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Engineering of electronic structure of boron-nitride nanotubes by covalent functionalization

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Electronic structure of boron-nitride nanotubes (BNNTs) can be tuned in a wide range through covalent functionalization, as experimentally and theoretically evidenced. Various functional groups were covalently attached to BNNTs. The ultraviolet-visible absorption spectra indicate that the electronic structure of BNNTs drastically changes under functionalization. First-principle calculations reveal that the covalently functionalized BNNTs can be either *n*- or *p*-doped depending on the electronegativity of molecules attached, and their energy gap can be adjusted from ultraviolet to visible optical range by varying concentration of functionalized species.

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In contrast to carbon nanotubes (CNTs), boron-nitride nanotubes (BNNTs) are constant-band-gap nanomaterials, independent of their radii and chiralities.[1] In addition, BNNTs possess excellent mechanical properties, high thermal conductivity, and superb resistance to oxidation.[2,3] However, a relatively large ~5.5 eV band gap of BNNT restricts its applications to sole dielectric performances.[4] Thus it is especially important to find a way to tune BNNT electronic properties in order to widen the application field. Although some methods have been predicted to be useful for BNNT band gap engineering using theoretical calculations,[5] in practice, such methods are very difficult to realize due to the extreme conditions involved, such as very high electric field or pressure.

Covalent functionalization of the nanotube sidewalls provides one of the most promising routes toward BNNT electronic structure adjustment. Much effort has been made with respect to the CNT-related works.[6–14] It is thought that BNNTs are more practical in this sense since they have a constant band gap and the influence of organic functional groups may be much more pronounced because carbon atoms are foreign atoms in BNNTs.[15] Recently, we have connected a long alkyl chain to a BNNT via a successful chemical reaction.[16] This may pave a way to further engineer BNNT electronic structure using on-demand covalent functionalization.

In this paper, we propose a practical way to tune BNNT electronic structure that has been verified experimentally and theoretically. Various organic functional groups were connected to BNNTs covalently via a chemical reaction between amino groups of BNNTs and –COCl groups of various additives. Dramatic changes in electronic structure of BNNTs were detected by UV-vis absorption spectroscopy. Then, the electronic structures of pristine and functionalized BNNT were compared using the first-principle calculations. The results indicate that covalently functionalized BNNTs may be *n*-doped or *p*-doped and the energy gap between the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) can be tuned in a wide range.

Multiwalled BNNTs grown by a chemical vapor deposition method were used for functionalization.[16,17] Naphthoyl chloride ($C_{10}H_7COCl$), Butyryl chloride ($CH_3(CH_2)_2COCl$), and stearoyl chloride ($CH_3(CH_2)_{16}COCl$) were used to consecutively fabricate $C_{10}H_7CO$-BNNT, $CH_3(CH_2)_2CO$-BNNT, and $CH_3(CH_2)_{16}CO$-BNNT. The Fourier-transformed infrared spectra confirm that the corresponding functional groups have been successfully attached to BNNTs.

UV-vis absorption experiments were performed on a Hitachi U-4100 spectrometer. The volume fraction of nanotubes within a product can reach 90 vol.% or more according to the electron microscopy observations,[17] which ensures the validity of our data. As shown in Fig. 1, for pristine BNNTs, a peak at 5.80 eV dominates. It corresponds to a band-gap transition and indicates a band gap in the range of 5.2 to 5.5 eV. After functional group attachment, this peak shifts to the lower energies, i.e., 5.56, 5.43, and 5.36 eV for $CH_3(CH_2)_2CO$-BNNT, $CH_3(CH_2)_{16}CO$-BNNT, and $C_{10}H_7CO$-BNNT, respectively. In addition, for $CH_3(CH_2)_{16}CO$-BNNT, two additional peaks at approximately 4.68 and 4.20 eV appear, and for $C_{10}H_7CO$-BNNT, a new peak at 4.34 eV becomes visible. It is suggested that a charge transfer may occur between the functional groups and BNNTs, which, in turn, induces doping effects in BNNTs. A HOMO-LUMO gap may be changed since carbon atoms may introduce some occupied or unoccupied levels in the large gap area.[18] These changes in the band structure of BNNTs may be the origin of new peak appearance and main peak shifts in the UV-vis absorption spectra. It should be noted that the concentration of functional groups on BNNTs is not uniform, because the chemical reactions are solely taking place at the amino group sites on BNNTs. These sites have been spontaneously formed during the BNNT growth.

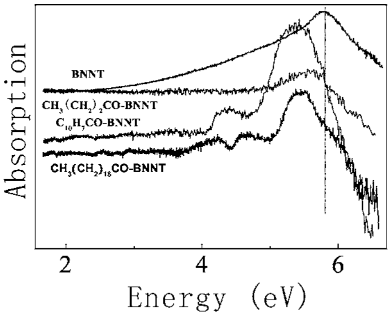

FIG. 1. Comparative UV-vis absorption spectra of pristine and functionalized BNNTs.

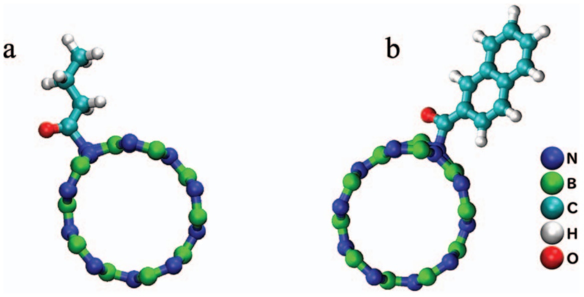

FIG. 2. (Color) The optimized structure of (a) $CH_3(CH_2)_2CO$-BNNT and (b) $C_{10}H_7CO$-BNNT.

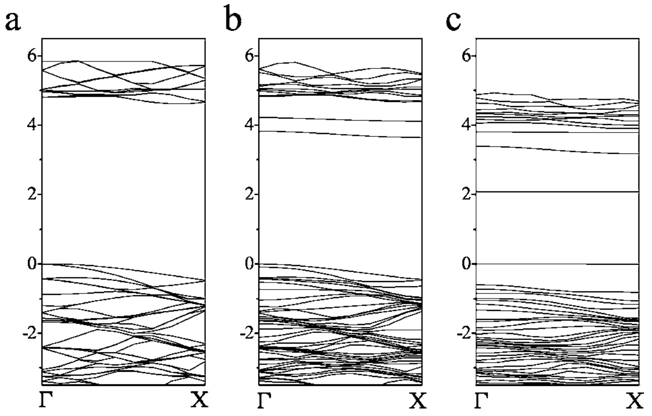

FIG. 3. Calculated bank structure of (a) a (5, 5) BNNT, (b) $CH_3(CH_2)_2CO$-BNNT, and (c) $C_{10}H_7CO$-BNNT.

In our experiments, the functional groups do not destroy the tubular morphology. This implies that there is an opportunity to change the nanotube electronic structure even more dramatically if more functional groups are introduced.

In order to investigate the effects of functional groups on BNNTs, the electronic structures of pristine and functionalized BNNTs were investigated by the first-principle calculations based on density functional theory (DFT) within the local density approximation (LDA).[19] The standard Troullier-Martins pseudopotentials were used with a plane-wave cutoff of 305 eV.[20] This method has already been successfully applied to study carbon and BN nanostructures.[21–23] A 20 Å wide vacuum region was included in a supercell.[24] The Fermi level is assigned to a zero energy value in our calculations. To sample the Brillouin zone, k points along the tube axis have been used. For the band structure calculations, a sampling of eight k points for the first Brillouin zone were used, and for DOS calculations, the Monkhorst-pack scheme, $3\times3\times9$, was found appropriate to represent all systems in our investigations.

The geometric structures of a (5,5) BNNT with different functional groups were allowed to relax completely until the residual forces become less than 0.05 eV/Å. The resultant structures are shown in Fig. 2. It can be seen that a local distortion occurs near the adsorption site, which can be understood by the local sp^3 rehybridization of a N atom at the absorption site.[7] The nitrogen atom and the nearest boron atom on the sidewall connected to the functional groups are extruded out. The B-N bond lengths in the nanotube beyond the first neighbors are found to be little affected by the functionalization. The naphthalene group plane has an angle of around 45° with the tube axis. Compared with $CH_3(CH_2)_2CO$, $C_{10}H_7CO$ induces a larger distortion which indicates that there is a stronger coupling interaction between the naphthalene group and BNNT.

The calculated band structures around the Fermi levels of pristine and functionalized (5,5) BNNT are shown in Fig. 3. The data were obtained at a density of one functional group per 31 B and 31 N atoms. Pristine (5,5) BNNT is an indirect gap material with a HOMO-LUMO gap of 4.5 eV.[25] It should be noted that these gap values are often underestimated due to the DFT-LDA calculations.[26] After the functional groups were introduced, the degenerated energy levels at the Γ point below the Fermi level split into two states. This energy level separation is due to the reduced symmetry of the system after introduction of functional groups.[27] The $CH_3(CH_2)_2CO$ attachment introduces two unoccupied bands under the bottom of the conduction band. For $C_{10}H_7CO$, not only are more bands introduced, but also the whole band shifts due to the larger symmetry breaking and stronger coupling interactions between the naphthalene group and BNNT. Detailed partial density of states (DOS) analysis reveals that

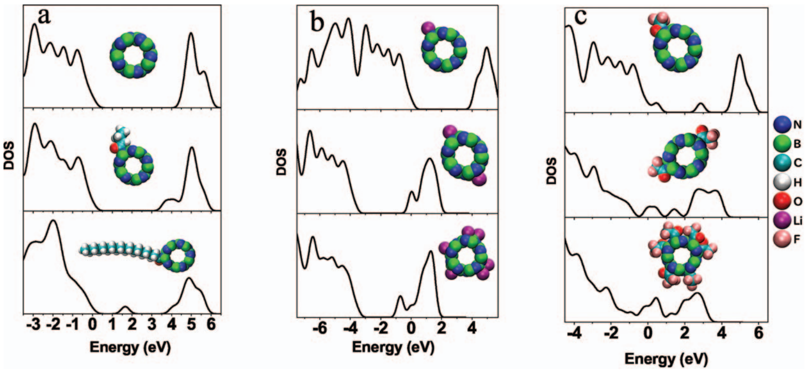

FIG. 4. (Color) (a) Comparative DOS of pristine (5,5) BNNT, $CH_3(CH_2)_2CO$-BNNT, and $CH_3(CH_2)_{16}CO$-BNNT from the top to bottom, respectively; (b) comparative DOS of Li functionalized BNNT, the concentration is one Li atom per 31 B and 31 N atoms, two- and sixfold, respectively, from the top to bottom; (c) comparative DOS of $COCF_3$ functionalized BNNT, the concentration is one $COCF_3$ per 31 B and 31 N atoms, two- and sixfold, respectively, from top to bottom. The insets are the optimized structures used for DOS calculations.

the new bands are mainly induced by the *s* orbital of carbon atoms bonded with N atoms for $CH_3(CH_2)_2CO$, whereas in the case of $C_{10}H_7CO$ all atoms contribute to the new bands.

The HOMO-LUMO gaps decrease dramatically after functionalization due to the bands introduced in the gap, which indicates that a charge transfer may take place and functional groups may have a dopant effect on BNNT. A Mulliken population analysis confirms that there are 0.13 electrons transfer from BNNT to $C_{10}H_7CO$, while 0.05 electrons transfer from $CH_3(CH_2)_2CO$ to BNNT. This implies that covalently functionalized BNNT may be either *p*-doped *n*-doped depending on the polarity and electronegativity of functional groups attached. In order to reveal the dopant effects more clearly, the calculations were performed on two special systems: F_3CCO-BNNT and Li-BNNT.[28] As expected, F_3CCO-BNNT is *p*-doped (0.20 electrons transferred) and Li-BNNT is *n*-doped (0.10 electrons transferred), which confirms that BNNTs of different dopant types can be fabricated through covalent functionalization.

In order to modify the BNNT electronic structure in a wider range, more heteroatoms should be introduced into a supercell. One possible way is to use a series of molecules with similar structure but multiplying a number of atoms. Figure 4(a) shows DOS of pristine BNNT, $CH_3(CH_2)_2CO$-BNNT, and $CH_3(CH_2)_{16}CO$-BNNT, respectively. It can be seen that except for the additional shoulder at the bottom of the conduction bands, one peak appears in the middle of the gap for $CH_3(CH_2)_{16}CO$-BNNT. Thus, it is suggested that it is difficult to obtain a controllable variation of the electronic structure using this route even when the molecules adopted have similar structure. A more reliable way is to connect more functional molecules to BNNTs. Concentration dependence calculations have been performed and the results are shown in Figs. 4(b) and 4(c). The top diagram in Figs. 4(b) and 4(c) is based on the concentration of one unit per 31 B and 31 N atoms. The following consecutive diagrams show the DOS when the concentrations are two- and sixfold. The insets display fully relaxed structures. The LUMO-HOMO gap of BNNT decreases to 3.75 eV after Li atom connection, and, then, further decreases to 3.08 eV and 2.01 eV when the concentrations become two- and sixfold. These values fall into the visible optical range. Although the bands shift occurs, the basic characteristics of the band structure are similar; the reduction of the LUMO-HOMO gap is due to the new bands appearing at the bottom of conduction band. The DOS variations of F_3CCO-BNNT exhibit similar characteristics: the density of impurity states becomes larger with the higher functional group concentration and the LUMO-HOMO gap is subsequently reduced. When the concentration is sixfold, no obvious energy gap can be identified. Thus such functionalized BNNT exhibit metallicity. These calculations indicate that the covalent functionalization at different concentrations is indeed an effective way to smoothly tune the BNNT electronic structure.

As revealed in our experiments, the optical properties of BNNT can in fact be changed by functionalization. Although it is difficult to strictly associate the absorption peaks with DOS diagrams because the BNNTs used in the experiments were multiwalled (while the calculations were run for single-walled nanotubes), some conclusions can still be drawn. The observed HOMO-LUMO gap reduction may be responsible for the redshifts of main adsorption peaks. For $CH_3(CH_2)_{16}CO$-BNNT and $C_{10}H_7CO$-BNNT, the additional bands appear in the middle of the energy gap and the transitions between these impurity states may lead to some new absorption peaks. However, for $CH_3(CH_2)_2CO$-BNNT, only a small additional shoulder, very close to the BNNT LUMO, is observed in Fig. 4(a). This would reduce the band gap and, therefore, only the redshift of the absorption peak is visible. Also, due to the dopant effects, the transport properties of functionalized BNNTs may be improved. High concentration functionalization would favor the overlap between the local molecular orbitals of the nearest dopants. Apparently, the electrical conductance of the outermost multiwalled BNNT layer can be adjusted by absorbing different molecules, which can be proved by further experiments. Recently, excitons in BNNTs were investigated theoretically and it was revealed that the optical absorption spectra of BNNTs are dominated by strongly bound excitons.[30] It is believed that after functionalization, new bound states appear in the gap, which changes that optical response of BNNTs.

In conclusion, the electronic structures of covalently functionalized BNNTs were experimentally and theoretically investigated. Their UV-vis absorption characteristics drastically change after the functionalization. The first-principle calculations indicate that the functionalized BNNTs can be either *p*-doped or *n*-doped dependent on electronegativity and polarity of the functional molecules attached. High-concentration covalent functionalization may effectively reduce a HOMO-LUMO gap of BNNTs from an ultraviolet to a visible optical range. Strongly polar molecule-functionalized BNNTs may even exhibit metallicity. In addition, it is envisaged that covalent functionalization may improve the BNNT transport properties due to doping effects. More calculations related to bonding energies and electronic structures of BNNTs absorbing molecules on different sites (such as on the top of B atoms) are still underway.[29]

Our studies provide a practical way to adjust the electronic structure of the constant-band-gap BNNTs. It can be proposed that, experimentally, BNNTs optical and transport properties can be tuned in a wide range by firstly introducing high concentration defects on their sidewalls using hydrogen plasma etching, for example, and, secondly, connecting proper molecules to the defects thus created. Because of the well-known difficulties in selection of a proper CNT for a specific device due to CNT electronic structure complexity, it is suggested that covalently functionalized BNNTs may be an effective and important substitute for conventional CNTs.

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