Enhanced optical transparency of films formed from sorted metallic or semiconducting single-walled carbon nanotubes filled with CuCl

Pavel V. Fedotov*1, Valentina A. Eremina1,2, Alexander A. Tonkikh1,3, Alexander I. Chernov1,4, and Elena D. Obraztsova**1,4

1 A.M. Prokhorov General Physics Institute, RAS, 38 Vavilov Street, 119991 Moscow, Russia
2 Department of Physics, M.V. Lomonosov Moscow State University, 1 Leninskie gory Street, 119234 Moscow, Russia
3 Faculty of Physics, Southern Federal University, Zorge Street 5, 344090 Rostov-on-Don, Russia
4 National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe hwy, 115409 Moscow, Russia

Received 15 April 2016, revised 27 May 2016, accepted 2 June 2016
Published online 22 June 2016

Keywords CuCl@SWCNT hybrid material, doped SWCNTs, sorted SWCNTs, transparent conductive material

* Corresponding author: e-mail: fedotpavel@mail.ru, Phone: +7 499 5038206, Fax: +7 499 1350270
** e-mail: elobr@mail.ru

Metallic and semiconducting fractions of single-walled carbon nanotubes (SWCNTs) sorted by an aqueous two-phase extraction technique and integrated into thin films were used to produce CuCl@SWCNT hybrid material via a gas phase filling the nanotubes with CuCl. As a result of doping, the SWCNTs in the hybrid material possess a higher optical transparency than the pristine ones. The hybrid material properties strongly depend on the metallic/semiconducting tube ratio in a pristine material. In this work, with UV-vis-NIR optical absorption and Raman techniques we show that upon filling with CuCl the solely metallic nanotubes provide much higher doping efficiency than the solely semiconducting SWCNTs. The CuCl@SWCNT hybrid material based on sorted nanotubes is more competitive as a transparent conductive material for the future photovoltaics.

1 Introduction Single-walled carbon nanotubes (SWCNTs) are very attractive for various fields of application [1]. Formation of transparent conductive material for future photovoltaics is one of the most promising fields [2, 3]. An ultimate flexibility, a high electrical conductivity and optical transparency of SWCNTs make them perfect candidates for high tech application areas. Thin film-like media formed from pristine SWCNTs have competitive performance characteristics [4]. Meanwhile, the SWCNT intrinsic properties can be significantly improved by various nanotube functionalization methods [5–8].
Filling the nanotubes is one of the ways to modify SWCNT properties [9–11]. In such technique, the nanotubes can serve as a nanoreactor for synthesis of nanostructured materials [12–14]. The material used as filler should demonstrate a strong acceptor/donor behavior to increase the SWCNT electrical conductivity and to decrease their optical absorption [15–18]. Upon such functionalization SWCNTs become highly doped. This leads to the increase of both optical transparency and electrical conductivity [19–21].

We have shown in the previous study that a gas-phase filling of SWCNTs with CuCl molecules is a simple and efficient method to improve the performance of SWCNT media [21]. For instance, CuCl@SWCNT hybrid material has a superb optical transparency comparing with that of the pristine nanotube media. The origin of this improvement is based on a strong p-type doping of SWCNTs through interaction with 1D CuCl nanocrystals formed inside nanotubes upon filling.

In this work, we perform the sorting of nanotubes over the electrical conductivity type using an aqueous two-phase extraction (ATPE) method. The fractions sorted are further filled with CuCl via a gas phase method to form CuCl@SWCNTs hybrid material. We study optical properties of CuCl@SWCNTs and show that there is a strong dependence on the metallic/semiconducting (m/s) type of nanotubes used for filling. The properties of hybrid materials can be further improved by controlling the m/s composition of SWCNT media.

2 Methods The home-grown arc discharge SWCNTs (average diameter 1.40 ± 0.15 nm) were purified and suspended by common procedures. Briefly, the raw SWCNT powder was dissolved in 2 w/w% sodium cholate (SC) in deionized water and sonicated for 2 h. In order to remove impurities (amorphous carbon and large bundles), the obtained suspension was centrifuged in the Beckman Coulter Ultra-Max-E centrifuge during 1 h with the acceleration 140,000 g. The supernatant was removed by filtration (220 nm pores) with a vacuum filtration technique. The obtained SWCNT film was finally transferred on a quartz substrate. Typically, before filling the films were composed of pure free-standing nanotubes (like a “buckypaper”). Formed SWCNT films possess a high optical homogeneity with a typical thickness below one micrometer.

Sorting of arc discharge SWCNTs over the electrical conductivity type (m/s sorting) was performed via a novel technique: an aqueous two-phase extraction (ATPE) [22].

In this method, we used two polymers: polyethylene glycol and dextran, and two surfactants: SC and sodium dodecyl sulfate (SDS), in appropriate concentrations. More details on SWCNT sorting procedure can be found elsewhere [23]. The yield of sorting can be seen in Fig. 1. The sorted metallic and semiconducting SWCNT fractions obtained were purified from residual polymers, surfactants, and finally transferred on the quartz substrate with the above-mentioned technique.

The filling process was performed by exposing SWCNT film to a gas-phase CuCl in the temperature range from 200 to 300 °C during different periods of time (from several hours up to 24 h) [21]. The filling procedure was carried out in air, inert atmosphere (argon) and vacuum. The obtained functionalized SWCNT films were washed and annealed to remove possible impurities.

The optical absorption spectra were recorded with the Lambda-950 (Perkin Elmer) instrument. The spectral resolution was 0.5 nm in the spectral range 200–3000 nm (6.2–0.41 eV).

The main Raman measurements have been performed with a spectrometer Jobin Yvon S3000 in a microconfiguration. The study of CuCl@SWCNT films was carried out using Ar–Kr ion laser at the wavelengths of 488 nm (2.54 eV), 514.5 nm (2.41 eV), and 647 nm (1.92 eV). The spectral resolution was 1 cm⁻¹. Additional Raman measurements have been performed with a LabRAM HR Evolution spectrometer equipped with HeNe laser (operating wavelength 632.8 nm).

Measurements of electrical sheet resistance of thin SWCNT films and CuCl@SWCNT hybrid material were performed via a common 4-probe resistivity technique on commercially available setup: Jandel RMS-EL/RMS-EL-Z. The measurement range of the setup is from 1 mΩ sq⁻¹ up to 500 MΩ sq⁻¹ with a typical accuracy of 0.3%.

3 Results and discussion The CuCl@SWCNT hybrid material has specific optical transmittance features being different from the features of pristine carbon nanotubes. In general, SWCNTs in a hybrid material are strongly p-type doped. The nanotubes act as an electron donor while the 1D CuCl nanocrystals formed inside SWCNTs act as an electron acceptor [17, 21]. Such phenomenon leads to suppression of the resonant optical
absorption of SWCNTs via the Pauli blocking mechanism. As the Fermi energy level of strongly p-type-doped nanotubes is located within a valence band, the electronic states above the Fermi level become depleted. So, there are no charge carriers at these states to absorb light, and the SWCNTs become optically transparent in the corresponding spectrum range.

To study the CuCl@SWCNTs system, thin films based on sorted s- and m-SWCNTs were functionalized via a gas-phase filling of nanotubes with CuCl. The filling process was carried out under the same conditions within the same chamber and was divided into several steps: 12 h exposure to a gas-phase CuCl at the first step, an additional exposure with the total time of 24 h at the second step and so forth.

By studying the optical transmittance features of the hybrid material synthesized from semiconducting (CuCl@s-SWCNTs) or metallic nanotubes (CuCl@m-SWCNTs) we discovered that both types of nanotubes are strongly affected by functionalization with CuCl (Figs. 2 and 3). It implies that, in general, the process of functionalization by filling nanotubes with CuCl occurs regardless of SWCNT conductivity type.

After the first step of filling (12 h), the CuCl@s-SWCNT sample has a totally suppressed S 11 nanotube absorption transition, whereas S 22 transition is barely suppressed (Fig. 2, red line). This spectrum corresponds to the Fermi energy location between the first and the second Van Hove singularities of semiconducting SWCNTs (Fig. 4b). We assume that such a noticeable change of the spectrum corresponding to a large shift of the nanotube Fermi energy (deep within the valence band) is a signature of strongly doped SWCNTs [17–19].

Moreover, after the second step (24 h) the effect is even more pronounced (Fig. 2, blue line): S 22 absorption transition is totally suppressed, and S 33 transition is also strongly suppressed. In the latter case, we assume that the Fermi level of nanotubes is around the third Van Hove singularity (Fig. 4c). Further exposure of the CuCl@s-SWCNT sample to the CuCl gas does not lead to observable changes in the transmittance spectra. We attribute this limitation to the maximum available filling level for the specific nanotube film.

In case of filling m-SWCNT sample, the effect of functionalization is even more pronounced. The system reaches the maximum filling level already during the first step of treatment with CuCl. At this point the CuCl@s-SWCNT sample demonstrates almost a totally suppressed M 11 nanotube optical absorption transition (Fig. 3) which corresponds to the Fermi level location below the first Van Hove singularity for metallic nanotubes (Fig. 5). So, the Fermi level shift for CuCl@m-SWCNT sample is significantly larger than in case of CuCl@s-SWCNT sample after the first step.

The metallic SWCNTs are more efficiently doped comparing with semiconducting SWCNTs upon n-type doping via a nanotube filling with ferrocene [24].

Figure 2 UV-vis-NIR optical transmittance spectra of s-SWCNT films depending on the exposition time to a gas-phase CuCl: the pristine s-SWCNT film (black), CuCl@s-SWCNT film formed during 12 h exposure to a gas-phase CuCl (red) and during 24 h exposure to a gas-phase CuCl (blue).

Figure 3 UV-vis-NIR optical transmittance spectra of m-SWCNT films depending on the exposition time to a gas-phase CuCl: the pristine m-SWCNT film (black) and CuCl@m-SWCNT film formed during 12 h exposure to a gas-phase CuCl (blue).

Figure 4 The scheme of electronic transitions upon the optical absorption for the pristine s-SWCNT film (a), CuCl@s-SWCNT film formed during 12 h exposure to a gas-phase CuCl (b) and during 24 h exposure to a gas-phase CuCl (c).
attribute an earlier reaching the filling limitation together with a larger Fermi energy shift in case of metallic SWCNTs (relative to semiconducting SWCNTs) to the more effective filling and the more efficient p-type doping of metallic nanotubes upon filling SWCNTs with CuCl. This assumption is further confirmed by Raman spectroscopy data.

In CuCl@SWCNT samples studied, it is typical that a transition in the optical transmittance spectrum between a highly optically transparent region and a region with a normal absorption is not sharp. One can attribute a widening of this transition to the effect of inhomogeneous filling of nanotubes with CuCl. Moreover, inhomogeneous filling of nanotubes can cause the charge transfer between the nanotubes inside the bundles and the appearance of doping level distribution between SWCNTs.

Raman features of both CuCl@s-SWCNT and m-SWCNT samples are in agreement with the known Raman features of highly p-type-doped SWCNTs (Figs. 6 and 7) [16, 17, 21, 25, 26]. The efficient nanotube doping and nanotube filling with other materials could be the reason of strong suppression of radial breathing mode (RBM) intensity. However, we suggest that in case of CuCl@SWCNT hybrid material, the doping effect plays the most important role. Only nanotube fragments (or part of nanotubes) are typically filled [21], and one can assume that, according to the filling mechanism, the RBM intensity of SWCNTs in the film cannot be fully suppressed. At the same time, due to a possibility of charge transfer between the filled and empty nanotubes in the bundles one can expect a doping of all the nanotubes in the bundles even under the partial filling. So for the full suppression of RBMs, the doping of all nanotubes is needed while the filling of all nanotubes is not crucial.

The frequency up-shift of Raman tangential mode (G-mode) of nanotubes is a fingerprint of p-type doping. Usually for the highly doped SWCNTs the frequency shift is higher [16, 26]. For the CuCl@s-SWCNT sample after the first step of filling the G-mode up-shift is 6 cm$^{-1}$ (Fig. 6). This up-shift value is quite high. It signifies a strong nanotube doping in the CuCl@s-SWCNT hybrid material.

At the same time, for the CuCl@m-SWCNT sample after the first step of doping the corresponding component of G-mode is up-shifted by 16 cm$^{-1}$ (Fig. 7). So, according to Raman data, the metallic SWCNT media upon filling with CuCl is more efficiently doped relative to the semiconducting SWCNT media. This difference in doping efficiency becomes more pronounced in Raman spectra in case of a resonant excitation of semiconducting nanotubes (their tiny amount is residual upon m/SWCNTs sorting) in CuCl@m-SWCNT sample (Fig. 8).

In this case, the G-mode upshift of semiconducting SWCNTs is 12 cm$^{-1}$, which is twice higher than in CuCl@s-SWCNT sample (Fig. 6). These observations imply that semiconducting nanotubes in CuCl@SWCNTs offer electrons not only to CuCl nanocrystals, but also to filled metallic nanotubes in the same bundle (e.g., the filled m-SWCNTs act as electron acceptors). A schematic view of this process imposed on the HRTEM image of CuCl@SWCNT bundle is represented in Fig. 9.

**Figure 5** The scheme of electronic transitions upon an optical absorption for the pristine m-SWCNT film (a) and for CuCl@m-SWCNT film formed during 12 h exposure to a gas-phase CuCl (b).

**Figure 6** The Raman spectra of pristine s-SWCNT film (black) and CuCl@s-SWCNT film formed during 12 h exposure to the gas-phase CuCl (red). The spectra are normalized to the G band intensity of s-SWCNTs. The excitation wavelength is 514.5 nm (semiconducting nanotubes are in resonance).

**Figure 7** The Raman spectra of pristine m-SWCNT film (black) and CuCl@m-SWCNT film formed during 12 h exposure to the gas-phase CuCl (green). The excitation wavelength is 632.8 nm (metallic nanotubes are in resonance).
The effect of charge transfer between filled s- and m-SWCNTs is important for understanding the optical transmittance features of CuCl@SWCNTs formed from the nanotubes with mixed conductivity types (Fig. 10).

One of the peculiar features of such CuCl@SWCNTs is a strong suppression of $M_{11}$ absorption transition while $S_{22}$ transition is suppressed very weakly. If the doping efficiency for m/s SWCNTs is similar and there is no charge transfer between filled m/s SWCNTs, then one should expect a gradual suppression of optical absorption transitions upon increasing the CuCl filling level: first $- S_1$, then $S_2$, $M_1$, $S_3$, etc. However, in case of strong enough charge transfer between filled m- and s-SWCNTs one might expect a microscopic charge separation and, therefore, the different order of the optical bands suppression (Fig. 11).

We assume that the effect of charge transfer between filled m- and s-SWCNTs plays an important role in decrease of efficiency of CuCl filling of the nanotubes. A relatively
poor nanotube doping efficiency for CuCl@SWCNT synthesized from m/s mixed nanotubes is clearly observed in Fig. 10: the blue line is a typical optical transmittance spectrum of CuCl@SWCNT sample upon the maximum reachable filling level (via a gas-phase method). According to the spectrum, Fermi level of doped nanotubes is located within $S_2$ Van Hove singularity which corresponds to approximately 0.62 eV Fermi level shift. This value is in agreement with previously reported results on mixed conductivity type SWCNTs filled with CuCl via a capillary filling method [17, 27]. However, this is far below what one can achieve with the CuCl@s-SWCNT (Fig. 2, blue line) or the CuCl@m-SWCNT sample (Fig. 3). For the better understanding, the nanotubes filling efficiency limitations a numerical modeling should be carried out.

An electrical conductivity of CuCl@SWCNT film is typically strongly improved comparing with the electrical conductivity of a pristine nanotube film. One of the origins of this improvement is a huge increase of charge carrier density of functionalized nanotubes. In case of CuCl@s-SWCNTs and CuCl@m-SWCNTs, the improvement of sheet resistance is large: the typical improvement factor is around 40 regardless the m/s mixed nanotubes. The absolute values of CuCl@SWCNT sheet resistance vary significantly in correlation with the morphology of films (below 100 $\Omega$ sq$^{-1}$ for the best samples): mainly, depending on a spatial homogeneity level of the film. The more detailed study of electric conductivity properties of CuCl@m-SWCNT and CuCl@s-SWCNT is under investigation.

4 Conclusions The functionalization of both semiconducting and metallic SWCNT films by filling nanotubes with CuCl leads to a significant increase of optical transmittance (above 90% in NIR). The best absolute optical transmittance is observed in CuCl@m-SWCNT films. The efficiency of filling with CuCl for metallic-enriched SWCNT fraction has been observed to be higher than that for semiconducting SWCNTs. According to the absorption spectroscopy and Raman studies, the metallic nanotubes filled with CuCl can serve as electron acceptors for neighboring semiconducting nanotubes in m/s mixed SWCNTs films.

Acknowledgements The work was supported in frames of project 15-12-30041 of Russian Science Foundation. P.V. Fedotov thanks grant SP-170.2015.3 of Ministry of Education and Science of Russian Federation. The authors are grateful to Prof. Andrey Chuvilin for help in HRTEM measurements. We thank Dr. Dmitry Rybkovskiy for useful discussion.

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