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Structure of the polyaniline–carbon nanotube interface

© *I.A. Lobov, N.A. Davletkildeev, S.N. Nesov, D.V. Sokolov*

Omsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Omsk, Russia
E-mail: LI_87@mail.ru

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The analysis of the structure and chemical state of the polyaniline/multi–walled carbon nanotube interface layer was carried out using the both methods of Near Edge X-Ray Absorption Fine Structure and X–Ray Photoelectron Spectroscopy. An analysis of the photoelectron spectra showed an increase in the content of covalently bound chlorine, which may be due to the functionalization of nanotubes during the polymer synthesis. The spectrum shows two states of the chloride anion, which are assigned to the polaron (Cl^*) and bipolaron (Cl^-) forms of polyaniline. The content of Cl^* increases in the interface layer, which indicates an increase in its electrical conductivity.

Keywords: polyaniline, multi–walled carbon nanotubes, composites, X–ray spectroscopy.

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Composites based on polyaniline (PANI) and carbon nanotubes (CNT) are promising as sensitive elements of gas sensors, supercapacitor electrodes, and protective coatings [1,2]. Many characteristics of heterophase composite materials are defined by the structure of their interfaces and nature of interaction between their components. CNTs are graphite–like structures containing structural defects of various types. For instance, multiwall CNTs (MWCNTs) with the bamboo arrangement contain a great number of fragments of graphene planes terminating on the surface [3]. The PANY/CNT interface layer has been studied experimentally only slightly. Using techniques with a large analysis depth, it is impossible to distinguish the signal from the interface since the its volume fraction is rather small. Surface–sensitive investigation methods do not provide reliable information on the interface layer structure because of too large thickness of the composite polymer layer. In this work, studies of the PANI/MWCNT composites with a polymer layer sufficiently thin to allow getting signals from the interface were performed by combining the X–Ray Photoelectron Sectroscopy (XPS) and Near Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS).

MWCNTs were synthesized by catalytic gas–phase deposition using acetonitrile as the carbon raw material. As a growth catalyst, we used nickel nanopowder obtained by the nickel oxalate ($\mathrm{NiC_2O_4}$) decomposition on a quartz substrate. The MWCNT synthesis was performed at 800°C for an hour. The obtained MWCNTs were rinsed with 15% hydrochloric acid to remove the catalyst, dried, and annealed in air at 390°C for 2 h in order to remove the amorphous phase. The PANI/MWCNT composites were synthesized by the method of *in situ* chemical oxidative polymerization of aniline in the HCl aqueous solution. The nanotubes were preliminary dispersed in isopropyl alcohol for an hour. After that, aniline and 3M HCl were added to the suspension, and dispersion was performed again for 30 min. By properly fitting the aniline/MWCNT ratio, composites with the polymer layer thicknesses not larger than 15 nm (composite PANI/MWCNT-1) and more than 100 nm (composite PANI/MWCNT-2) were synthesized. As an oxidizer, ammonium persulfate (with the equimolar ratio to aniline) dissolved in 3M HCl was used. Both mixtures were cooled in an ice bath to 0°C. The oxidizer was added to the first mixture in drops with continuous stirring. The reaction time was 1 h. The reaction product was rinsed many times with water, alcohol and acetone, and then dried in air at room temperature.

The thickness of the polymer layer on the MWCNT surface was controlled by transmission electron spectroscopy (TEM) with microscope JEOL JEM2200FS. To analyze the structural–chemical state of the nanotubes and composites, we used techniques NEXAFS and XPS based on the synchrotron radiation of the electron storage ring BESSY II (Germany, Berlin) and RGL-PES station equipment. NEXAFS spectra were detected in the mode of measuring the sample–leakage current.

Initial MWCTs have the bamboo structure with the mean outer diameter of ~ 100 nm. Detailed characteristics of the initial MWCNTs are presented in [4]. Analysis of TEM images of composites PANI/MWCNT-1 (Fig. 1, *a*) showed that the polymer layer on the nanotube surfaces varies from several units to two tens of nanometers. This makes it possible to analyze the material electronic structure near the PANI/MWCNT interface by NEXAFS (with the probing depth of $\sim 20{-}40$ nm) and XPS (with the probing depth of $\sim 2{-}3$ nm). The polymer layer thickness in the PANI/MWCNT-2 composites (Fig. 1, *b*) exceeds 100 nm, which allows using their spectra as reference ones for the PANI description.

NEXAFS spectra C 1*s* exhibit transitions from the C 1*s* core level to unoccupied conductivity–band C 2*s*, 2*p* states possessing the π^*— and σ^*-symmetry. The MWCNT

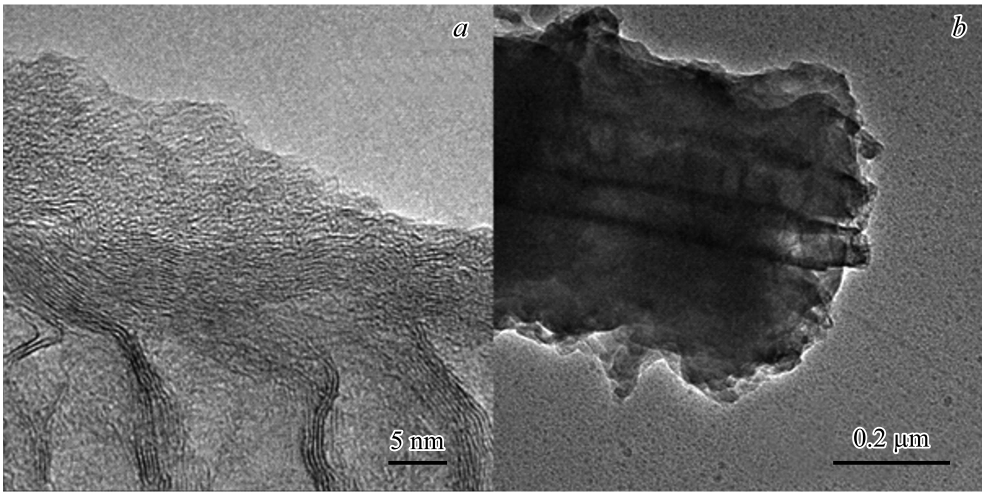

Figure 1. TEM image of the PANI/MWCNT-1 composite interface (*a*) and PANI/MWCNT-2 interface (*b*).

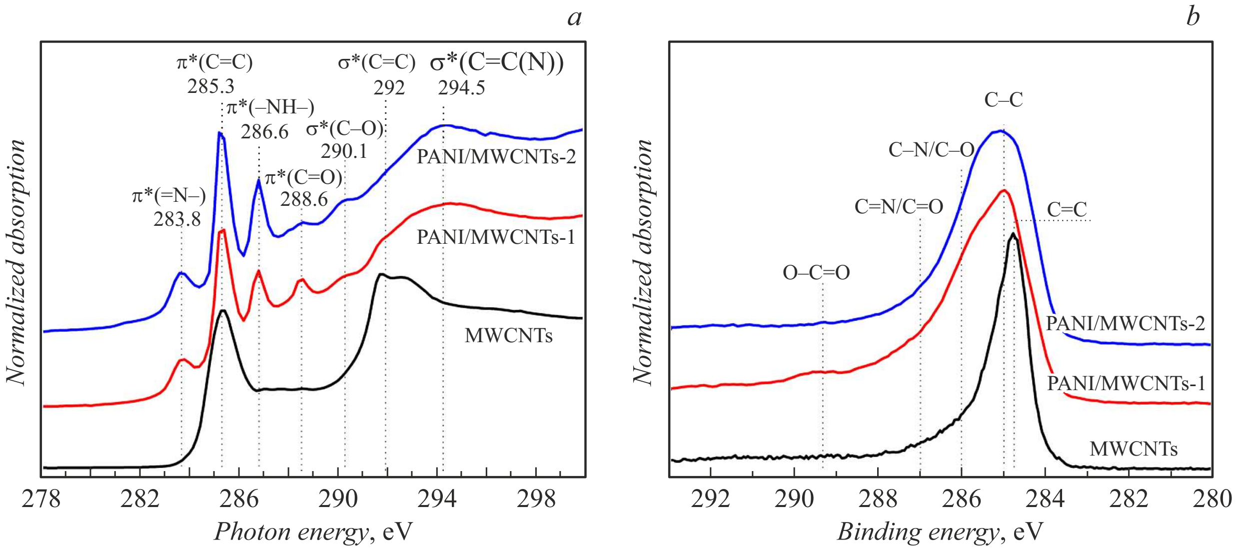

Figure 2. NEXAFS C 1*s* spectra (*a*) and XPS C 1*s* spectra (*b*) of MWCNTs and composites PANI/MWCNT-1, PANI/MWCNT-2.

NEXAFS C 1*s* spectrum (Fig. 2, *a*) has two local maxima at the photon energies of ~ 285.3 and ~ 292 eV corresponding to the π^*— and σ^*-resonances, respectively [5]. The MWCNT spectrum evidences for a high extent of the crystal structure ordering in the initial MWCNT walls and for the absence of functional oxygen–containing groups on their surfaces. The main peaks of the composite C 1*s* spectra are well consistent with the PANI spectra presented in literature [6]. The most intense maximum at the photon energy of ~ 285.3 eV corresponds to the π^*-states of carbon within the carbon–carbon bonds. The low–energy maximum at the photon energy of ~ 283.8 eV corresponds to the π^*-states of carbon bound with nitrogen within the imine groups (=N–). The maximum at the photon energy of ~ 286.6 eV corresponds to the π^*-states of carbon bound with nitrogen within the amine groups (–NH–). Maxima at the ~ 288.6 and 290.1 eV photon energies correspond to the π^*(C=O)— and σ^*(C–O)-states of carbon within the carbon–oxygen groups [4]. Maxima at the photon energies of ~ 294.5 and 302 eV correspond to the states of carbon possessing the σ^*-symmetry within the polymer benzene rings. The composite PANI/MWCNT-1 spectrum has some specific features. For instance, at the photon energies of ~ 292 eV there is a spectral line kink that is evidently a signal of the σ^*(C=C)-states of carbon forming the MWCNT wall skeletons. The intensity increase at the photon energies of ~ 288.6 eV indicates the increase in the number of carbonyl and carboxyl groups that are most probably fixed on the carbon nanotube surfaces near the MWCNT/PANI interfaces. This study used MWCNTs with the bamboo structure comprising surface–terminating graphene wall edges that may get oxidized during storage in

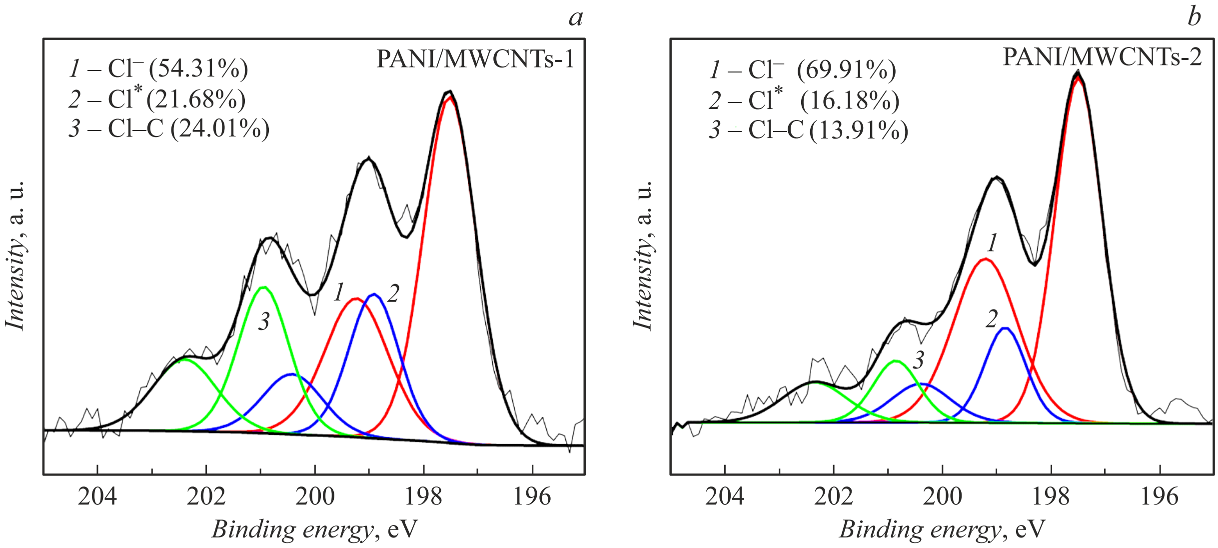

Figure 3. XPS Cl $2p$ spectra of composites PANI/MWCNT-1 (*a*) and PANI/MWCNT-2 (*b*).

air. In addition, formation of COOH groups on MWCNTs of this type takes place in treating them in hydrochloric acid [4] and, hence, in the process of the composite synthesis.

The XPS C $1s$ spectrum of MWCNT (Fig. 2, *b*) has an asymmetric shape characteristic of conducting carbon nanotubes [7]. The position of the main maximum at the binding energy of ~ 284.7 eV is characteristic of the carbon–carbon bonds in the carbon nanotube walls doped with nitrogen. At the binding energies of ~ 286 and ~ 287 eV there exist states corresponding to carbon within C–N/C–O and C=N/C=O, respectively. States at the ~ 289.4 eV energy correspond to carbon within the O–C=O bonds that typically arise on the MWCNT structural defects and ends and also at the graphene wall edges terminating on the multiwall carbon nanotube surfaces. The XPS C $1s$ spectrum of PANI/MWCNT-2 exhibits a more pronounced broadening in the range of high binding energies where the states corresponding to the carbon–nitrogen chemical bonds are located. It is clearly seen that the PANI/MWCNT-1 XPS C $1s$ spectrum is contributed by MWCNTs. This manifests itself in the existence of an intense feature at the ~ 285 eV energy and in the intensity growth in the range of binding energies corresponding to carbonyl groups (COOH), which agrees well with the NEXAFS results.

The XPS Cl $2p$ spectrum is a doublet with the spin–orbit splitting of ~ 1.6 eV and the $\sim 1:2$ ratio between the areas of lines Cl $2p_{1/2}$ and Cl $2p_{3/2}$ (Fig. 3). Component Cl $2p_{3/2}$ at the binding energy of ~ 197.5 eV correspond to the states of the Cl^- anion, while the peak at ~ 201 eV is associated with the presence of covalently bound chlorine [8]. One more component is distinguished in the PANI Cl $2p$ spectra with the Cl $2p_{3/2}$ maximum at the ~ 199 eV binding energy [8,9]. It is related to the states of anion chloride (Cl^*) arising due to the charge exchange between chlorine and PANI polymer chain with formation of a delocalized positive charge on nitrogen. The Cl^* and Cl^- states are related to the polaron and bipolaron energy states of PANI, respectively [9].

Quantitative ratios between the components are demonstrated in Fig. 3. The increase in the intensity of covalently bound Cl in the PANI/MWCNT-1 XPS spectrum (Fig. 3, *a*) may be caused by formation of the Cl–C bonds on the nanotube surfaces during the synthesis of composites. A significant increase in the Cl^* fraction is a specific feature of the PANI–MWCNT interface layer. As noticed in [9], PANI whose predominant component is Cl^- has a lower electrical conductivity. Therefore, the increase in the Cl^* component content in the composite PANI/MWCNT-1 XPS spectrum may evidence for a higher conductivity of the interface layer than that of the bulk polymer layer.

Thus, specific features of the structures and chemical states on interfaces in the PANI/MWCNTcomposites were studied using a complex of experimental methods (TEM, NEXAFS, XPS). It was established that carbonyl and carboxyl groups exist near the interface on the carbon nanotube surfaces. These groups are assumed to be formed in the process of the composite synthesis. Analysis of the chlorine XPS spectra demonstrated a signal intensity increase of the interface layer Cl–C component, which may be caused by the MWCNT functionalization during the composite synthesis. There was revealed an increase in the content of chloride anion connected with the PANI polaron energy states, which evidenced for an increase in the PANI interface layer conductivity relative to the bulk layer conductivity in the PANI/MWCNT composites.

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Conflict of interests

The authors declare that they have no conflict of interests.

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