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Modification of the electronic structure in single-walled carbon nanotubes with aromatic amines

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We investigated the interactions of two aromatic amines, N,N,N'-tetramethyl-p-phenylenediamine (TMPD) and tetramethylpyrazine (TMP) with single-walled carbon nanotube (SWNT) networks. Adsorption and intercalation of amine molecules in bundled SWNTs is expected to modify the electronic structure of nanotubes in a similar way as has already been observed for alkali metals. Our *ab initio* density functional calculations demonstrate that TMPD donates electron to the nanotube and produces donor-like states below the conduction band whereas the effect of the TMP treatment is very weak. The electron transfer to the nanotubes has been supported experimentally by the XPS valence band spectra

which show strongly modified spectral features. Especially an increase of the electronic density at the Fermi level upon adsorption of TMPD and TMP is clearly demonstrated. Rather intensive features between π^* and σ^* transitions in the NEXAFS spectrum of the pristine SWNTs attributed to the oxidized carbon functional groups are chemically modified upon adsorption of amines on the networks. This fact suggests that the aromatic amines evidently react with the defects, remove or replace oxygen species responsible for the p-type doping of SWNTs, and therefore are acting as a de-doping agent for the naturally p-type doped semiconducting SWNTs.

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1 Introduction The electrical properties of single-walled carbon nanotubes (SWNTs) being of interest for a variety of applications, ranging from nanoelectronics and sensing systems to nanocomposites, are highly sensitive to the interactions with chemical species constituting the nanotube environment. Even simply adsorbed atoms, ions and neutral molecules are able to modify the conducting π system of carbon nanotubes providing a convenient opportunity for controllable doping. Whereas the p-type doping due to the oxidation at ambient conditions is very common, the n-type doping is typically related to alkali metals under a vacuum environment and is not stable in air [1]. However, it has been shown that chemical reactants possessing strong reducing properties are able to donate electrons to carbon nanotubes [2]. Thereby the doping efficiency is correlated to the electrochemical redox

potential of the involved reactants [3]. In a similar way, several organic molecules typically containing sulphur or nitrogen atoms may behave like electron donors of carbon nanotubes. Especially amine-rich polymers such as poly(ethyleneimine) have demonstrated electron donation effects [4]. In our previous research on chemical doping of SWNTs using N,N,N'-tetramethyl-p-phenylenediamine (TMPD) and tetramethylpyrazine (TMP), both small aromatic molecules comprising nitrogen atoms, we have observed a characteristic shift of the carbon C 1s peak to higher binding energy in the XPS spectra, and a corresponding shift of the G-line to a lower frequency in the Raman spectra indicating an n-type doping [5].

In this work, we analyse the electron transfer from TMPD and TMP to SWNTs and their effect on the electronic structure of SWNTs, both theoretically by performing

ab initio density functional calculations, and experimentally using valence band X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS). The following sections are focused on the electronic and structural characterization of the charge transfer complexes formed on the SWNT surface after adsorption of amines considering also the role of the oxidized carbon functionalities in the pristine sample.

2 Materials and methods Single-walled carbon nanotubes were purchased as a purified arc discharge material from Hanwha Nanotech Co. Ltd. Thin films of SWNTs have been prepared by vacuum filtration of a suspension in 1 wt% of sodium dodecylsulfate and subsequent rising with de-ionized water and drying. The amines, TMPD and TMP were purchased from Aldrich and used in a form of a 3 wt% solution in the anhydrous tetrahydrofuran. The doping was performed by dipping the SWNT films in the amine solution for 24 h and drying at room temperature in air.

The XPS and NEXAFS experiments were performed at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using radiation from the Russian-German beamline and the MUSTANG experimental station. The XPS valence band spectra were collected using a hemispherical analyser VG CLAM-4 at the incident photon energy of 100 eV with the experimental resolution better than 0.1 eV (full width at a half maximum, FWHM). NEXAFS spectra near the C K-edge were acquired in the total-electron yield mode. The spectra were normalized to the primary photon current from a gold-covered grid recorded simultaneously. The monochromatization of the incident radiation was ~ 80 meV, FWHM. During the experiments, the pressure in the chamber was $\sim 10^{-8}$ Pa.

For the theoretical study, we calculated the electronic structures of the SWNTs doped with TMPD and TMP, based on the density functional theory [6]. Norm-conserving Troullier–Martins pseudopotentials [7] were employed and wave functions were expanded using the pseudo-atomic orbital basis set implemented in the OpenMX package. For the exchange–correlation term, the Ceperley–Alder type local density approximation [8] was used. The energy cutoff for real space mesh points was 200 Ry. As a model system, the semiconducting (8,0) carbon nanotube was used for studying the doping properties of TMPD and TMP. The supercell size in the lateral direction was 20 Å to avoid the interaction between the neighbour cell, and the size in the axial direction was 12.78 Å. The atomic positions were relaxed until the forces on the atoms were reduced to 0.05 V/Å.

3 Results and discussion

3.1 Theoretical results The chemical structure and the highest occupied molecular orbitals (HOMO) of the doping materials are shown in Fig. 1. Considering only the elemental composition, both molecules containing nitrogen heteroatoms are supposed to act as a potential donor material.

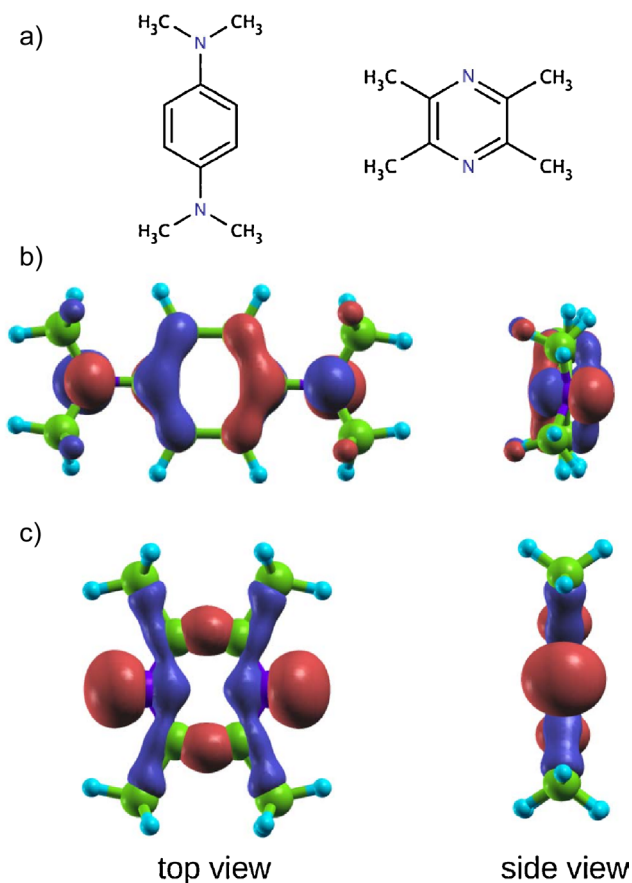


Figure 1 (online colour at: www.pss-b.com) (a) Chemical structure of TMPD (left) and TMP (right). Top and side views of isosurfaces of the HOMOs of TMPD (b), and of TMP (c).

However, our first-principles study shows that the symmetry and the distribution of the electron density over these molecules have significant differences. One can clearly see in the side views of Fig. 1b and c that the HOMO of TMPD has a π -bonding character, whereas that of TMP has a σ -bonding character. As a consequence, the molecular orbitals accommodating the lone pairs of nitrogen in TMPD can easily align and overlap with the π orbitals of carbon nanotubes, and thus stronger molecular interactions of adsorbed molecules with the SWNT are possible. Formation of the charge-transfer complexes leads to charge redistribution in the system, resulting in increasing electron density in the sp^2 -bonded carbon nanotubes. In contrast, weak interaction with nitrogen orbitals in pyrazine ring are expected for TMP. Moreover, the TMPD with the lowest ionization potential (6.2 eV) [9] among of a variety of aliphatic and aromatic amines has already demonstrated an electron transfer to acceptor compounds or even to non-polar solvents [10]. Therefore this amine has been selected as a suitable n-type dopant for nanotube networks.

The electronic structure of the (8,0) CNT with the adsorbed TMPD and TMP molecules is presented in Fig. 2. A corresponding band structure of the bare (8,0) CNT is not

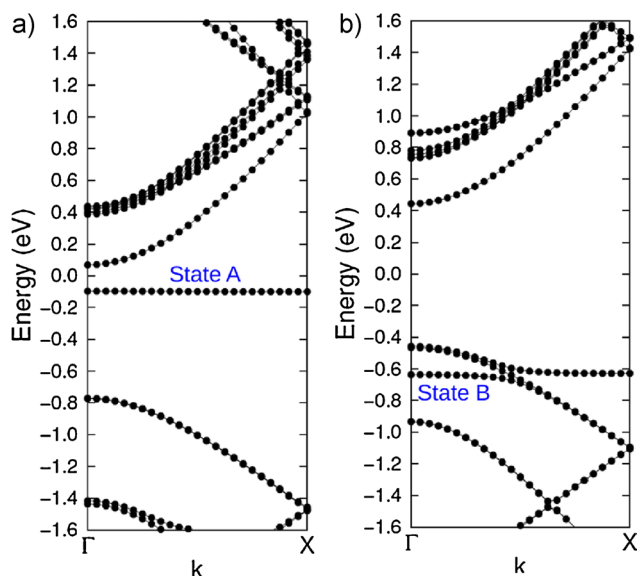


Figure 2 (online colour at: www.pss-b.com) Band structures of the (8,0) CNT interacting with (a) TMPD and (b) TMP. The Fermi level is set to zero.

shown here, because it is almost identical to that shown in Fig. 2b, where the conduction band minimum is located at ~ 0.4 eV. In contrast, Fig. 2a demonstrates that the conduction bands are downshifted by ~ 0.35 eV, and a donor-like state (state A) is placed below the conduction band minimum in the TMPD-doped case. This means that the electron transfer occurs from TMPD to the tube, resulting in the n-type doping. On the contrary, the band structure of the TMP-doped CNT (Fig. 2b) shows no gap state originating from the TMP molecule. A TMP-derived localized state (state B) is located at about -0.6 eV and is weakly hybridized with the valence band of the tube. There is no downward band shift implying electron donation, so that the n-type doping cannot be demonstrated for the TMP doping. This observation is in accordance with the σ -bonding character of the HOMO of TMP in Fig. 1c.

Figure 3 shows that the two flat bands (states A and B) originate from the HOMOs of TMPD and TMP, respectively. Consequently, we can conclude that the characters of molecular orbitals of the dopant play a crucial role in controlling the doping level of the semiconducting CNT.

3.2 NEXAFS and XPS spectroscopy Electronic and structural information about carbon atoms and local functionalities in carbon nanotubes can be deduced from the C K-edge X-ray absorption fine structure spectra. The spectra of the pristine and the dopant treated carbon nanotube network (left panel in Fig. 4) are dominated by two sharp peaks located at around 285.4 and 291.8 eV, and associated with $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions, respectively [11]. In order to visualize the changes in the spectral C K-edge range with deposition of amine molecules the spectra were normalized on the intensity of the σ^* -resonance (right panel

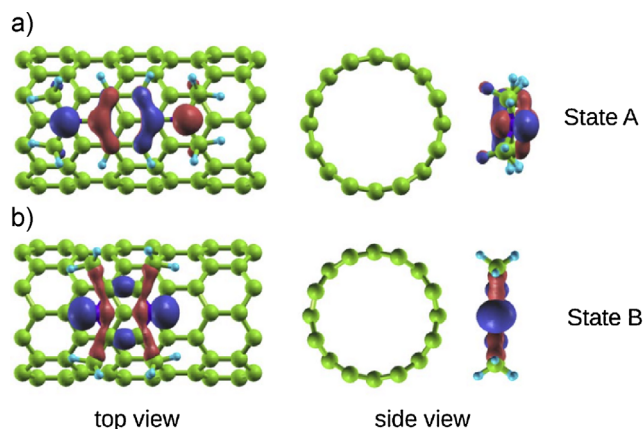


Figure 3 (online colour at: www.pss-b.com) Wave functions of the localized states in the band structures in Fig. 2 corresponding to dopant molecules on the surface of the (8,0) carbon nanotube: (a) TMPD and (b) TMP.

in Fig. 4). The relative intensity of the π^* -resonance is practically unchanged with the TMP adsorption, while it markedly increases in the spectrum of the TMPD + SWNT complex. The latter effect may be related to the charge transfer from the phenylene ring of the TMPD resulting from the higher concentration of TMPD molecules on the SWNT surface due their stronger interaction with SWNTs. Discussing the NEXAFS spectrum of the pristine sample it is worth to notice the spectral features in the range between the π and σ transitions. These bands are assigned to three types of oxidized carbon functional groups. The right panel of Fig. 4 shows the changes in this region in comparison to the reference pristine SWNTs sample. Both amines affect this spectral region, but the TMPD has a stronger influence on these bands. This fact suggests that the TMPD may undergo ionization forming the contact ion pairs $\text{TMPD}^+ \text{X}^-$ in the presence of oxygen functionalities (X: oxygen atom of carbonyl, carboxyl or hydroxyl groups). The ionization of

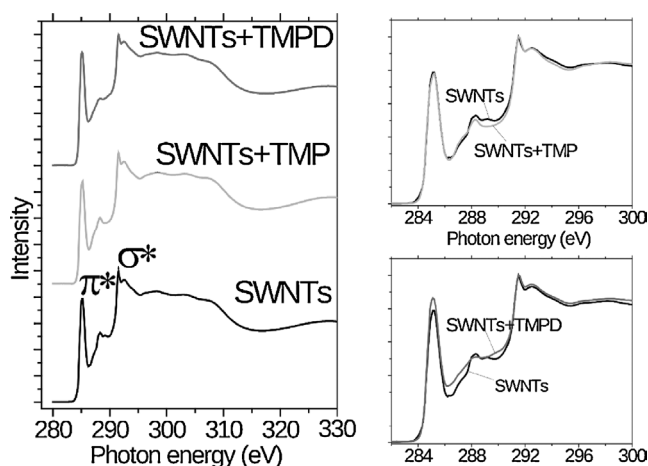


Figure 4 The C K-edge NEXAFS spectra of the pristine and amine modified SWNT networks.

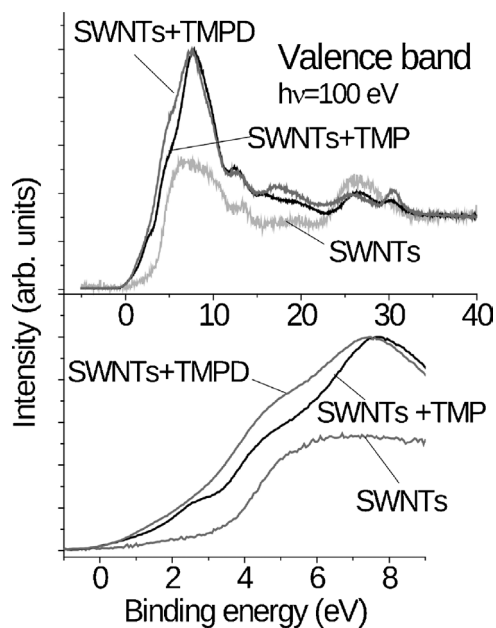


Figure 5 The XPS C valence band spectra of the pristine and the modified by aromatic amines SWNT networks.

aromatic amines and electron transfer to oxygen containing polar molecules has been already observed when methanol and water were used as a solvent [12]. A removal or chemical modification of oxygen containing groups in the SWNTs which are responsible for the p-type doping is equal to de-doping. Thus the investigated aromatic amines are able to affect the SWNT electronic properties on two ways: directly through the electron transfer to the sp^2 system of SWNTs, and indirectly through passivation of the oxygen terminated defects.

The chemical modification of SWNTs by TMPD and TMP has been further studied by the XPS. The photoemission process at 100 eV provides direct information about energy distribution and density of state of the valence electrons. Figure 5 shows the changes in the spectra of SWNT sample following the chemical treatment.

The strong difference in shape and intensity of the spectral features in respect to the pristine sample provides clear evidence that the SWNTs have been chemically modified with corresponding changes in the electronic structure when the amines were adsorbed. An increase of the electron density visible in Fig. 5 is characteristic for formation of SWNT/amine surface complexes. A detailed analysis of the spectrum near to the zero energy (lower panel of the Fig. 5) demonstrates the charge accumulation and an increase of the density of states at the Fermi level

implying the donation of electrons to SWNTs, and an n-type doping.

4 Conclusions A new method for chemical modification of entangled SWNT networks has been studied. It has been shown that adsorption of aromatic amines such as TMPD and TMP leads to an increase of the electronic density near the Fermi level confirming n-type doping. Moreover, it has been demonstrated by NEXAFS that amines cause significant changes in the oxidized functional groups removing or chemically modifying them. Removal of the oxygen species which are actually determining the p-type semiconducting properties of SWNTs means that these amines behave as a potential reducing or de-doping reactant for the naturally p-type doped SWNTs.

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