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Selective Covalent Functionalization of Carbon Nanobuds

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The unique properties of carbon nanotubes (CNTs) such as a high aspect ratio and excellent thermal, optical, and electrical conductivities have been utilized in a broad range of applications from electric circuits to biomedical devices. For incorporating CNTs to applications there is, however, a major obstacle due to their poor solubility in many solvents, particularly in water.[1−3] The CNT solubility can be increased by using hydrophilic molecules that are either adsorbed, for example, surfactants,[4] or chemically bound to the tubes[5,6] of which the latter approach often requires pretreatment of inert CNT sidewalls in order to increase their reactivity. This changes the carbon−carbon bond configuration (sp^2-hybridization) of the CNT which may alter its properties.[7] The tube ends with pentagons offer sites for a noninvasive bonding, but this restricts the chemical modifications to low concentrations that are localized only at the tube ends.

Recently, Nasibulin et al.[8] synthesized a novel carbon hybrid material—carbon nanobud (CNB)—wherein fullerenes were formed and covalently bonded to the tube sidewall simultaneously with the growth of single walled carbon nanotubes (SWCNTs). These fullerenes with different cage sizes (dominant cage C$_{60}$, ∼25%)[8] and shapes are expected to provide exquisite sites for a noninvasive, covalent modification of CNTs.

Our aim is to demonstrate by theoretical and experimental means the feasibility of chemical modification of CNBs taking place exclusively on the CNB fullerenes. Amine compounds are known to react with C$_{60}$[9−12] but not with pristine CNTs. It is worth noting that CNBs contain a negligible amount of defects,[8,13] and thus any sidewall reactions can be excluded.

The selectivity of the reaction between an amine (CH$_3$NH$_2$) and CNB is studied computationally using density functional theory (DFT) utilizing the CPMD and Turbomole program packages.[14,15] A hypothetical CNB model originally proposed by Nasibulin et al.[8] has been used in which a C$_{60}$ is fused to a SWCNT by removing internal carbon atoms (Figure 1). The reactivity is studied by comparing calculated binding energies on different CNB sites (sidewall, neck, and fullerene top). The top of the fullerene is shown to be the most favorable binding site for the amine (Figure 1). When the primary amine binds to the fullerene, two species, N-HR and H, are added to the fullerene top in either ortho, meta, or para positions, that is, they are separated by one, two, or three bonds, respectively.[12] By obeying to the local symmetry of the C$_{60}$, this reaction could give rise to six different stereoisomers. Our calculations predict that the structure where the additions are in the ortho position with respect to a six-membered ring is the most stable with the lowest binding energy (close to thermoneutral). Other sites of the CNB are clearly unfavored with endothermicity within 150−250 kJ/mol. Computational studies also show that the reactions taking place at the top of the CNB fullerene could be well described with a simplified model involving an amine and C$_{60}$. This is based on the similarity

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(14) CPMD (http://www.cpmd.org). Computational details: PBE functional; 80 Ry energy cutoff for the wavefunction expansion in plane waves; simulation cell, 19.7 × 20 × 26 Å.
(15) Turbomole 6 (http://www.cosmologic.de/QuantumChemistry/main_turbomole.html). Using C$_{60}$ as a simplified, nonperiodic model of the CNB bud top was also tested with CH$_3$,H addition using four unique conformations (relative positions as in ortho, meta, para). The results of the two methods agree very well. The correlation of CPMD energies calculated with the full periodic model and corresponding C$_{60}$ energies calculated with Turbomole can be expressed as $E_{\mathrm{CPMD}}[\mathrm{kJ/mol}] = 1.1468 \times (E_{\mathrm{Turbomole}}) - 7.467$, $R^2 = 0.968$.

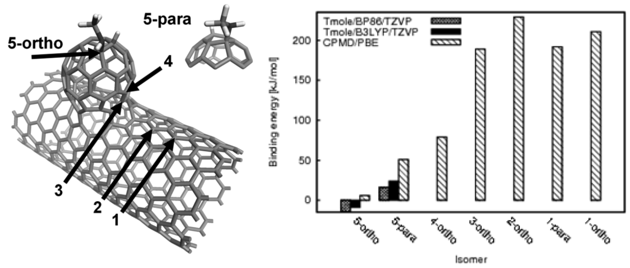

Figure 1. Studied reaction sites and the corresponding binding energies for NH_2CH_3+CNB→CNB-$NHCH_3$,H. The arrows show nitrogen addition sites.

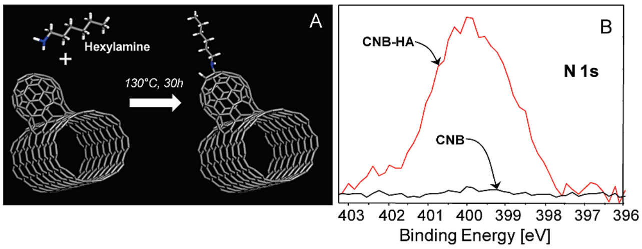

Figure 2. (A) Model for a nucleophilic addition reaction between hexylamine and C_{60} fullerene of CNB (blue part denotes to nitrogen atom). (B) N 1s band in the XPS (X-ray photon spectroscopy) of CNB−HA.

of energies calculated with the full periodic model and C_{60}; see Figure 1.[16] This allows more accurate theories to be used and more detailed studies on this particular reaction site to be performed.

SWCNTs[17] and CNBs[8,18] are synthesized using a floating catalyst process. The CNB sample is characterized by TEM (transmission electron microscopy) to ensure the formation of covalently bonded fullerenes.

Hexylamine (HA) is chosen for a nucleophilic addition to CNB fullerenes (Figure 2a). The CNBs are dispersed in HA (7.6 mL) and refluxed at 130 °C under nitrogen purge for 30 h in the presence of light. After the reaction, the major fraction of unreacted HA is removed by vacuum treatment followed by flushing the crude CNB−HA with deionized water to remove any traces of HA. The CNB−HA is dried in vacuum over silica. The same procedure is carried out with SWCNT and C_{60} except that the resulting C_{60}−HA is purified by column chromatography.

The CNB−HA consists of 1.5 molar % of nitrogen which corresponds to 1 HA molecule per 51 CNB carbon atoms (Figure 2b). This high nitrogen quantity may result from multiple HA additions to a single fullerene.[9−12] No nitrogen is observed with HA-treated SWCNT.

To gain more information on the nature of the CNB−HA interaction IR spectra measurements were performed and compared with corresponding spectra from DFT calculations (Figure 3). CNB−HA expresses ultimately similar IR characteristics as C_{60}−HA: a broad band at 3340 cm^{-1} for the secondary amine (calculated N−H stretch for C_{60}−HA at 3438 cm^{-1}) and a strong stretching

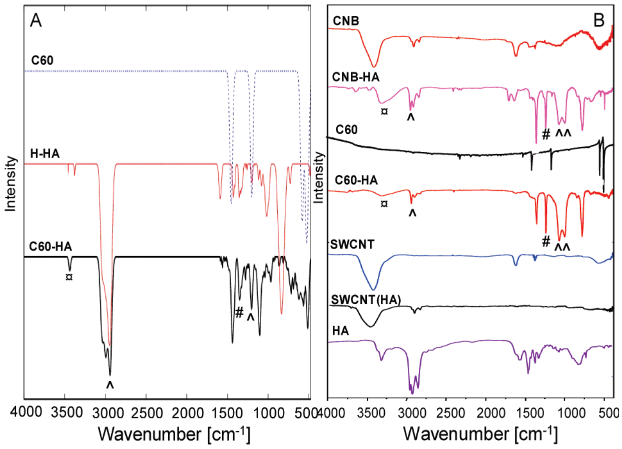

Figure 3. (A) Simulated IR spectra (A) based on the calculated DFT harmonic frequencies and intensities and (B) measured IR spectra of the samples. Symbol (¤) denotes to the bands at 3438 (part A), 3340 (B) and 3343 cm^{-1} (B), (#) denotes 1342 (A) and 1261 cm^{-1} (B), and (^) denotes 2955 (A), 1201 (A), 2964 (B), 2966 (B), 1095 (B), and 1023 cm^{-1} (B).

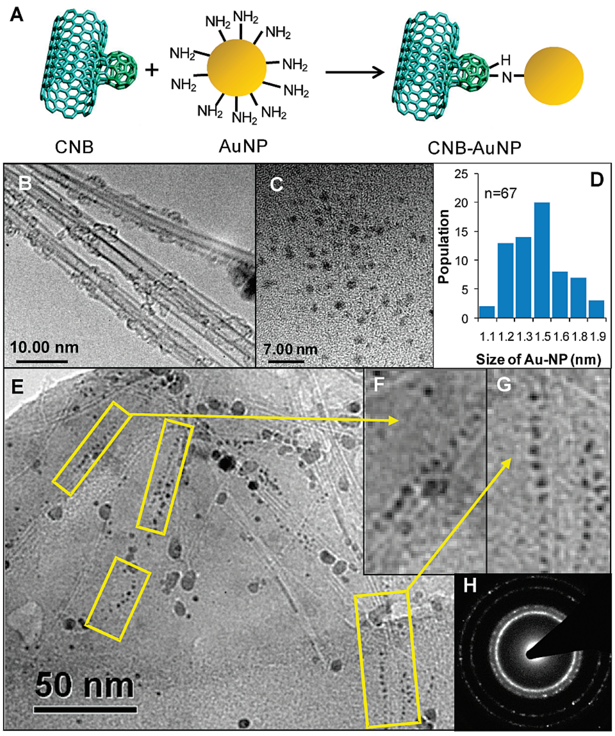

Figure 4. (A) A reaction scheme of CNB+AuNP; TEM images of (B) CNBs and (C) AuNPs; (D) the size distribution of AuNP; (E) TEM image of CNB−AuNPs; (F and G) close-ups showing AuNPs along CNB; and (H) the diffraction pattern of AuNPs in CNB−AuNP. Yellow boxes show few AuNP arrays in CNB−AuNP. Large clusters of approximately 5 nm in size seen in E are Fe catalyst particles used in the CNB synthesis.

vibration at 1261 cm^{-1} for C−N of a secondary amine[19] (calculated frequency is 1342 cm^{-1}). Note that the latter band does not exist in the HA spectrum. Both the measured and the calculated spectra support the absence of the scissoring and weakening of H−N−H modes of CNB−HA and C_{60}−HA once the amine has reacted.[20]

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(16) See Supporting Information.

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These changes are taken as a strong evidence of selective amine reaction on the fullerenes of CNBs since no such bands appeared in the spectrum of SWCNT(HA).

The intensity of the vibrational modes of fullerenes changes when the symmetry of the fullerene cage structure changes.[1] Three strong bands at the region of 3000–2800 cm^{-1} belong to the stretches of C–H bond in hydrogenated C_{60}.[21] The highest frequency band (2964 cm^{-1} and 2966 cm^{-1}) is the strongest in both CNB–HA and C_{60}–HA resulting from a change in the vibrational modes of C_{60} by the added H atom. The DFT calculations give a localized C_{60}–H weak stretching mode at 2955 cm^{-1} and a strong bending mode at 1201 cm^{-1}. Moreover, CNB–HA and C_{60}–HA show strong bands at 1095 cm^{-1} and 1023 cm^{-1} related to the modified symmetry of C_{60}.[1,20,22,23] Accordingly, the symmetry of fullerenes is evidently affected by HA molecule.

We have also conducted a reaction between CNBs and amine-terminated gold nanoclusters (AuNP) with diameter of approximately 1.5 nm (Figure 4). The CNB–AuNP derivatives are found on the amorphous part of the holey carbon grid (Figure 4e) from which the existence of the CNB and Au is verified by their electron diffraction. Although the visual observation of "AuNP on the top of fullerene" is not possible to make, the AuNPs are found along the CNB sidewall. Note that the gold nanoparticles have a tendency to agglomerate themselves, and thus their localization along the sidewall hypothesizes a strong interaction between CNBs and AuNPs. The random and blocky localizations of AuNPs result from similar localization of the fullerenes (Figure 4b). We believe that AuNPs are chemically grafted to fullerene parts of the CNBs.

By combining experimental and computational methods we have demonstrated for the first time a chemical reaction to take place selectively on the fullerenes of the nanobuds. This opens up new possibilities for the noninvasive functionalization of SWCNT. In other words, the fullerenes of the nanobud can be utilized to functionalize the parent SWCNT without introducing defects into the tube sidewall. This is utmost important for applications, for instance, in the field of flexible electronics, transparent conducting films, and biomedicine, where the original properties of the tubes are essential to preserve.

Supporting Information Available: Description of the syntheses of SWCNT, CNB, and CNB–AuNP (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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