range of 5 to 300 K. For this purpose the holder was placed in a blown-through helium cryostat for intermediate temperatures.

The thermoelectric power (TEP) was measured using an ordinary integral two-probe method⁵⁰ in a specialized vacuum chamber containing a custom-made TEP probe holder. On gradient heating holder plate the sample temperatures and the potential differences across the sample are measured with the thermocouples. The chromel–alumel thermocouples were utilized as probes, but the potential differences were measured by chromel wires. The samples of “pristine”, iodine- and copper chloride-filled SWCNT films were held under the ambient conditions before the TEP measurements. The measurements were conducted for a temperature range of 300–425K (temperature of hot point of the sample) and in air. The treated SWCNT films were studied by scanning electron microscopy (SEM) using the JEOL-7600F instrument and by high resolution transmission electron microscopy (HRTEM) using the instrument JEM-2100F equipped with a delta corrector and a cold field emission gun operated at 60 kV.

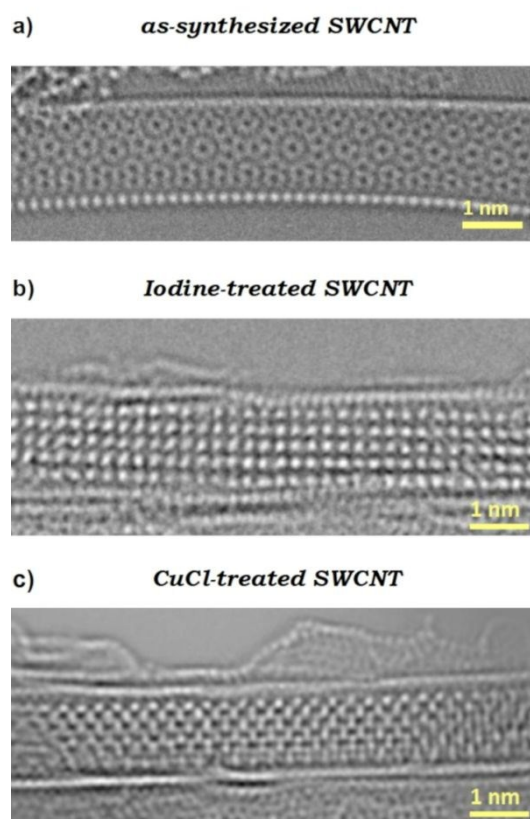


Fig. 2 HRTEM images of (a) initial SWCNT; (b) SWCNT filled with iodine; (c) SWCNT filled with CuCl.

TEM studies should reveal the filling of interior channels of SWCNTs after gaseous treatment of both types. For iodine we already have observed this earlier²⁴. As it was shown, the gaseous treatment leads to filling of nanotube channels and formation of one-dimensional (1D) structures inside. In case of

iodine the 1D crystals or polyiodide chains were observed depending on diameters of SWCNTs⁴⁹. In our work we used the coarse aerosol-grown SWCNTs with mean diameter of 1.8 nm (Figure 2 (a) shows an example of a «pristine» nanotube). In our case only 1D crystals were observed inside nanotubes after iodine or copper chloride treatment (Figure 2 (b), (c)). The atomic structure of 1D-crystals of iodine and copper halides, formed within carbon nanotubes with diameters up to ~1.6 nm, has been studied in numerous experimental and theoretical works^{51–55}. In relatively thin nanotubes, the filling molecules may arrange in unique 1D-structures, not existing as free-standing objects. For large-diameter tubes it is often believed, that the filled material resembles the structure of the corresponding bulk crystal. However, recent studies revealed an unexpected complexity of the 1D nanocrystals grown inside the nanotube inner channels⁵⁶. Treatment of the CNT-samples with binary compounds may result in growth of different substances with various chemical compositions. An unambiguous determination of the chemical composition and precise atomic arrangement of the 1D-crystals grown inside the carbon nanotubes requires a more detailed study including theoretical modeling and analysis of different TEM projections.

Results and discussion

Many properties of carbon nanotube are affected by chemical doping. Due to a large difference between the work function values of carbon nanotubes (~4.95–5.05 eV^{57,58}) and strong acceptor solids like iodine (~5.5 eV⁵⁹) and copper chloride (~6.8–7.0 eV⁶⁰), the electrons from the CNTs are transferred to the lower-lying states of the acceptor structures. The consequence of this charge transfer is the depletion of the highest occupied nanotube electronic states and Fermi level shift inside the valence band of the CNTs^{25,53}, which leads to metallization of the semiconducting fraction of the macroscopic sample. Besides the enlarged electrical conductivity^{47,61,62}, this also significantly affects the optical properties of the samples – the Burstein-Moss shift^{63,64}, observed in degenerate semiconductors, manifests itself in the suppression of optical absorption bands of the nanotubes^{49,65,66}. In the context of transparent conductive films fabrication, the acceptor doping leads, therefore, to the overall improvement of the SWCNT films characteristics, making them both more conductive and more transparent. We now turn to the detailed discussion of the properties of the produced films, probed by optical absorption, thermoelectric and conductivity measurements.

Raman and UV-vis-NIR spectra

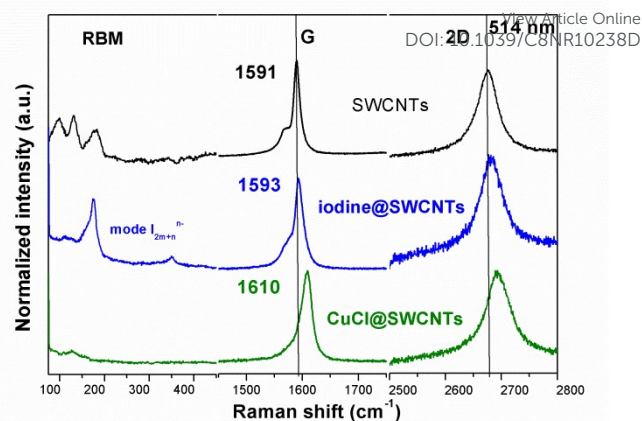


Fig. 3 The normalized Raman spectra of SWCNT films formed from initial and acceptor-filled (iodine or CuCl) nanotubes. The excitation wavelength is 514 nm (2.41 eV).

The Raman spectra of pristine and gas-phase treated SWCNT films were recorded at 514 nm (2.41 eV) excitation wavelength (Figure 3). The normalized Raman spectra of treated SWCNTs show a significant change in phonon and electron structure of SWCNTs. In case of iodine, the G-band was shifted toward high frequencies by 2–3 cm⁻¹. The right shift of G-band was associated with the charge transfer from SWCNT to dopant structures^{67–69}. In the low frequency range a significant suppression of radial breathing mode (RBM) bands and an appearance of a new line were detected⁷⁰. The suppression of SWCNT modes could be associated both with a charge transfer and a strong mechanical interaction between nanotubes and 1D structure inside them. Some contribution could come from dopant clusters outside the tube walls. As it was reported⁴⁹, the new peaks in RBM region are lines of polyiodide structures, formed inside nanotube inner channels and, probably, in space between individual tubes in bundles. Moreover, because the I₂ iodine lines were not discovered in the spectra, we could conclude that adsorbed or intercalated I₂ is absent⁴⁹.

The Raman spectra of copper chloride-treated SWCNTs exhibited similar effects. In case of copper chloride, the significant suppression of RBM, 2D and G bands was observed⁴⁸. As well as in case of iodine the right shift of G-band associated with charge transfer was detected. As it was expected, the shift was higher than that in case of iodine by an order of magnitude (up to 20 cm⁻¹) as a consequence of higher charge transfer in case of copper chloride.

UV-vis-NIR spectra (in spectral range 200–3000 nm) were recorded for SWCNT films of different density, and, as a result, of different optical transparency. Figure 4 (a) shows the optical features of «pristine» SWCNTs. The bands marked as E11s, E22s and E11m are associated with electron transitions for semiconducting (s) and metallic (m) SWCNTs, respectively. It was determined that the measured samples (60–90% transparency) demonstrated T_{tr} of 67, 74, 84, 87% and 90% at 514 nm, depending on film density.

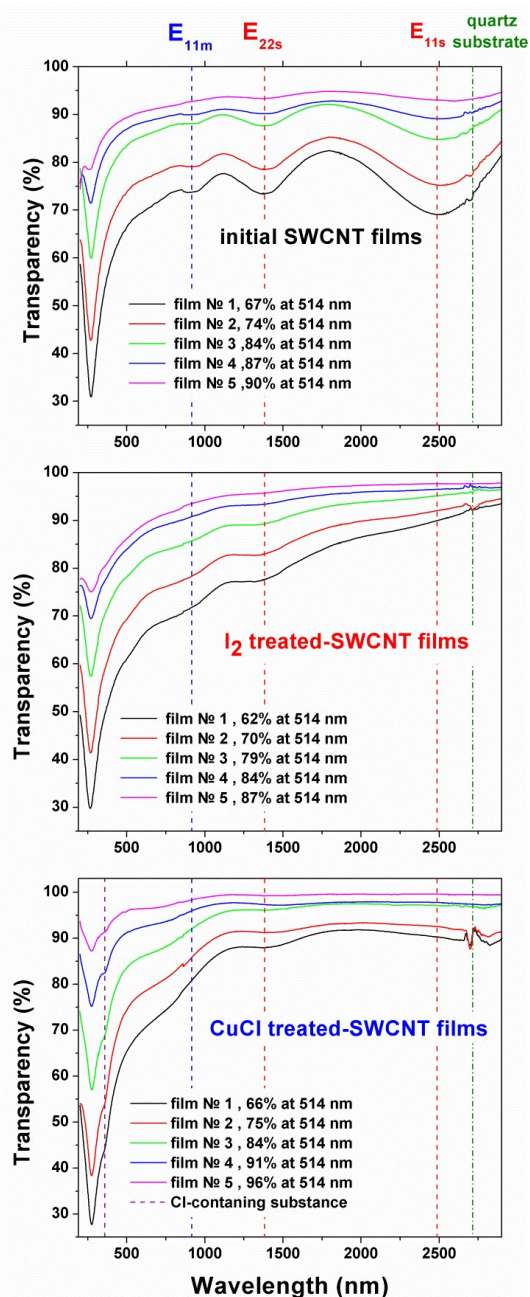


Fig. 4 UV-vis-NIR optical absorption spectra for the set of SWCNT films with different optical transparency (films №1-5): (a) initial; (b) filled with iodine; (c) filled with CuCl.

After gas-phase iodine treatment the changes of optical properties triggered by the charge transfer from SWCNT to iodine structures were observed (Figure 4 (b)). The first electron transition for semiconducting SWCNTs was completely suppressed. The second electron transition for semiconducting SWCNTs was suppressed partially. The suppression of electron transition occurs due to the charge transfer which empties the states in the top of valence band. In these states there are no electrons which could absorb photons anymore. The suppression of E_{11s} and E_{22s} is related

to the position of the Fermi energy and allows estimating the efficiency of electron transfer from the nanotube. Another effect is a decrease of T_{tr} in spectral region 200-1500 nm. A reduce of transparency (of 3% in average) was observed for all samples at 514 nm (Figure 4 (b)). The increase of absorption in the entire visible range may be attributed to the absorption of 1D – polyiodide structures, formed inside nanotubes⁷¹.

Figure 4 (c) presents UV-vis-NIR spectra of copper chloride-treated SWCNTs. As in case of iodination, the electron transitions for semiconducting SWCNTs were also suppressed. However, for the copper chloride the suppression effect was higher. This correlates with the Raman results for both cases (Figure 3). Thus, for copper chloride a higher value of charge transfer was observed, as in the previous studies^{47,49,53}. As for the optical transparency, the opposite effect takes place. The samples with initial T_{tr} 67%, 74% and 84 % at 514 nm were not remarkably affected, while for the samples with initial T_{tr} 87% and 90 % the increase of T_{tr} about 4% was detected. In case of copper chloride, the effect of transparency increase, resulted from the charge transfer, was observed up to ultraviolet range, where the copper chloride absorbs. After the copper chloride treatment a new band appeared in UV region at position of about 360 nm. We attribute this band to absorption of a chlorine-containing substance⁷². Also, the position of the observed band is close to that known for nano-objects of CuCl and CuCl₂^{73,74}.

Improving transparency and expanding the spectral transparency window is one of the significant advantages of filled-SWCNTs over materials being leaders for TCF formation. This work and our recent⁷⁵ investigations show that film of filled SWCNTs is highly transparent within the wide range - from 200 up to 10000 nm. The organic materials (as PEDOT:PSS) have a narrow transparent spectral window (from 300 up to 1000 nm)⁷⁶. Also, the ITO and FTO/ITO structures are transparent within the visible range, but they have an extremely high light absorption in UV and NIR ranges⁷⁷.

Stability of doped SWCNT films

The stability of single-walled carbon nanotube films filled with CuCl and iodine was estimated by thermoelectric power (TEP) measurements. TEP is extremely sensitive to the Fermi energy shift. Moreover, for semiconductors, the TEP sign yields the type of predominant carriers as well as the value of energy gap.

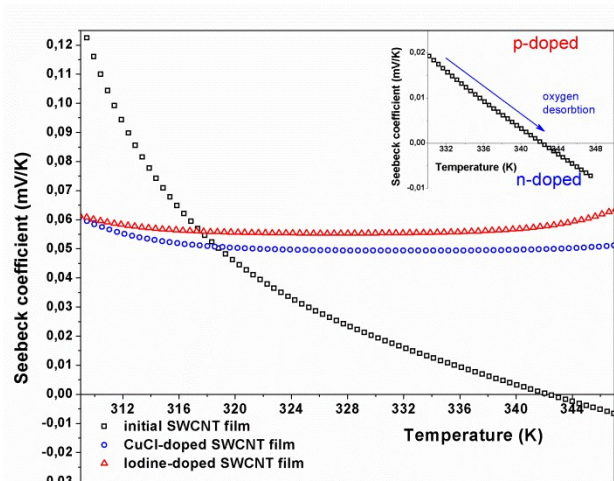


Fig. 5 Temperature dependence of thermopower for initial, iodine- and CuCl-doped SWCNT films. Insertion: thermopower for initial SWCNT films in the region of TEP sign switching.

The plots of Figure 5 demonstrate the measured TEP (Seebeck coefficient) as a function of average temperature for initial, iodine- and copper chloride-doped SWCNT films. Here all measurements were made in the narrow temperature range from 298 to 373 K and under air conditions during 20 minutes. The Seebeck coefficient of initial SWCNT film shows the exponential change from about +120 $\mu\text{V/K}$ to -7 $\mu\text{V/K}$ at the slight heating. Such behavior is easily explained by the extreme sensitivity of SWCNT electronic properties to the presence of physisorbed or/and chemisorbed oxygen^{78,79}. The oxygen is known to show acceptor properties for carbon nanotubes. So in our case, the physical desorption of oxygen, caused by heating, leads to the change of carrier type from holes to electrons with a switching of the Seebeck coefficient sign – TEP sign are switching from plus to minus.

Despite the fact that physisorbed oxygen is present in the copper chloride and iodine treated samples, the TEP temperature-induced behavior of initial and intentionally doped samples was significantly different. TEP of copper chloride and iodine-doped SWCNT films showed a weak dependence on the temperature within the whole range. Such temperature dependence is usual for metal SWCNT⁸⁰. Presumably, the effect of oxygen desorption for a filled-SWCNT film is negligible. Primarily, it is due to a strong doping and a significant Fermi level shift for iodine-(0.6 eV) and copper chloride-(0.9 eV) doped samples⁴⁷.

Based on the TEP results we claim the rise of stability of SWCNT films under the filling process. In this case, stability depends on evaporation temperature and doping ability of fillers. The initial samples are doped by physisorbed oxygen, so the heating above 300 K leads to its desorption having a negative effect on transport properties: a rise of the resistance is triggered by the change of the carrier type. The filling (physisorption) with iodine and copper chloride were carried out at 403 and 503 K, respectively. Thus, the intentionally doped films demonstrate the stable transport properties

below 400 K. In the case of simultaneous physisorption of few acceptors (or donors), the main contribution to the transport properties is determined by the strongest one. It happens due to highest carrier density under the stronger doping effect. The additional oxygen doping leads to a minor change in carrier density. Therefore iodine- and copper chloride- doped samples are stable within the temperature range investigated. Such insensitivity to the environment makes the filled tubes a very promising material for electronics applications.

Sheet resistance of doped SWCNT films

Four-probe DC measurements were carried out at room temperature for the untreated, iodine-treated and copper chloride-treated SWCNTs assembled in films of different optical transparency. To investigate the improvement of film electrical conductivity after the gas-phase treatment by iodine or copper chloride, the strips of samples with 60-90% transparency have been placed on quartz substrates and connected by 30 μm -diameter copper wire, attached with a self-solidifying silver paste. As it was expected a high charge transfer should lead to a remarkable improvement of electrical conductive properties of filled SWCNT films. Previously, we and other groups observed a substantial increase of the film electrical conductivity, triggered by the charge transfer between the nanotube and dopant^{24,47,62}.

The 4-probe measurements have demonstrated an extremely high decrease of R_{sq} for both iodine- and copper chloride-treated SWCNT films. The film with the initial couple of characteristics: R_{sq} and T_{tr} of 147 Ohm|67% after the iodine treatment changed the parameters to 31 Ohm|62%, correspondently. The same "pristine" film after the copper chloride treatment demonstrates R_{sq} and T_{tr} of 28 Ohm|66%. So, the improvement of R_{sq} by an order of magnitude was observed in both cases. On the other hands, in case of initially more transparent films the difference between the nanotube filling with copper chloride and iodine is clearly detected. The film with initial R_{sq} and T_{tr} of 4800 Ohm|90% after the iodine treatment changed parameters to 359 Ohm|87%, after the copper chloride treatment – 208 Ohm|96% (Table 1). In comparison with the iodine treatment, the copper chloride filling led to the higher (about two-fold) decrease of R_{sq} . The higher effect on R_{sq} of SWCNT films in case of copper chloride treatment could be assigned to the higher value of charge transfer in this case, confirmed earlier by Raman and UV-vis-IR studies of the same films. The difference in the R_{sq} and T_{tr} changes for different SWCNT films may be explained by the features of filling degree and percolation effects. With the rise of film density (toward to lower T_{tr}) the number of metal current pathways should rise. Thus the effect of SWCNT film doping should be lower for the high density films containing both metal and semiconducting tubes.

Table 1 The electrical sheet resistance (R_{sq}) at room temperature and optical transparency (T_{tr}) at 514 nm for initial and filled SWCNT films.

SWCNT films		Iodine-treated SWCNT films		Copper chloride-treated SWCNT films	
T_{tr} (%)	R_{sq} (Ohm)	T_{tr} (%)	R_{sq} (Ohm)	T_{tr} (%)	R_{sq} (Ohm)
67	147	62	31	66	28
74	261	70	61	75	31
84	362	79	68	84	60
87	862	84	151	91	98
90	4807	90	359	96	208

From point of view of transparent conductive films the most important results concern the samples with initial couple of parameters $T_{tr}|R_{sq}$ of 84%|362 Ohm as well as 87%|862 Ohm. Iodine doping of these samples led to change of $T_{tr}|R_{sq}$ from 79%|68 Ohm to 84%|151 Ohm. The copper chloride doping of these samples led to these characteristics changing to 84%|60 Ohm and 91%|98 Ohm, respectively. Thus, the highest parameter of $T_{tr}|R_{sq}$ at the transparency closest to 90% has been observed for SWCNT film treated by copper chloride. This film demonstrated $T_{tr}|R_{sq}$ characteristics close to that of ITO. Moreover, these new films formed from assembled doped SWCNTs turned out to be very stable. As it was specially tested, their T_{tr} and corresponding R_{sq} values remain unchanged during several years. The control measurements of sheet resistance at room temperature have been performed in a few years. The films SWCNT, treated by copper chloride, with 84 and 91% transparency, demonstrated a rise of sheet resistance from 60 to 63 Ohms and from 98 to 102 Ohms, respectively. So, the variation of resistance did not exceed 6% after five years.

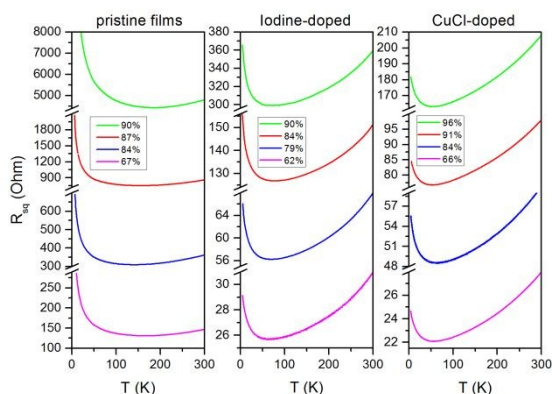


Fig. 6 Temperature dependencies of the sheet resistance of pristine and doped SWCNT films with the different values of optical transparency.

The temperature dependencies of the sheet resistance of the investigated SWCNT films are shown in Figure 6. As seen, all the curves have a non-monotonic temperature behavior with a strongly pronounced metallic run ($dR/dT > 0$) at high temperatures and an abrupt up-turn at low temperatures. It is seen also that a weak metallic run at $T > 200$ K is observed even for «pristine» SWCNT films. However, as it was mentioned by us in Ref. ²⁴, such a behavior appears to be

observed only for the films consisting of SWCNTs with an average diameter equal or greater than 2 nm. For the films made from SWCNT of lower average diameter the up-turn $R(T)$ began directly from room temperature.

After modification by doping, the films resistance appeared to drop down by one order of magnitude, to change the non-monotonic temperature behavior, and to reduce the crossover temperature. The greatest effect is observed in case of using copper chloride as a dopant. The metallic behavior of $R(T)$ is extended down to 50 K.

As follows from the data shown in Ref. ⁴⁷ the forms of reduced $R(T)/R(300\text{ K})$ dependencies almost do not depend on optical transparency, i.e. on the density of nanotube cells in the nanotube net. In turn, this fact argues a presence of two contributions to the total resistance: (1) the contribution from SWCNT bundles with a quasi-one-dimensional conductivity; (2) the contribution from the inter-bundle electron tunneling in the places of their crossing. As it was shown in Ref. ⁴⁷ these contributions are perfectly fitted in frames of known heterogeneous model ^{81,82}. The modification of SWCNT by doping decreases the values of both contributions. The behavior of nanotube contribution can be described in frames of model for suppression of backscattering of the charge carriers by phonons. The shift of the Fermi energy from the gap center into valence band was determined in Ref. ⁴⁷ as -0.6 eV in case of iodine doping and as -0.9 eV in case of copper chloride doping. It was shown also that in case of SWCNT films modification the energy barriers for electron tunneling between SWCNT bundles are essentially diminished. That means the significant decrease of contact resistance between SWCNT bundles. In addition, the dropping down of the energy barriers for electron tunneling by one order of magnitude substantially exceeds the decreasing of nanotube contribution specified by a low energy phonon participation.

Thus, from the physical point of view the significant decrease of the electrical resistance of acceptor-doped SWCNTs assembled into transparent films can be connected with the shift of the Fermi level down into the valence band in the region of quasi-one-dimensional density of states. The level of doping corresponding to the Fermi energy shift below the top of the first metallic sub-band, provides the increase of conductivity of metallic nanotubes, and simultaneously, the opening of metallic channel for p type doped semiconducting nanotubes. Thereto it is very important that the doping leads to the significant decrease of the energy barriers for electron tunneling between SWCNT bundles, and therefore to essential diminishing of the contact resistance between SWCNT bundles.

Advantages of filled SWCNT films

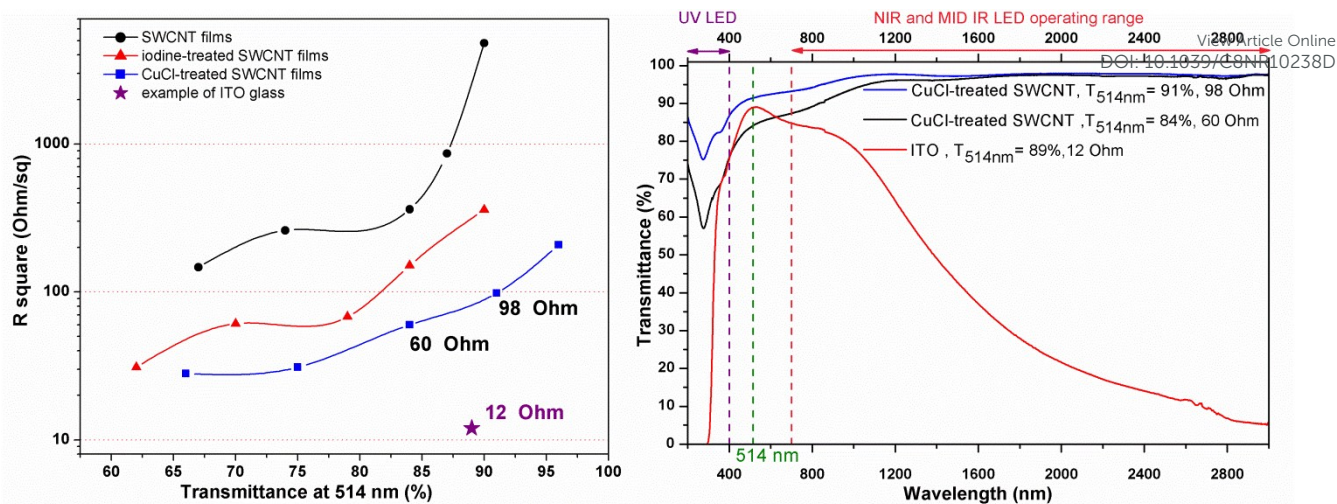


Fig. 7 (Left) The electrical sheet resistance (R_{sq}) at room temperature versus optical transparency (T_{tr}) at 514 nm for films assembled from pristine and filled SWCNTs. (Right) UV-vis-NIR optical absorption spectra for ITO glass and copper chloride-doped films.

The discussed changes in conductive and optical properties of SWCNT films arising after acceptor-doping are summarized in Figure 7. The SWCNT films treated with copper chloride demonstrate the lowest sheet resistance, which is, however, 5–8 times higher than that of ITO glass sample used for comparison. The ITO glass with a transparency of 89% at a wavelength of 514 nm and a sheet resistance of 12 Ohm was used as a reference sample. These values are better than ones observed for the filled nanotube films. Nevertheless such films are still promising for formation of conductive transparent electrodes. The final resistance of the transparent doped nanotube film is strongly depended on the initial parameters of the sample before doping. We believe that by optimizing the methods of synthesis and film formation it is possible to achieve much lower values of resistance of initial samples. As a result, a minimal resistance of these films after treatment with copper chloride will be decreased. In general, such films demonstrate significant advantages comparing with ITO and other organic and nanotube transparent electrodes. They have a higher transparency in the wide spectral range from 200 to 10,000 nm. This makes it possible to use such films for UV, IR and MID IR LED, as well as other photosensitive elements where it is necessary to make a transparent conductive "window"^{83–88} From our point of view, the other most important advantage of such films is a possibility of their simple non-disturbing incorporation into many technological processes for the formation of layered structures (especially organic ones). Such ability exists due to the simplicity of transferring of aerosol CVD grown films on any surface without additional thermal treatment, participation of solvents and organic materials.^{4,89} Also the filling technique can be optimized for doping of free-standing films anywhere with the subsequent transfer to the formed layered structure. This eliminates the contamination of photosensitive layered elements and the destruction of fragile organic structures. Another equally important advantage is a temporary stability and insensitivity to the environment, even in course of longstanding temperature processes. According to

thermoelectric measurements, the filled carbon nanotubes are almost not sensitive to absorption and desorption of oxygen. Moreover, a longstanding storage in air (5 years) leads to the electrical resistance increase not more than 6%.

Conclusions

In present work we demonstrate the advantages of networks of single-wall carbon nanotubes filled with acceptor molecules (iodine, copper chloride) from gas phase. The gaseous treatment results in encapsulation of iodine or copper chloride in SWCNT channels, followed by formation of 1D-structures based on them. These 1D-structures accept electrons from the nanotubes. We have revealed the effective charge transfer between the nanotubes and inner structures. This led to the remarkable improvement of characteristics of «pristine» conductive SWCNT networks: sheet resistance, wide-range optical transparency and air sustainability. The higher charge transfer leads to the higher improvement of electrical sheet resistance of the film formed from hybrid (nanotube + dopant) structures. Thus, the copper chloride encapsulation improves R_{sq} of the aerosol-synthesized SWCNT films more than the iodine treatment. A unique set of conductive films with a step-by-step changed transmission (60–95%) has been prepared in this work on the base of aerosol-synthesized single-wall carbon nanotubes. The nanotubes were filled with iodine or copper chloride under the same conditions. The effect of transparency and sheet resistance improvement in films of filled nanotubes (comparing with parent pristine ones) was observed for all films in the set. The highest couples of values of $T_{\text{tr}}/R_{\text{sq}}$ - 84% / 60 Ohm and 91% / 98 Ohm have been registered. These characteristics sound very promising for applications in optoelectronics. Thus, the filling procedure is not only a method for conductivity increasing. We demonstrate that filling is a comprehensive method of improving transparency, conductivity, and stability of nanotube networks for using as conductive transparent flexible electrodes in optoelectronic devices operating in

ultraviolet, visible and infrared spectral ranges in different environments.

Conflicts of interest

There are no conflicts to declare.

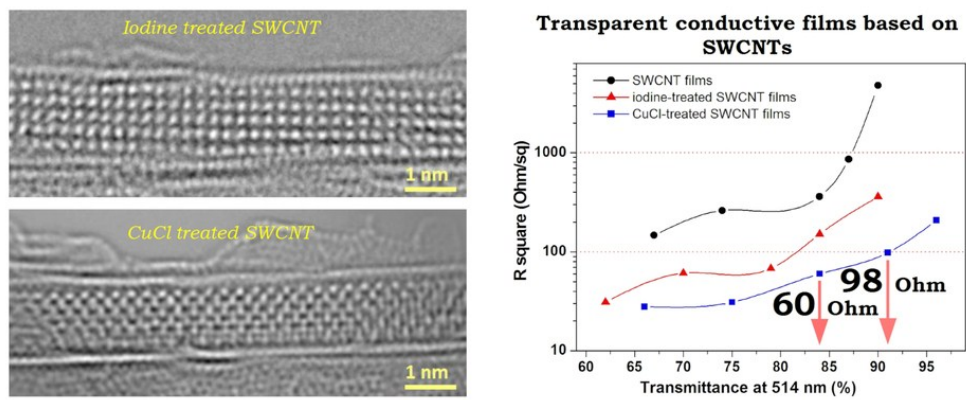
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