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Valentina A. Eremina
Pavel V. Fedotov
Elena D. Obraztsova

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Copper chloride functionalization of semiconducting and metallic fractions of single-walled carbon nanotubes

Valentina A. Eremina,[a,b,*] Pavel V. Fedotov,[b] and Elena D. Obraztsova[a,b]
[a]M.V. Lomonosov Moscow State University, Faculty of Physics, Leninskie Gory Strasse 1, Moscow 119991, Russia
[b]A.M. Prokhorov General Physics Institute of Russian Academy of Sciences, Vavilov Strasse 38, Moscow 119991, Russia

Abstract. In this work, a separation of arc-grown single-walled carbon nanotubes (SWNTs) over conductivity type has been performed with an aqueous two-phase separation method. The separated fractions were used to synthesize copper chloride (CuCl) at SWNTs hybrid materials. These nanohybrids were studied using UV-vis-NIR optical absorption and Raman techniques. The changes in electronic and optical properties of functionalized SWNTs were revealed. A significant p-type doping of SWNTs by CuCl was considered as a main reason for modification of nanotube optical properties. [DOI: 10.1117/1.JNP.10.012515]

Keywords: single-walled carbon nanotubes; aqueous two phase separation method; copper chloride.

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1 Introduction

Single-walled carbon nanotubes (SWNTs) are interesting for researchers due to their unique optical, electronic, and other properties controlled by tube geometry and by various functionalization methods.

A majority of existing synthesis methods provide SWNTs with a wide range of geometries. However, many fundamental and technological applications of SWNTs require the nanotube fractions with a certain geometry. A number of methods can provide almost a single chirality or conductivity type separation. A gradient density ultracentrifugation[1] and a gel chromatography[2] are among them. Recently, a new method for an easily accessible separation of SWNTs has been proposed. This aqueous two-phase separation method[3] is based on the spontaneous formation of two phases (with two polymers—polyethylene glycol and dextran)—the top and the bottom water phases, containing two different conductivity types of nanotubes.

2 Experimental Details

In this work, the nanotubes synthesized by arc discharge technique were used. A 2 w/w% water solution of sodium cholate (SC) was used for the initial suspending of SWNTs. To obtain a stable suspension of the individualized nanotubes, the prepared mixture was exposed to the ultrasonication for 3 h and then to the ultracentrifugation (with the acceleration of 150,000 g) for 1 h. In order to achieve the separation by type of conductivity, two aqueous polymers were used: 50 w/w% water solution of polyethelene glycol (PEG) and 20 w/w% water solution of dextran. The aqueous 10 w/w% solutions of SC and sodium dodecyl sulphate (SDS) were used for the control of the total surfactant composition in the mixture.

At the second step of the experiment, films were formed from the obtained top (semiconducting) and bottom (metallic) phases using MCE (Millipore) filters with pores diameter of

*Address all correspondence to: Valentina A. Eremina, E-mail: erjomina@physics.msu.ru

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100 nm. Then, these films were transferred from the filters to the quartz substrates. To achieve filling of the nanotubes with copper chloride (CuCl), the SWNTs films on quartz substrates and CuCl powder were heated at 230°C in the air during 13 h. The exposition time and the temperature were selected to optimize the SWNT functionalization.

UV-vis-NIR optical absorption spectra have been registered with a PerkinElmer Lambda 900 spectrometer and Raman scattering measurements have been made with Jobin Yvon spectrometer S3000 with Ar–Kr laser at excitation wavelength of 488 nm (2.54 eV), 514 nm (2.41 eV), and 647 nm (1.92 eV).

3 Results and Discussions

In order to achieve the separation of nanotubes by metallic and semiconducting types of conductivity, we used two surfactants—SC and SDS, as they promote the separation by conductivity type.[3] A well separation of the top and the bottom phases in the vial has been reached by adjusting the concentrations of polymers and surfactants (Fig. 1). The obtained value of the concentrations (w/w%) at which the separation was the most efficient was 8.64% Dx, 7.4% PEG, 1.21% SDS, and 1.24% SC.

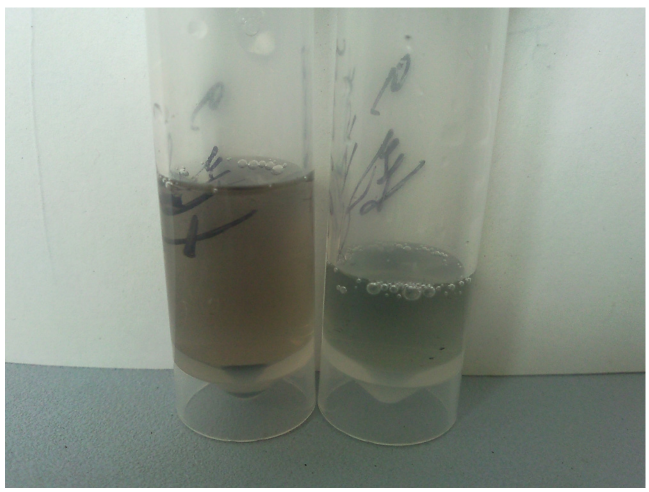

Fig. 1 The photo of the (a) top and the (b) bottom phases.

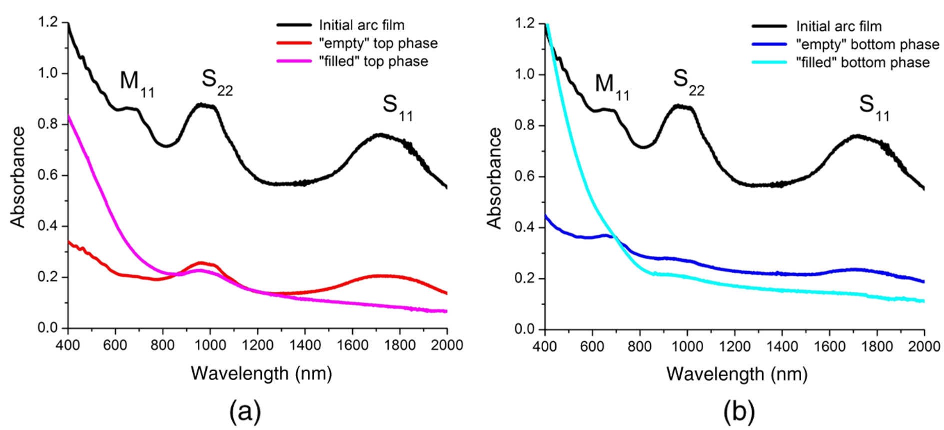

Fig. 2 The UV-vis-NIR absorption spectra: (a) of the initial arc film (black curve), the "empty" top phase film (red), and after filling with CuCl (magenta); (b) of the initial arc single-walled nanotubes (SWNTs) film (black curve), the "empty" bottom phase film (blue), and after filling with CuCl (light blue).

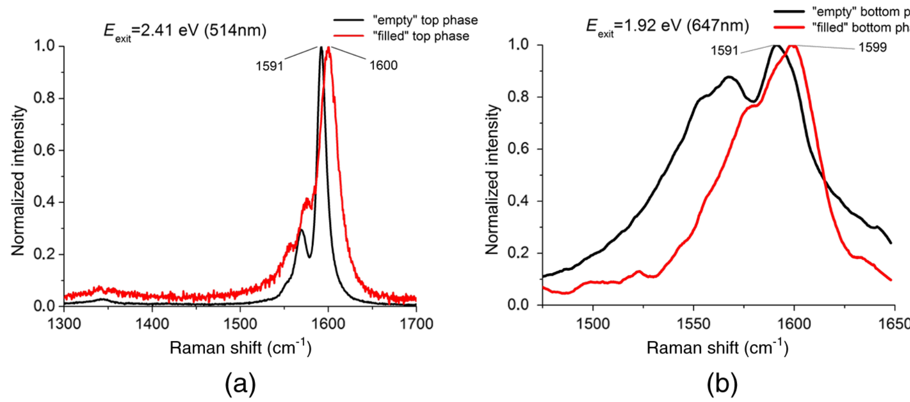

Fig. 3 The normalized Raman spectra of the SWNTs G-modes: (a) for the "empty" (black curve) and the "filled" (red curve) top phase $E_{exit} = 2.41$ eV and (b) for the "empty" (black curve) and the "filled" (red curve) bottom phase on $E_{exit} = 1.92$ eV.

We did not perform repeated procedures of nanotube separation, because faced with certain difficulties associated with the polymer presence in suspension. Nevertheless, the NIR-vis-UV absorption and Raman scattering spectra have shown that the obtained top phase predominantly contains semiconducting nanotubes and the bottom phase contains metallic ones. The Raman scattering measurements showed that in the initial film, the ratio of semiconducting to metallic nanotubes was equal to 1.82. This ratio became equal to 12 and 0.41 for the top and the bottom phases respectively.

After the filling process, which was performed by exposing SWNT films to CuCl gas for 13 h under 230°C, we found that the optical properties of the functionalized nanotubes have altered. In the absorption spectrum of semiconducting nanotubes, a strong suppression of S_{11} absorption band is seen. The suppression of S_{22} is not so significant [Fig. 2(a)].

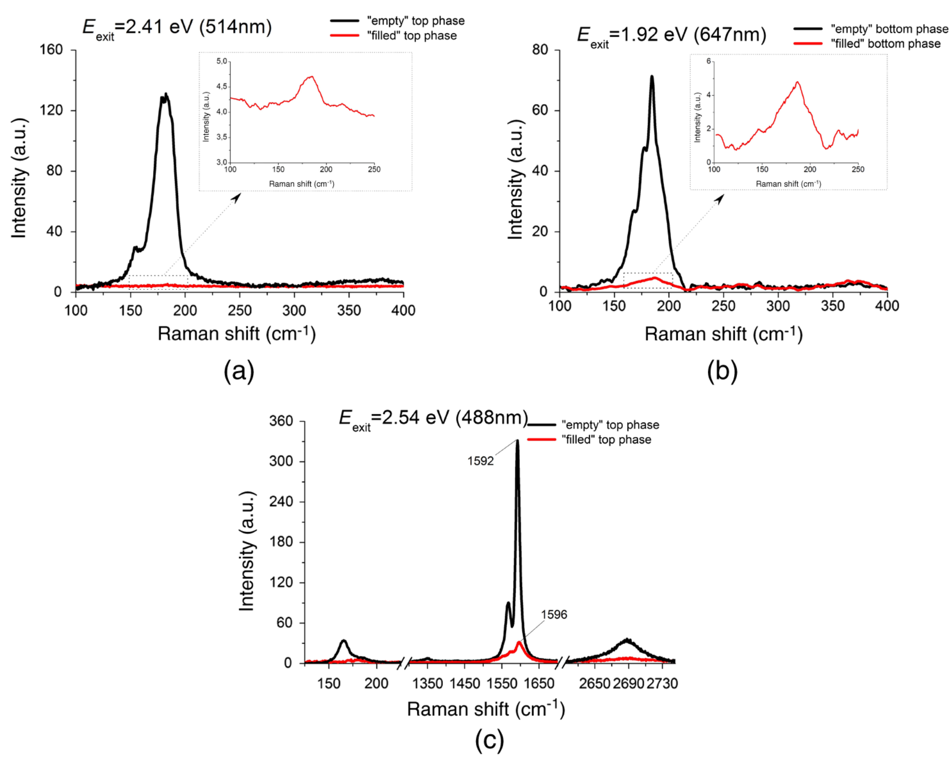

Fig. 4 The radial breathing modes: (a) of the "empty" (black curve) and the "filled" (red curve) top phase on $E_{exit} = 2.41$ eV; (b) of the "empty" (black curve) and the "filled" (red curve) bottom phase on $E_{exit} = 1.92$ eV. (c) The Raman spectra of the "empty" (black curve) and the "filled" (red curve) top phase film on $E_{exit} = 2.54$ eV.

Due to the presence of a small amount of semiconducting nanotubes in the initial metallic fraction, the suppression of S_{11} and S_{22} bands in this film can also be observed as well as the suppression of M_{11} absorption band [Fig. 2(b)]. This means that the Fermi level in such functionalized SWNTs becomes lower due to the electron transfer from the nanotube to the CuCl, which has a higher electronegativity. This leads to a decrease in the light absorption.[4]

The optical properties of the nanotubes have noticeably altered in the Raman spectra too. In the normalized Raman spectra in spectral range of nanotube G-mode [Fig. 3(a)], one can notice that the semiconducting SWNTs peak (being in resonance under 514-nm excitation wavelength) after functionalization became wider (due to the effect of different degrees of filling with CuCl for different nanotubes) and shifted by 9 cm^{-1} toward high frequencies. The form of this peak became more "metallic" due to the changes in the nanotube band structure.[5]

The peak profile of the metallic nanotubes (being in resonance under 647-nm excitation wavelength) became more like "semiconducting" due to the loss of the resonant excitation[6,7] or due to opening a band gap at the Fermi level position.[5] This peak is also shifted by 8 cm^{-1} toward high frequencies [Fig. 3(b)].

The radial breathing modes (RBM) [Figs. 4(a) and 4(b)] are suppressed due to the changes of resonance conditions.[8] This means that the filling efficiency is high. The ratio of intensities G/RBM bands after filling relates to G/RBM of "empty" nanotubes as 1.5 for the top phase (semiconducting) and as 5.6 for the bottom phase (metallic). For the SWNTs 2-D mode a small shift is also observed.

4 Conclusion

In this work, the fractions of arc SWNTs separated over conductivity type have been obtained and studied. The aqueous two-phase separation method was used to get two fractions: one, enriched with semiconducting nanotubes (from the top phase) and another one, enriched with the metallic SWNTs (from the bottom phase).

These fractions have been filled with CuCl from gas phase. The optical properties of CuCl at SWNTs hybrid materials were studied with UV-vis-NIR optical absorption and Raman techniques. The electronic properties of CuCl at SWNTs hybrid materials appeared to be changed. In the absorbance spectra of filled semiconducting nanotubes, a strong suppression of S_{11} transition and a small suppression of S_{22} transition were observed, whereas for the metallic SWNTs functionalized with CuCl even the suppression of M_{11} transition was observed side by side with almost full suppression of S_{11} and S_{22} transitions from the residual semiconducting nanotubes. In the Raman spectra, the changes in the position, width, and form of G-band both for metallic and semiconducting nanotubes were observed. A character of these changes was different. The shape of Raman G-band of semiconducting nanotubes became more "metallic" and vice versa. In summary, we attribute the changes in the optical properties of filled fractions of SWNTs to the strong p-doping mechanism. Further studies will be focused on understanding the changes in the electronic structure and optical properties of separated fractions of SWNTs.

Acknowledgments

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Valentina A. Eremina graduated from the physics faculty of M.V. Lomonosov Moscow State University in 2014. Now, she is a second year PhD student at this faculty in the Quantum Electronics Department. She has specialized on the optical spectroscopy of single-walled carbon nanotubes, separation of carbon nanotubes by aqueous two-phase extraction technique, and functionalization of carbon nanomaterials and is studying their optical properties.

Pavel V. Fedotov is a PhD student in A.M. Prokhorov General Physics Institute of Russian Academy of Sciences. He graduated from the Physics Department of M.V. Lomonosov Moscow State University (2012) with honors. He specializes in the optical spectroscopy of carbon-based nanomaterials (nanotubes, graphene nanoribbons, etc.), characterization of the SWCNT synthesis yield, and optical properties of the functionalized SWCNTs.

Elena D. Obraztsova was graduated from the Quantum Radiophysics Chair of the Physics Department of M.V. Lomonosov Moscow State University (MSU) in 1981. She received her PhD in optics at MSU in 1990. Since 1992, she has worked at A.M. Prokhorov General Physics Institute of the Russian Academy of Sciences, heading the nanomaterials spectroscopy laboratory. She is a coauthor of more than 230 papers in peer-reviewed journals. She was a supervisor of 10 PhD defended theses.