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# Study of composite MWCNT/pyrolytic Cr interface by NEXAFS spectroscopy

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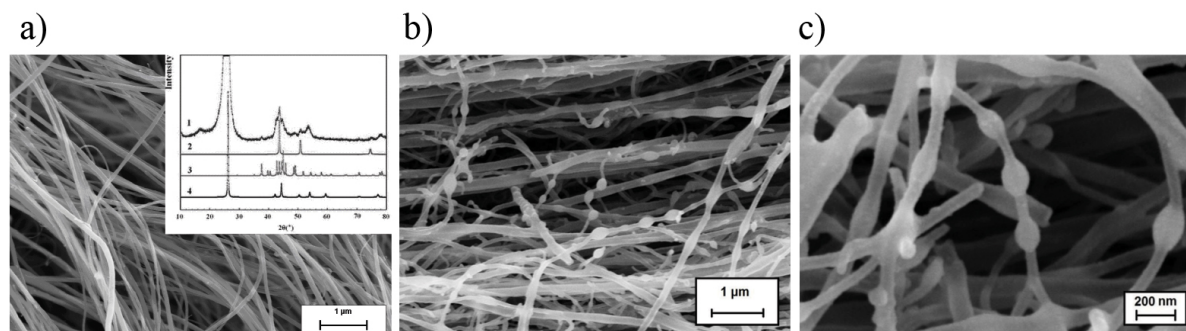
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**Abstract.** A composite material based on MWCNT covered by pyrolytic Cr has been prepared by MOCVD growth technique using bis(arene)chromium compounds as the pyrolytic Cr source. Their structures and morphologies were preliminarily studied by X-ray diffraction and scanning and scanning electron microscopy. The atomic and chemical composition of the interface, MWCNT surface and Cr-coating of the composite were studied by total electron yield mode in the range NEXAFS C1s - and Cr2p - absorption edge with use of synchrotron radiation of RBL at BESSY-II. The study has shown that top layers of the MWCNT in composite have no essential destruction, the coating of the MWCNT surfaces is continuous and consists of Cr<sub>2</sub>O<sub>3</sub>. The chromium oxide adhesion is provided by chemical binding between the carbon atoms of the MWCNT top layer and the oxygen atoms of the coating.

## 1. Introduction

Coating the surface of the MWCNT with specific metal films gives them unique physical and chemical properties and leads to the creation of new heterogeneous materials that will have good adhesion to the matrix. Such materials can be used as nanostructured heterogeneous catalysts of various chemical processes, sensors, chemical power sources, elements of various electronic devices and other active elements in many scientific and technical applications. Therefore, the development of methods of synthesis and investigations of nanostructured composite material based on MWCNTs is an actual problem. In our earlier work we have demonstrated for the first time the possibility of synthesis on the MWCNT surfaces of the nanosized Fe<sub>3</sub>O<sub>4</sub> coating by the metal organic chemical vapour deposition (MOCVD) growth technique [1] and have shown the informativity of the near edge x-ray fine structure (NEXAFS) spectroscopy for the experimental investigation of the MWCNT/pyrolytic metals heterogeneous systems. The present paper is the extension of these researches regarding the development of the metal and metal oxide deposition methods and improvement of the carbon nanotube/matrix interface properties. The MWCNT/pyrolytic Cr composite has been prepared by the MOCVD growth technique using decomposition of the bis(arene)chromium compounds at temperature 400°C. It should be noted that the spectral investigation of the NEXAFS C1s - edge is difficult due to overlaying





**Figure 1.** SEM image and XRPD of pristine MWCNTs (a) and SEM image of the MWCNT/chromium composite material prepared by the MOCVD method, using pyrolytic decomposition of chromium-organic liquid (b,c). **1.a** (insert): pristine MWCNT's experimental diffractogram (curve 1) compared with theoretical diffractograms of  $\gamma$ -Fe (curve 2),  $\text{Fe}_3\text{C}$  (curve 3) and graphite (curve 4).

with NEXAFS Cr 2p - edge in the two order diffraction. Therefore, aims of our research were both development of the MOCVD technology for MWCNT coating with pyrolytic chromium and modification of the NEXAFS C1s - edge investigation method. The NEXAFS spectroscopy allows probing the atomic composition and angular momentum character specific densities of unoccupied electronic states and may give information about chemical bonds in the investigated samples. After the absorption of X-rays in the range 250–600 eV the electron escape depths of the primary photoelectrons and Auger electrons in materials are less than 1 nm, in contrast to the secondary electron area occupying a few nm. Therefore NEXAFS spectroscopy by the total electron yield (TEY) method can be used for studies of both the thin coating and coating-substrate interlayer without sample destruction. In case of the composite MWCNT's - pyrolytic Cr the coating and substrate include chromium and carbon atoms, respectively, that enable us to study the state of the MWCNT top layer and to measure the chromium coating effective thickness by the NEXAFS C1s - spectrum, while the coating state can be analyzed from the NEXAFS Cr2p - spectrum.

## 2. Experimental details

MWCNT's were prepared by the MOCVD method from a toluene-ferrocene mixture in a tubular quartz reactor in the flow of argon at atmospheric pressure. The detailed procedure is described in [2]. The samples produced in the central region of a quartz reactor for MWCNT deposition at 800°C were selected for the study. The averaged MWCNT diameter was  $\sim 70$  nm, and the MWCNT length was 0.2–2 mm. The laboratory apparatus and the MOCVD technology for the coating of MWCNT's with chromium were developed for the nanostructured composite materials. The chromium-organic liquid (COL) "Barkhos" available from commercial sources was used as an organometallic precursor. COL represents a mixture of alkyl-substituted derivatives of bis(arene)chromium (the average molecular weight is 292, the total chromium content is 15–16 wt %). The technique for deposition of pyrolytic chromium has been described earlier [3]. Briefly, pyrolytic chromium coatings were deposited onto the MWCNT surface as follows. MWCNTs portion of 50 mg was placed into a Pyrex-glass ampoule (10–12 cm<sup>3</sup> in volume) and heated at 200°C for one hour with continuous vacuum pumping. Then the ampoule was cooled, filled with argon, and 0.1–0.2 cm<sup>3</sup> COL was poured into it. Then the ampoule was sealed using a gas burner and temperature was gradually increased to 400°C to obtain high-quality pyrolytic chromium coatings. The ampoule was kept at this temperature for two hours, then it was cooled to room

temperature, unsealed, and MWCNT samples with deposited pyrolytic chromium coatings were removed.

This method allows controlling the Cr coating thickness from a few nm to tens of nanometers. The MWCNT's and MWCNT's composite samples were characterized by various methods. The X-Ray phase analysis was carried out on a DRON-3M diffractometer with use of Cu-K $\alpha$  radiation and a graphite monochromator. The thermochemical characteristics of MWCNTs were studied using the Pyris 6TGA thermoscales. The surface morphology of MWCNTs and the composite material was studied on the scanning electron microscope (SEM) ZEISS Supra 50 VP.

The study of the pristine MWCNT's surface, chemical composition, coating thickness and surface coating interaction was carried out by NEXAFS spectroscopy method with using synchrotron radiation of Russian-Germany beamline (RGLB) at BESSY-II [4]. The absorption cross section (CS) spectral dependences in the wide energy interval 250–900 eV and C1s - edge and Cr2p - edge ranges of the pristine MWCNT's and composite MWCNT's/pyrolytic chromium were measured in TEY mode. The samples for studies were prepared by pressing the MWCNT and composite powders into the surface of a pure Cu plate. Additional Ti-film of the 160 nm thickness mounted onto Au grid with small mesh were used in the capacity of absorption (transmission) filter for the effective suppression and measurement of the second-order light and the VUV-stray radiation [5]. The incident photon flux was measured using the clean Au-photocathode. The incident monochromatic SR intensity in arbitrary units was obtained by means of the division the TEY monochromatic signal of Au plate by the Au atomic cross section [5]. The CS in arbitrary units was obtained by means of the division the TEY by the SR intensity. In all cases TEY - signal measurements were carried out considering nonmonochromatic stray.

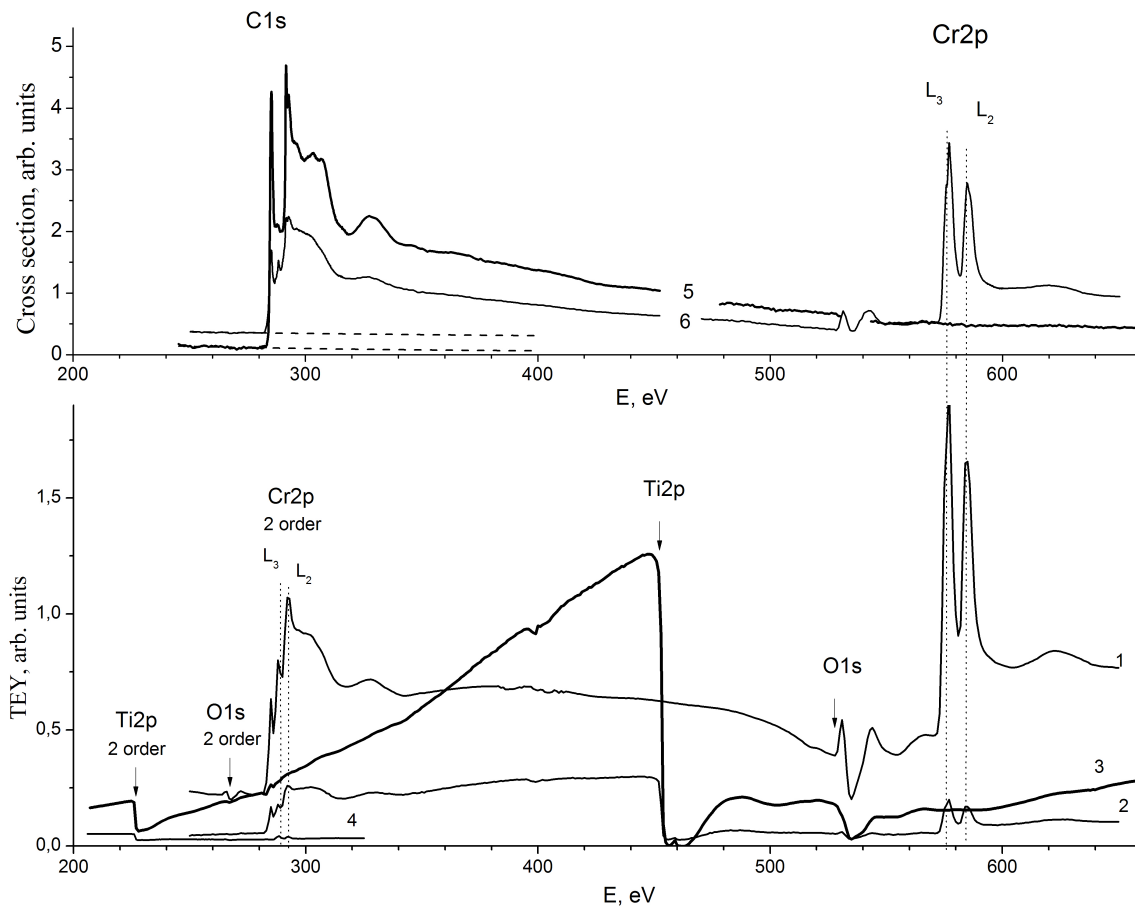
### 3. Results and discussion

The bottom of figure 2 illustrates the CS measurement problems in the range NEXAFS C1s absorption edge of the chromium-contained compounds. The composite MWCNT/chromium CS dependence without the Ti-filter (curve 1) shows clearly that NEXAFS Cr 2p - edge and O1s - edge observe in the low order diffraction. Meanwhile the strong Cr L<sub>2,3</sub> - lines overlap exactly with NEXAFS C1s - edge. The Ti-absorption filter decreases the Cr L<sub>2,3</sub> - line and the O1s - fine structure intensities by an order of magnitude. Their intensities were decreased very strongly on the monochromator optical elements, too. This suppression factor is calculated as a ratio of the intensity jumps in the Ti 2p - edge in the first and second orders by the spectral dependence Au (curve 3). This factor is 9.5.

The contribution of the two order diffraction intensity to the range NEXAFS C1s edge (curve 4) can be obtained by dividing the NEXAFS Cr 2p edge intensity by 9.5. As a result the nondistorting TEY-signal in the range NEXAFS C1s absorption edge of composite MWCNT's/pyrolytic chromium was obtained by subtraction of curve 4 from curve 2. The CS of the composite (arb.units) was obtained by dividing the TEY to the SR intensity.

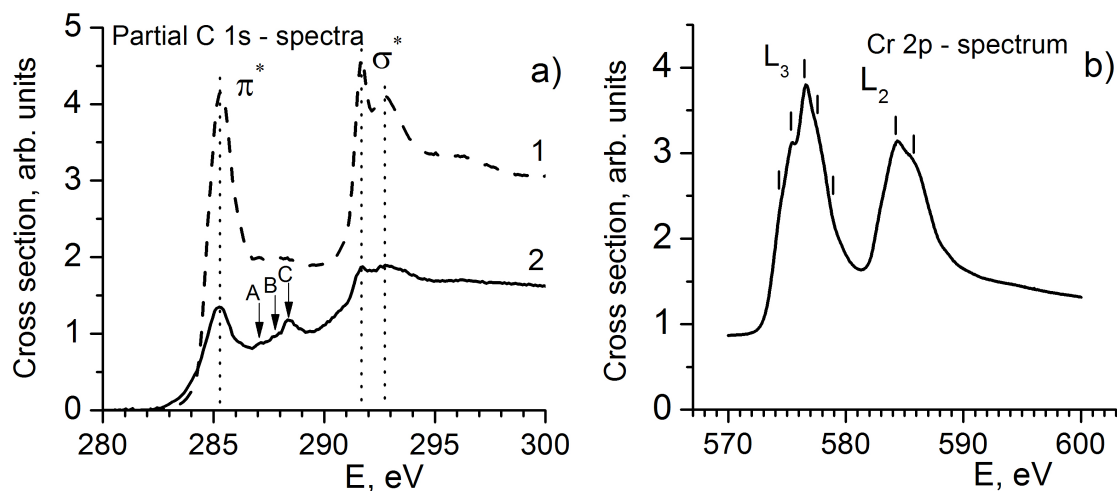
The top of Figure 2 shows the measured CS spectral dependences in the energy interval 250–700eV for the pristine MWCNT's and composite MWCNT/pyrolytic chromium. Examining the CS in Figure 2 one can see, that (i) the pristine MWCNT's dependence has the NEXAFS in the C1s-edge range only and (ii) the composite dependence has the NEXAFS in the C1s-, O1s- and Cr2p-edge ranges.

The first point indicates that the pristine MWCNT surface is clean and the iron compounds detected by x-ray diffractometry method must be contained inside MWCNT's volume. The second point and continuity of the pyrolytic chromium coating suggest that the coating has nanosized thickness and contains chromium oxide. This conclusion based on facts, that the photoelectron's escape depth in metals is about 1 nm only [6] and the NEXAFS Cr2p - spectrum of the composite completely coincides with the Cr2p - spectrum of the pure Cr<sub>2</sub>O<sub>3</sub> (in Figure 3 is not shown). Figure 3 shows the decrease of the composite CS dependent area (S<sub>2</sub>) by a



**Figure 2.** Bottom: TEY of the composite without (curve 1) and with (curve 2) Ti- absorption filter and Au-plate (curve 3) in the range 250–660 eV. Dotted line - interpolation contribution

factor of 2.12 in the NEXAFS C1s-edge range in comparison with the pristine MWCNT area ( $S_1$ ). However, NEXAFS C1s - spectra of pristine MWCNTs and the composite are similar. This decrease is a result of the photoelectron scattering by the atoms of the chromium oxide coating. The photoelectron escape depth in pure  $\text{Cr}_2\text{O}_3$  is  $\lambda=1.0$  nm [7]. Using this value we can calculate the minimal effective thickness of  $\text{Cr}_2\text{O}_3$  coating on the MWCNT's surface as product of  $\lambda$  and  $\ln(S_1/S_2)$  and it is equal to 0.75nm. NEXAFS C1s-spectrum of composite has new weak peaks A, B and C with the energy 287.1 eV, 287.8 eV and 288.4eV, respectively. The energies of these peaks coincide with the energies of transitions from C1s - level to  $\pi^*$ -unoccupied orbital of C-O-C, C-O and C=O groups, respectively [4,5]. Taking into account these facts one can believe, that the adhesion of the chromium oxide coating on the MWCNT's surface is a result of double and single bond formation between the surface MWCNT's atoms and oxygen atoms of the  $\text{Cr}_2\text{O}_3$  coating without destruction of the MWCNT outside surface, and that a small amount of oxygen atoms embedded in the surface of the nanotubes form the epoxy bonds.



**Figure 3.** (a) NEXAFS partial C1s - spectra of pristine MWCNTs (curve 1) and MWCNT/chromium composite (curve 2); (b) the NEXAFS Cr2p - spectrum of MWCNT/chromium composite.

#### 4. Conclusion

The study has shown that top layers of the MWCNT's in composite reveal no essential destruction, coating of MWCNT's-surface is  $\text{Cr}_2\text{O}_3$  and this coating is continuous. The chromium oxide adhesion is provided by chemical binding between the carbon atoms of the MWCNT's top layer and the oxygen atoms of the coating.

#### Acknowledgments

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