Synthesis of nanocomposites on basis of single-walled carbon nanotubes intercalated by manganese halogenides

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Abstract. In this work MnCl$_2$@SWNT and MnBr$_2$@SWNT nanocomposites were prepared via capillary filling of single-walled carbon nanotube channels by melts of manganese halogenides with slow cooling to room temperature for better crystallization. Electronic properties of MnHal$_2$@SWNT nanocomposites have been investigated by X-ray photoelectron spectroscopy, optical absorption spectroscopy and Raman spectroscopy. It was found that the manganese halogenides show acceptor behavior and there is the charge transfer from the carbon nanotube walls to intercalated nanocrystals.

1. Introduction

Today single-walled carbon nanotubes (SWNTs) are an example of one of the most interesting nanomaterials, which attract the close attention of the research community due to their unusual electronic, chemical and structural properties accompanied by extraordinary mechanical behavior depending on the diameter and conformation of tubes [1-5]. However, the strong dependence that the functional properties have on the diameter and rolling vector of the nanotube, in combination with the practical difficulty of extracting of SWNTs of definite chirality, makes it necessary to develop methods for a directed change in their electron structure. Modifying of SWNT properties by introducing of various substances into the internal channels of nanotubes is of special interest. Moreover, single-walled carbon nanotubes have an extra small diameter and maximal anisotropy parameters, compared to other known nanostructures, which make them extremely attractive templates for forming of one-dimensional nanocrystals in the internal channels [6].

It should be noted that the filling of nanotube internal channels makes it possible to change the structure and properties of SWNTs without the necessity of separating them with respect to their chirality and electronic characteristics [7]. For instance, an intercalation of electron-donors (with Fermi level located in the conductance band of SWNTs) to the metallic tubes will lead to increase of electron density on carbon nanotube walls resulting in better conductance through the composite wire, while an intercalation of electron-acceptors (with Fermi level below the one of SWNTs) may cause the decrease of carrier density (and Fermi energy) in the system [7]. Moreover, the electronic properties of the obtained composites will be determined by the generalized electron density of the SWNT and the electron density on the one-dimensional crystal associated with it. Therefore, this approach, which is based on the charge transfer in X@SWNT system after introducing of one-dimensional nanocrystals of the electron-donor or electron-acceptor compounds into SWNT channels, makes it possible to control the electronic structure of single-walled carbon nanotubes and produce heterotransitions inside a single nanotube in the case of partially filled channels.
An extensive application of SWNT-based composites is unfortunately limited due to the absence of universal synthetic approaches for infilling of nanotube channels [7]. The traditional techniques include *in situ* filling of nanotubes by catalytic metals during CVD process and *ex situ* procedure (so-called capillary technique) via impregnation of pre-opened SWNTs [8, 9, 10, 11-16]. However, in many cases the formation of discrete clusters inside carbon nanotubes instead of the formation of continuous one-dimensional nanocrystals was observed, especially when *in situ* intercalation or wet-chemistry methods were applied [17]. Homogeneous filling of nanotube channels can be achieved when molten guest compounds are crystallized slowly inside SWNTs [18, 11, 19, 20]. This approach can be used if the surface tension of the guest compound is low ($\gamma=130-170$ mN/m) in order to enable the wetting of nanotube surface, as well as if it has a relatively low melting point ($<800^\circ$C) to prevent the destruction of carbon nanotubes in the course of impregnation [15]. At present, a great number of studies report the filling of carbon nanotubes with halides, metals, oxides, hydroxides, chalcogenides, fullerenes and other materials [19H26]. However, in most of these works, most attention was paid to the studying of atomic structure of the obtained nanocomposites, whereas the electronic properties of intercalated nanotubes remained practically unknown. At the same time, these characteristics determine the practical application of nanomaterials on basis of single-walled carbon nanotubes. Therefore, in this work nanostructures on basis of SWNTs filled with MnCl$_2$ and MnBr$_2$ were synthesized and the influence of intercalated salts on the electronic structure of nanotubes was studied.

2. Experimental part

SWNTs were obtained by catalytic arc-discharge method using 0.8 cm diameter graphite rods with Y/Ni powder catalyst under the following conditions: helium pressure of 73.3 kPa and current of 100-110 A. Nanotubes were purified by multistage procedure consisting of oxygenation in air and rinsing with HCl to remove the catalyst. The purified samples with SWNTs content of 78 wt.% and catalyst content of 0.12 wt.% were pre-opened by heat treatment at 500ºC in dry air for 0.5 hour.

Pre-opened SWNTs (0.025 g) were grinded in agate mortar with MnCl$_2$ or MnBr$_2$ (Aldrich, 99,999 wt. %) in molar ratio of 1:1. In view of hygroscopic properties of these compounds this experimental stage was carried out in dry box. Then obtained mixture was evacuated in quartz ampoules at 1 Pa for 1 hour and sealed. The ampoules were heated at a rate of 1K/min up to the temperature of 100K above the melting point of MnHal$_2$. This temperature was maintained for 10 hours, whereupon the samples were slowly cooled at a rate of 0.1K/min. We believe that slow cooling provides better conditions for MnHal$_2$ crystallization inside the nanotube channels. The obtained samples were denoted by MnCl$_2$@SWNT and MnBr$_2$@SWNT, respectively.

The Raman spectra were acquired using a Renishaw InVia Raman microscope equipped with 20 mW 514 nm argon, 17 mW 633 nm HeNe and 300 mW 785 nm NIR diode lasers, variable power ND filters (power range 0.00005-100%) and near-excitation tunable (NeXT) filters. In Raman spectra the positions of all resonance lines were determined by least-square fitting of the experimental data with sets of Gaussian/Lorentzian convolution functions using “WiRE 2.0” software. Optical absorption spectra were acquired using Perkin-Elmer Lambda 950 spectrometer in the spectral range of 200-2500 nm with a spectral resolution of 1-4 nm. HRTEM was performed on JEOL 2100 microscope at 300 kV. For this study the samples were prepared by dispersing of nanotubes onto a carbon-coated copper grid. X-ray photoelectron spectra were obtained using monochromatic Al K$_\alpha$ irradiation at Axis Ultra (Kratos) spectrometer at pass energy of 5 eV. The samples were placed on metallic indium surface. The size of analyzed area equaled 300x700 microns.

3. Results and Discussion

The HRTEM images obtained for MnCl$_2$@SWNT and MnBr$_2$@SWNT samples are represented in Fig. 1. These data show a bundle of single-walled carbon nanotubes with an internal diameter of 1.4 nm. These data give evidence that nanotube channels are filled; moreover, the formation of one-dimensional crystals with an ordered structure is observed inside the channels in the case of MnCl$_2$. In the observed projection for MnCl$_2$@SWNT nanocomposite the motive of image is formed by two
rows of contrast elements with the distance between them of 0.33-0.35 nm and periodicity of fragments repeating along SWNT axis of 0.30 nm.

![HRTEM images of MnHal2@SWNT nanocomposites](image1)

**Figure 1.** HRTEM images of MnHal2@SWNT nanocomposites

The optical absorption spectra of SWNTs (Fig. 2) in the visible and near-IR regions illustrate the set of characteristic stripes corresponding to transitions between the van Hove singularities in semiconductor (S1–S2) and metal (M1) nanotubes with a diameter of 1.2–1.5 nm. In the spectra of MnCl2@SWNT nanocomposite a partial quenching of optical transitions between the first van Hove singularities of semiconductor SWNTs takes place (S1 in Fig. 2). Such behavior of the system can be caused by the electron transfer between the nanotube and the crystal with either devastation or filling of the first van Hove singularities with electron density, which was observed earlier in our previous works [20, 21]. Also a strong shift (0.15-0.25 eV) of all peaks in composites towards lower energies takes place. This shift corresponds to the narrowing of energy gaps between the van Hove singularities in nanotubes after the filling of channels. Thus, the described changes in the spectra of composites (as opposed to unfilled SWNTs) evidence the charge transfer between the nanotube walls and the introduced nanocrystals, which leads to a significant change in the electronic structure of SWNTs.

![Optical spectra of MnCl2@SWNT nanocomposite](image2)

**Figure 2.** Optical spectra of MnCl2@SWNT nanocomposite (a), the schemes of optical transitions between the van Hove singularities in semiconducting (b) and metallic SWNTs (c)

Figure 3 shows the characteristic RBM and G bands of Raman spectra of pristine SWNTs and MnCl2@SWNT and MnBr2@SWNT composites, which were obtained upon the excitation of samples by laser radiation with an energy of 1.96 eV and 1.58 eV (λex = 633, and 785 nm, respectively) in the frequency region of 100–1700 cm−1. Both RBM and G band positions for nanocomposites are up shifted relative to those of pristine SWNTs and it indicates the change in C-C bond energy. Also it may indicate the change of electronic structure of carbon nanotubes in course of intercalation. It should be noted that besides the significant shifts of RBM and G bands in Raman spectra of the MnCl2@SWNT and MnBr2@SWNT nanocomposites, which evidence the mechanical and electronic
interaction between SWNT walls and intercalated nanocrystals, a substantial change in the profile of G band takes place. The profile of G band changes from typical for metallic nanotube form to the form that is typical for SWNTs of the semiconductor type. A possible explanation for the changes in G band profile is the transition of metallic SWNTs to a semiconductor state after the filling them with one-dimensional MnCl$_2$ and MnBr$_2$ crystals as a result of the charge transfer between SWNT walls and the intercalated nanocrystals.

![Raman spectra of MnHal$_2$@SWNT nanocomposites obtained at laser energies of 1.96 eV (a) and 1.58 eV (b)](image)

**Figure 3.** Raman spectra of MnHal$_2$@SWNT nanocomposites obtained at laser energies of 1.96 eV (a) and 1.58 eV (b)

Fig. 4 shows x-ray photoelectron spectra of pristine SWNTs and MnBr$_2$@SWNT sample. The C 1s spectrum of nanocomposite has a multicomponent structure. Component C I positioned at binding energy of 284.38 eV can be assigned to the pristine unfilled SWNT. Besides, new components C II and C III appear, with BE being lower for C II and higher for C III. Both components are evidently related to the filled nanotubes. The possible origin of C II component is the variation of SWNT work function as a result of Fermi level downshift and the corresponding shift of all peaks related to MnBr$_2$@SWNT to lower binding energies. Thus, the manganese halogenide show acceptor behavior. Moreover, this assumption is consistent with the whole dataset discussed above. The nature of the less intensive and broad component C III is evidently different. It is positioned at binding energy of 0.63 eV higher than C II. Probably it can be assigned to the local effects [20].

![C 1s x-ray photoelectron spectra of pristine SWNTs and MnBr$_2$@SWNT sample](image)

**Figure 4.** C 1s x-ray photoelectron spectra of pristine SWNTs and MnBr$_2$@SWNT sample

4. Conclusions

Thus, in present work MnCl$_2$@SWNT and MnBr$_2$@SWNT nanocomposites were obtained by the capillary filling of the internal channels of single-walled nanotubes with melts of manganese halogenides and subsequent slow cooling in order to obtain better crystallization of nanoparticles in
SWNT channels. It was found that the manganese halogenides show acceptor behavior and there is the charge transfer from the carbon nanotube walls to intercalated nanocrystals.

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