Optical properties of single-walled carbon nanotubes filled with CuCl by gas-phase technique

Pavel V. Fedotov*,1, Alexander A. Tonkikh1, Ekaterina A. Obraztsova1,2, Albert G. Nasibulin3, Esko I. Kauppinen3, Andrey L. Chuvilin4, and Elena D. Obraztsova1

1 A.M. Prokhorov General Physics Institute, RAS, Vavilov Str. 38, Moscow 119991, Russia
2 National University of Science and Technology “MISIS”, Leninskii Prospect 4, Moscow 119049, Russia
3 Aalto University, Espoo, Finland
4 CIC nanoGUNE Consolider, San Sebastian, Spain

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* Corresponding author: e-mail fedotov@physics.msu.ru, Phone: +7 4991353002, Fax: +7 4991353002

Single-walled carbon nanotubes (SWCNTs) have unique electronic and optical properties, which are attractive in various applications. These properties can be further improved by functionalization. In this work, it is shown that filling nanotubes with CuCl leads to improvement of their electro-conductive and optical transmission properties up to outstanding level. The improvement is due to the significant p-type doping of the functionalized nanotubes. That leads to a huge increase in nanotubes charge carrier density and the considerable decrease of the nanotubes absorption via Pauli blocking. The functionalization was realized via a gas-phase filling of SWCNTs with CuCl. We demonstrate the effect of huge doping on optical properties of nanotubes with different average diameters. The observed sufficient stability of the CuCl@SWCNT composite is proved to be due to the formation of quasi-one-dimensional (1D) CuCl crystal inside nanotubes.

1 Introduction

Single-walled carbon nanotubes (SWCNTs) represent a very attractive material promising in various fields of application [1]. One of the most attractive applications is utilizing nanotubes as a transparent conductive material for the future photovoltaic [2, 3]. The ultimate mechanical, chemical, and physical properties of SWCNTs, basically, their stability upon various stresses, a specific quasi-one-dimensional (1D) electronic structure [4] and a tunability of their properties, make them perfect candidates for such high tech application areas.

It is possible to apply different media based on SWCNTs: large diameter nanotube bundles – as a mechanically strong and electrically conductive material, thin nanotube films – as an optically transparent and electrically and thermo conductive material [2, 3]. Such media formed from pure SWCNTs have quite good performance characteristics [5]. However, their properties can be significantly improved by various nanotube functionalization methods.

One of the ways to modify SWCNTs properties is to fill them with other material [6–8] and utilize them as nano scale reactors [9–11]. To increase their electric conductivity and decrease optical absorption, it is crucial to use a material with a strong acceptor/donor behavior. In this case, SWCNTs become highly doped, which leads to increase of both transparency and electro conductivity [12].
In this work, we show for the first time the simple and efficient method of improving performance of SWCNT media by filling them with CuCl molecules through a gas phase. Due to functionalization SWCNT films become significantly more electrically conductive [13] and optically transparent. It is very important that in our method the modification of nanotubes is introduced after the formation of SWCNT film. The mild treatment during the process almost do not damage the structure of the media, gas-phase approach leads to much cleaner SWCNT surface comparing with a liquid method of filling.

2 Experimental section

2.1 Preparation SWCNT with large diameter (average diameter 2 and 2.2 nm) were synthesized by an aerosol method [14]. They were used (as-grown) by a simple transfer from a filter to a quartz substrate. Arc discharge (average diameter 1.4 nm) and HiPCO (average diameter 1.1 nm) SWCNTs were purified and suspended by common procedures.

Briefly, a raw SWCNTs powder was dissolved in 2 w/w% sodium cholate (SC) deionized water and sonicated for 2 h. In order to remove impurities (amorphous carbon and large bundles), the obtained suspension was centrifuged in Beckman Coulter Ultra-Max-E centrifuge during 1 h with the acceleration 140 000 g. The supernatant was filtrated through cellulose filters (100 nm pores). The obtained SWCNTs film was finally transferred on a quartz substrate.

2.2 Filling In brief, the filling process was performed by exposing SWCNT film to CuCl gas under the temperature ranging from 200 to 300 °C for different periods of time (from a few hours up to 24 h). Obtained modified films were rinsed and annealed to remove possible impurities.

2.3 Characterization The optical absorption spectra were recorded with a spectral resolution 0.5 nm in a spectral range of 200–3000 nm (6.2–0.41 eV). The Raman investigations of the CuCl@SWCNT films were carried out using Ar–Kr ion laser at the wavelengths of 488 nm (2.54 eV), 514.5 nm (2.41 eV), 568 nm (2.18 eV), and 647 nm (1.92 eV). The spectral resolution was 0.5 cm⁻¹.

3 Results and discussion

3.1 Large diameter SWCNTs In order to study the effect of functionalization of large diameter SWCNTs (average diameter 2 and 2.2 nm) via CuCl filling we used films with different nanotube stuffing. The average optical transmittances of these samples were tuned from 10 to 80% due to different nanotube densities.

Typically, all films were very thin with a spatially low dense nanotube bundle distribution. According to estimations, an average thickness of most films did not exceed 100 nm. As seen from the SEM image of the typical large diameter SWCNT film, nanotubes in such media tend to form thick bundles (Fig. 1).

After functionalization by filling with CuCl, the nanotubes demonstrate changes in the optical properties. For instance, the absorption spectra of the modified large diameter SWCNT films are significantly different from those of unfilled nanotubes (Fig. 2).

In case of large diameter nanotubes, absorption bands (S₁₁, S₂₂, M₁₁, partly S₃₃) are strongly suppressed. This phenomenon is due to a strong p-type doping, when the Fermi energy level enters the valence band of SWCNT and depletes the electronic states. Such depletion leads to suppression of absorption as there are fewer electrons in the valence band to absorb light (Pauli blocking). One can notice in the Fig. 2 that the effect of nanotube functionalization depends on the CuCl gas exposition time. While a fraction of filled SWCNTs increases with the exposition time increase, an average optical transmittance of the modified films is increasing noticeably (from initial 70% up to 98% after filling).
A high level of doping leads to significant changes in the Raman spectra of films with functionalized SWCNT (Fig. 3). For instance, RBM peaks of nanotubes in modified films are strongly suppressed and shifted, which implies the encapsulation of molecules inside nanotubes and a high efficiency of doping. The G mode has different shape and is largely shifted (up to 20 cm\(^{-1}\)). The same is valid for 2D band.

This implies that filling SWCNT with CuCl modifies its phonon dispersion: bending of the dispersion curves and, possible, appearance of Kohn anomaly in highly doped semiconducting nanotubes. One can assume an efficient charge transfer between the nanotube surface and the encapsulated CuCl. The effect of a strong doping in CuCl@SWCNT composite is complex and well pronounced. All these specific optical features observed in the composite are in agreement with typical features of doped SWNT reported previously in different works [15–18]. A further investigation of modified electron and phonon systems in functionalized nanotubes is required.

The specific optical properties of the large diameter SWCNT filled with CuCl appeared to be sufficiently stable upon various treatments (the medium temperature annealing and the rinsing with various solvents). One of the basic reasons for this stability is formation of well-ordered crystalline CuCl structures within nanotubes. The formation of quasi-1D CuCl crystals is confirmed by a high-resolution transmission electron microscopy (HRTEM) imaging (Fig. 4).

The HRTEM analysis of functionalized SWCNTs has demonstrated that statistically only a small fraction of nanotubes (less than 10%) is filled with CuCl crystals while other nanotubes are empty. At the same time, the optical investigation has demonstrated an overall and homogenous modification of nanotube film properties due to doping. We assume that in functionalized film all the SWCNTs are efficiently doped: the filled nanotubes are doped by encapsulated 1D CuCl crystals while the unfilled nanotubes are doped by other surrounding nanotubes in the bundles via charge transfer.

3.2 Medium and small diameter SWCNTs It is also possible to encapsulate CuCl molecules inside SWCNT with the small and medium average diameters (1.1 nm –
HiPCO, 1.4 nm – arc discharge SWCNT). In this case, the difference between initial and functionalized SWCNT films looks very similar to what is observed for large diameter nanotubes (see Fig. 5, cf. Fig. 2).

For instance, in arc discharge nanotubes S11, S22, and M11 absorption bands are strongly suppressed, though a certain part of light is still absorbed by the functionalized SWCNT film (Fig. 5a). At the same time, for the functionalized HiPCO nanotubes (Fig. 5) the even S11 absorption band is only partially suppressed. So the suppression of the SWCNT absorption bands upon filling with CuCl is less pronounced in films formed by small diameter nanotubes. The filling process in arc discharge and, especially, in HiPCO SWCNTs appears to be less efficient (requires much higher temperature and exposition time). One of the reasons of less efficient functionalization of the small diameter SWCNT is a strong spatial restriction, which makes 1D CuCl crystal formation less favorable [15]. Amorphous CuCl structure is weaker as an electron acceptor and, therefore, the charge transfer from the nanotube is less efficient in this case. They are also less stable upon various post-treatments: it is possible to remove them by annealing or rinsing with different solvents.

4 Conclusions In this paper, we show that it is possible to functionalize SWCNTs of different diameters by a gas-phase filling them with CuCl. Such functionalization leads to a significant increase in transmittance (up to 98%) of the initial nanotube films. The suppression of optical absorption happens due to a huge p-type doping of SWCNTs induced by CuCl crystals. We show that such type of filling allows to improve the optical properties of macroscopic samples of SWCNTs (for instance, films) without their damaging and even without a noticeable harm to the SWCNT crystalline structure. The efficiency of doping-induced transparency is significantly higher for the large diameter nanotubes (2.0–2.2 nm). A smaller enhancement of transparency is observed as well in the small diameter nanotubes (1.0–1.4 nm). The CuCl filling of the large diameter SWCNTs under certain conditions leads to formation of well-ordered 1D crystal inside the nanotubes. Modification of the specific optical properties of CuCl@SWCNT composite is sufficiently homogenous due to a charge transfer between the nanotubes filled with CuCl and empty ones in the bundles. According to our optical investigation, the transparent CuCl@SWCNT films are composed of strongly doped nanotubes, and, therefore, have a big potential for application as highly conductive transparent media.

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References