2013

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Guiling Zhang
Harbin University of Science and Technology

Rulong Zhou
Hefei University of Technology

Xiao Cheng Zeng
University of Nebraska-Lincoln, xzeng1@unl.edu

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Zhang, Guiling; Zhou, Rulong; and Zeng, Xiao Cheng, "Carbon nanotube and boron nitride nanotube hosted C_{60}–V nanopeapods" (2013). Xiao Cheng Zeng Publications. 116.
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Carbon nanotube and boron nitride nanotube hosted C\textsubscript{60}–V nanopeapods†

Guiling Zhang, a,b Rulong Zhou b,c and Xiao Cheng Zeng a,c

We investigate electronic and transport properties of a novel form of nanopeapod structure, where the “pod” component is either a carbon nanotube (CNT) or a boron-nitride nanotube (BNNT) while the “pea” component is a chain of C\textsubscript{60}–V dimers. Compared to the conventional carbon peapod where the “pea” is a chain of C\textsubscript{60} fullerenes, marked changes in the electronic structures are found due to the formation of coordination bonds between V and two neighboring C\textsubscript{60} molecules. The local spins in the (\eta\textsubscript{6}–C\textsubscript{60}−V)@CNT or (\eta\textsubscript{6}–C\textsubscript{60}−V)@BNNT peapod are coupled via antiferromagnetic (AFM) exchange interaction. In particular, the C\textsubscript{60}–V chain in BNNT yields a well-defined spin qubit. Density-functional theory calculation suggests that the (\eta\textsubscript{6}–C\textsubscript{60}−V)@CNT peapod is metallic with characteristics of multiple carriers contributed from CNTs, C\textsubscript{60}, and V. The (\eta\textsubscript{6}–C\textsubscript{60}−V)@BNNT peapod is predicted to be semiconducting with a narrow band gap, and its charge carriers are contributed by the C\textsubscript{60}–V chain. Evidently, the insertion of a V atom between every two C\textsubscript{60} fullerenes can enhance the conductivity of the peapod. Binding H atoms on all the \(\alpha\) positions of the pentagons in C\textsubscript{60} can further strengthen the V–C\textsubscript{60} interaction. Both AFM and FM states of the H-containing peapod are nearly degenerate in energy. The FM state gives rise to a magnetic moment of 3.0 \(\mu_B\) per unit cell, three times greater than that of the V–benzene or V–cyclopentadiene multidecker complexes. The binding of H atoms to the C\textsubscript{60} however cannot enhance electron transport due to the removal of the \(\pi\) channel of C\textsubscript{60}. Previous experiments have demonstrated that C\textsubscript{60} molecules can enter BNNTs through the open tips of the BNNTs, offering a strategy that the V–C\textsubscript{60} dimers may be encapsulated into nanotubes through the open tips of the nanotubes to form M–C\textsubscript{60} peapods.

Introduction

Nanopeapods, nanotubes (NT) filled with fullerene molecules (C\textsubscript{60}@NT), have attracted intensive interest due to their potential applications in field-effect transistors,1−3 magnetic nanodevices,4−7 data storage nanodevices,8,9 and nanoscale lasers.10 Being trapped in the cylindrical interior of nanotubes, the fullerene molecules may form a one-dimensional (1D) wire structure. In contrast to the 1D structure assembled on a substrate, the confined 1D structure within a nanotube exhibits exceptional thermal stability owing to the spatial protection by the host nanotube.11 This hybrid core/sheath structure enables the development of a novel class of 1D nanostructures unavailable in open environment. Moreover, the electronic coupling between various components, including fullerene–nanotube and fullerene–fullerene, may lead to new physical phenomena that cannot be observed with isolated nanotubes and fullerenes. For example, recent scanning tunneling microscopy (STM) imaging on the carbon nanotube (CNT) peapod, C\textsubscript{60}@CNT, shows the modulation of density of states (DOS) in the conduction band with the same period as the 1D C\textsubscript{60} array,12,13 which can affect the electron transport property of the CNT.14−17 CNT peapods have been successfully synthesized in many laboratories.18 The first evidence of C\textsubscript{60} nested inside carbon nanotubes was reported in 1998.19 Later, higher fullerenes, e.g. C\textsubscript{70},20,21 C\textsubscript{82},19 and C\textsubscript{84},22 endohedral fullerenes, e.g. Gd@C\textsubscript{82},23,24 PrSc@C\textsubscript{84},25 and N@C\textsubscript{60},26,27 and other modified fullerenes, e.g. C\textsubscript{59}N (ref. 28) and C\textsubscript{59}R (\(R = \text{alkyl}\)),29 were also experimentally detected inside CNTs. Theoretical computations have yielded additional details of the energetics,30,31 electronic structures,30,36 and transport properties37−39 of CNT peapods. However, few studies have reported boron–nitrogen nanotube (BNNT) peapods. Note that BNNTs were first reported by Okada et al. in 2001.40 Soon after, this nanomaterial was fabricated in the laboratory by Mickelson et al.41 Since then, structural and electronic properties of BNNT peapods have been explored theoretically.52,43 The BNNT peapods can be viewed as a single-file fullerene chain, where the fullerene molecules are confined to form a linear chain.

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3tc30800f
which interacts with the BNNT host through weak van der Waals interaction.\textsuperscript{42} It is known that the CNTs can be either metallic or semiconducting, depending on their diameter and chirality, while the BNNTs are always insulating with band gaps of 4–5 eV.\textsuperscript{44–47} Such a striking difference in electronic properties between CNTs and BNNTs will inevitably lead to different physical properties of the corresponding peapods. For the CNT peapods, there are two conducting pathways: one along the CNTs and the other along the encapsulated fullerene chain.\textsuperscript{48} However, for the BNNT peapods, the electron transport is expected to be only through the fullerene t\text{1u}-derived bands.\textsuperscript{42}

A possible experimental strategy to endow either CNT or BNNT peapods with new properties is to encage exohedral or endohedral fullerenes. Recently, fullerene derivatives containing transition metal atoms adsorbed on the outer surface of the carbon cage have received increasing interest because such complexes can possess properties of transition metals and fullerenes.\textsuperscript{48–51} It is known that transition metal (TM) atoms can be coordinated with benzenes (η\text{6}-type) or cyclopentadienes (η\text{5}-type) and form 1D sandwich multidecker clusters. However, it is still a challenge to synthesize η\text{6}- and η\text{5}-type transition metal-fullerene complexes due to the curved surface of fullerene and associated weak polarizability.\textsuperscript{48–51} Here, the superscript of η denotes the number of carbon atoms that are bonded to a metal atom. Two research groups have synthesized both neutral and cationic clusters, η\text{6}-M\text{m}(C\text{60})\text{m} and η\text{5}-M\text{m}(C\text{60})\text{n} (M = Sc, Ti, V, Cr, Fe, Ni, Ag; m and n are integers).\textsuperscript{48,53} Only small-sized clusters (n ≤ 4) were proposed to form a stable multi-pod structure in the gas-phase. For large-sized clusters (n > 4), the TM-fullerene complexes favor either a multiple dumbbell or a ring configuration. Hence, it is unlikely to fabricate a long-chain of M–C\text{60} multi-pods due to multiple facets of fullerenes, as each facet can coordinate with a transition metal atom. On the other hand, the nanotube can be a perfect cylindrical host to enclose a 1D M–C\text{60} multi-pod nanowire. In addition, previous diffraction measurements\textsuperscript{54–57} and high resolution transmission electron microscopy (HRTEM) imaging\textsuperscript{54–57} show that the distance between the C\text{60} molecules within nanotubes almost always falls into the range of 9.7–10.0 Å, a sufficient interval for inserting a transition metal atom to form M–C\text{60} multi-pod complexes. Furthermore, both experimental and theoretical studies have demonstrated that exohedral functional groups (e.g. –H and –Me) of fullerenes can also stabilize the M-fullerene complexes.\textsuperscript{49,50} Various transition metal–fullerene complexes, e.g., Re(η\text{5}-C\text{60}H\text{5})(CO)\text{3} (ref. 58) and (η\text{5}-C\text{5}H\text{5})MC\text{60}R\text{5} (M = Fe, Ru, R = Me, Ph),\textsuperscript{59} have already been successfully encapsulated into CNTs. Based on the aforementioned results and our calculations, we expect that 1D M–C\text{60} peapods in either CNT or BNNT may be realized in the laboratory.

In this work, we compute properties of eight V-containing CNT peapods 1a–1h and eight V-containing BNNT peapods 2a–2h at different spin states (Fig. 1 and ESI Fig. S1†) using the density functional theory (DFT) method. For the host nanotubes, we consider the metallic (10,10) CNT and the insulating (10,10) BNNT. The transition metal element V is selected in view

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Optimized multi-pod structures of V-containing peapods, 1a–d and 2a–d. 1a also illustrates a two-probe system for electron transport calculation. The most stable structures 1a, 2a, 1b, and 2b are discussed in this text.}
\end{figure}
of the fact that most benzene and cyclopentadiene sandwich multideckers are V complexes. The (10,10) nanotube and C60 fullerenes are chosen because they have been subjected to extensive studies both theoretically and experimentally.14 For the purpose of comparison, we also compute properties of the V-free C60@CNT and C60@BNNT peapods. In particular, the electronic and transport properties of the two most stable CNT peapods 1a and 1b and the two most stable BNNT peapods 2a and 2b are discussed in detail. Particular attention is placed on the effects of the V element on the electronic and transport properties of the peapods, as well as the effects of the attachment of H atoms to the C60, and the difference between the CNT and BNNT peapods.

Results and discussion

We use a supercell containing two repeated units (i.e., containing two C60s and two V atoms; see 1a in Fig. 1) in the axial direction to account for the magnetic exchange interaction due to the presence of the V element.

Favorable location for V binding

We first consider the systems without H (1a, 2a, 1c and 2c in Fig. 1, 1e-h and 2e-h in the ESI Fig. S1†). To confirm that the favorable location for the V atom is just between the C60s (sandwich multi-pod structure), 1a, 2a, 1c, and 2c, we also optimize peapods with every V atom being located in the space between the tube and the C60 (ESI Fig. S1†). These side-V-binding structures can be divided into two groups: (1) the pvH structure, if the V atom is located between a pentagon of C60 and a hexagon of nanotube, and (2) the hvH structure if the V atom is between a hexagon of C60 and a hexagon of nanotube (ESI Fig. S1†). For the pvH and hvH structures, all the cis and trans structures of 1c-h and 2c-h are examined. In the cis structure, the V atoms are aligned on the same side of the C60 along the axial direction, while in the trans structure the V atoms are located alternatively on the opposite side of the C60 along the axial direction. Both the antiferromagnetic state (AFM) and the ferromagnetic state (FM) are examined for the eight CNT peapods 1a-h and eight BNNT peapods 2a-h. The computed total energies E per supercell are listed in the ESI Table S1.† Note that all the sandwich multi-pod structures possess lower energies than the corresponding side-V-binding structures, indicating that the V atom favors to be located between C60s and link the fullerenes to form a 1D V–C60 hybrid multi-pod chain within either CNT or BNNT. Clearly, the hybrid multi-pod structure of the η⁶-type (C60–V)@NT is more stable than that of the η⁵-type one (1a vs. 1c and 2a vs. 2c). Time of flight mass spectroscopy measurements22,33 and ab initio calculation60 also confirm that the C60 behaves as a η⁶-ligand for the V atom. Therefore, the η⁵-type hybrid multi-pod structures 1a and 2a are energetically most favorable for the peapods (without H), which will be discussed in the following sections.

The chemical stability for the V-binding with peapods (without H) is evaluated by computing the reaction energy per supercell for the net reaction [nanotube (NT) + 2C60 + 2V → peapod − ΔEv].

The computed reaction energies for all peapods are listed in the ESI Table S1.† As a comparison, the reaction energies of V-free C60@NT peapods (based on the reaction [NT + 2C60 → peapod − ΔEv]) are also given in the ESI Table S1.† The ΔEv of C60@CNTs are in the range of −6.66 to −6.92 eV, in agreement with the experimental value of −6.0 eV.44 Importantly, the V-free C60@NT multi-pods prefer a pentagon-facing-pentagon (denoted as pfp) configuration for C60s rather than a hexagon-facing-hexagon (hfh) configuration. The formation of the V-containing structures releases 16–20 eV energies per supercell, much more than the V-free ones, implying that incorporation of the V atom into either C60@CNT or C60@BNNT is energetically favorable.

Next, we examine reaction energies of two types of H-containing peapods, (η⁵-C60@H6–V)@NT (1b and 2b) and (η⁶-C60@H12–V)@NT (1d and 2d). Similarly, the reaction energy ΔEv per supercell is computed through the reaction formula [NT + 2C60@H12/2C60@H10 + 2V → peapod − ΔEv]. The computed reaction energies for the H-containing peapods are given in the ESI Table S1.† Apparently, the attachment of the H atoms in the manner described above is more exothermic for the C60–V binding reaction. This is because with the H atoms attaching two opposing pentagons or hexagons of a C60 (forming C60@H10 or C60@H12), a structure of the cyclopentadiene type or a benzene type is formed. These exohedral H atoms can modify the local structure of the molecular orbitals. As a result, a favorable condition arises to the formation of the complex of the fullerene with the V atom through the η⁵ or η⁶-type bond. The formation of (η⁵-C60@H6–V)@NT gives rise to more negative ΔEv than the formation of (η⁶-C60@H12–V)@NT, suggesting that the η⁵-H-substitution is energetically more favorable for binding with V atoms. Hereafter, for H-containing multi-pods, only the η⁵-H-substituted 1b and 2b systems will be discussed.

Geometric structures and chemical bonding

The optimized supercell length in the axial direction (L) (1a in Fig. 1), the face-to-face distances between adjacent fullerenes (r), and the distances between the wall of the nanotube and the nearest atom of C60 (R) of 1a, 2a, 1b, and 2b are given in Table 1. The distances r are within the range of 3.43–3.64 Å, similar to the ligand-to-ligand separation in the V–benzene (3.3–3.4 Å)22 or V-cyclopentadiene (3.54 Å)44 multidecker clusters. The C60s in BNNT have a slightly longer separation than in CNT. The values of R are in the range of 3.30–3.49 Å, suggesting a van der Waals interaction between the CNT and the fullerene. There are no major geometry differences between the AFM and FM states of the four V-containing systems. No significant structural change is observed with the V doping except slight elongation of the r, indicating that the V atom can be sandwiched between C60s without deforming either the nanotube or the C60 structure. Therefore, the formation of the 1D V–C60 multi-pod chain would not require much structural distortion from the original V-free peapod.

Table 2 shows the charge populations in the peapods 1a, 2a, 1b, and 2b. About 1.2 electrons move from the V 4s orbital to the fullerene cage, while about 2.0 C60 electrons move to the empty V 3d and 4p orbitals, indicative of a typical V-cage coordination bond. Overall, a V atom bears a net negative charge. The V–C60
interaction can also be reflected from the projected density of states (PDOS) shown in Fig. 2. The 3d state of the V atom hybrids significantly with the π states of the fullerene. The Kohn–Sham orbitals corresponding to the energy levels near the Fermi level (EF) at the Γ point for 1a, 2a, 1b, and 2b are shown in Fig. 3, where it clearly shows the hybridization of the V 3d and fullerene π orbitals. In the carbon nanotube peapods 1a and 1b, the CNTs exhibit positive charges and thus the fullerene cages serve as the electron acceptor (Table 2). This conclusion is consistent with previous theoretical calculations.\textsuperscript{36,31,38} Conversely, the BNNT is an electron acceptor for the peapods 2a and 2b. The encapsulation of the V atoms and the addition of the H atoms have little effect on the charge transfer between the nanotube and the fullerene.

Magnetism

The calculated energy differences between the AFM and FM states are listed in Table 1 and ESI Table S1.\textsuperscript{1} Besides GGA calculation, the GGA + U calculation (see Computational methods) is also performed to confirm no appreciable change in the magnetic moments (see ESI Table S1).\textsuperscript{7} The (η\textsuperscript{6}C\textsubscript{60}−V)@CNT and (η\textsuperscript{6}C\textsubscript{60}−V)@BNNT peapods possess the AFM ground state with zero magnetic moment, in contrast to the FM ground state in the V–benzene or V–cyclopentadiene multidecker nanowire.\textsuperscript{63–65} This apparent difference in magnetic behavior may be attributed to the difference in the interaction between the 3d electrons of the V atom and the π electrons of the carbon rings; the d–π interaction is discontinuous in the peapod (⋯d–π–d–π–⋯ bonding type), but is continuous in the V–benzene and V–cyclopentadiene multidecker nanowires (⋯d–d–d–⋯ bonding type). In other words, each unit cell of (η\textsuperscript{6}C\textsubscript{60}−V)@NT has a spin \( \frac{1}{2} \), and the neighboring unpaired electron is antiferromagnetically coupled due to the exchange interaction of the intervening C\textsubscript{60}. In (η\textsuperscript{6}C\textsubscript{60}−V)@BNNT, the spin moment is mainly contributed by C\textsubscript{60}. As shown in Fig. 3, both valence band maximum (VBM) and

\[ ΔE_{AFM}/ΔE_{FM} (eV) \]

\[ ΔE_{EFM-AM}(meV) \]

\[ J (meV) \]

\[ T_{\text{AFM}}/T_{\text{FM}} (K) \]

\[ S_{\text{AFM}}/S_{\text{FM}} (μB) \]

\[ S_{\text{FM}}^\text{V} (μB) \]

\[ S_{\text{FM}}^\text{C} (μB) \]

\[ L_{\text{AFM}}/L_{\text{FM}} (Å) \]

\[ r_{\text{AFM}}/r_{\text{FM}} (Å) \]

\[ R_{\text{AFM}}/R_{\text{FM}} (Å) \]

\[ \text{Table 1} \] Calculation results for V–C\textsubscript{60} peapods 1a, 2a, 1b, and 2b. Those for V-free C\textsubscript{60}@CNT(PP) and C\textsubscript{60}@BNNT(PP) are listed for comparison

\[ \text{Table 2} \] Charge populations in V–C\textsubscript{60} peapods 1a, 2a, 1b, and 2b. Those for V-free C\textsubscript{60}@CNT(PP) and C\textsubscript{60}@BNNT(PP) are listed for comparison

![Fig. 2](image_url) Computed projected density of states (PDOS) of 1a, 2a, 1b, and 2b peapods.
conduction band minimum (CBM) of \((\eta^6-C_{60}-V)@BNNT\) can be attributed to the coupling of the V 3d and C_{60} \pi orbitals. The C_{60}–V chain in 2a gives rise to a 0.43 eV band gap at the \(\Gamma\) point (Fig. 3). Therefore, the \((\eta^6-C_{60}-V)@BNNT\) valence band is well separated from other energy bands above and below, leading to a well-defined spin qubit. However, in \((\eta^6-C_{60}-V)@CNT\), the energy band due to C_{60}–V crosses with other bands due to CNTs and thus cannot form an effective spin qubit.

The exchange parameter \(J\), which can be estimated by the energy difference between FM and AFM configurations, is over 60 meV per supercell (containing two spins). The values of \(J\) calculated for \((\eta^6-C_{60}-V)@NT\) peapods (>80 meV) as shown in Table 1, are much larger than those of the endohedral fullerene Sc@C_{82} peapods (<17 meV). We also estimate the Curie or Neél temperatures, \(T_{CN}\), of the peapods using the formula \(3/2k_B T_{CN} = J/2\) (see Table 1). The estimated Curie or Neél temperatures of \((\eta^6-C_{60}-V)@CNT\) and \((\eta^6-C_{60}-V)@BNNT\) are higher than 300 K, suggesting that the AFM state of the \((\eta^6-C_{60}-V)@NT\) peapod may be thermally stable at room temperature.

It is worth noting that the AFM and FM states of the H-substituted system, either \((\eta^5-C_{60}H_{10}-V)@CNT\) or \((\eta^5-C_{60}H_{10}-V)@BNNT\), are nearly degenerate in energy. The binding of five H atoms to the C_{60} leads to the formation of a radical of the cyclopentadienyl type. In the FM state, the unpaired electrons of the H-substituted C_{60}H_{10} are coupled with the 3d electrons of the V atom. Consequently, the FM state shows a magnetic moment \(S > 2.0 \mu_B\) per V atom and \(S < 1.0 \mu_B\) per C_{60}H_{10}, giving rise to a total \(S = 6.0 \mu_B\) per supercell (i.e., \(S = 3.0 \mu_B\) per unit cell), three times larger than that of the V–benzene or V–cyclopentadiene multidecker complex. The magnetic behavior of the AFM and FM states is reflected in the projected density of states (PDOS) shown in Fig. 2. For the AFM states, the majority spin and the minority spin are nearly the same near the Fermi level so that their net magnetic moments are nearly zero. For the FM

Fig. 3  Computed band structures (right panels) of 1a, 2a, 1b, and 2b peapods and the Kohn–Sham orbitals (left and middle panels) corresponding to the energy levels (highlighted in red and/or green lines) near \(E_F\) at \(\Gamma\) point. The value of the iso-surface is 0.05 (e \(\AA^{-3}\)).
state, the majority spin below the Fermi level is greater than the minority spin. The spin polarization is mainly due to the V atoms. These novel magnetic properties of the H-substituted \((\eta^5-C_{60}H_{10-V})@CNT\) and \((\eta^5-C_{60}H_{10-V})@BNNT\) peapods may have potential applications for magnetic nanodevices.

**Transport property**

Fig. 3 plots the band structures of 1a, 2a, 1b, and 2b. For the purpose of comparison, the band structures of the V-free \(C_{60}@CNT\) and \(C_{60}@BNNT\) peapods are given in the ESI Fig. S2.† For the \(C_{60}@CNT\) peapod, two bands cross the Fermi level \(E_F\) with large and linear dispersion, retaining the character of the \(\pi\) orbitals of the CNT. Hence, the \(C_{60}@CNT\) is a metal. The flat \(h_u\) and \(t_{1u}\) bands originated from the \(\pi\) orbitals of \(C_{60}\) and lie within the valence and the conduction bands, as clearly seen from the PDOS (Fig. 2). This is different from an earlier study that the \(t_{1u}\) bands of \(C_{60}\) also cross the Fermi level.† In that study, the lattice parameter was constrained to be 9.824 Å and the band structures were computed based on the local-density approximation (LDA), while in this study a full geometry optimization is performed based on the spin-polarized generalized gradient approximation (GGA). Note that a topographic STM image of the \(C_{60}@CNT(17,0)\) also shows that the \(t_{1u}\) state of \(C_{60}\) corresponds to the conduction band. From the PDOS, one can see that only the \(\pi\) states of the CNT make a contribution at the Fermi level. The fullerene \(h_u\) (~1.2 eV), \(t_{1u}\) (~0.4 eV), and \(t_{1g}\) (~1.4 eV) states hybridize with the \(\pi\) states of the CNT to different extent. This result is consistent with the STM study of the \(C_{60}\) peapods. Therefore, the fullerene \(\pi\) states can also participate in the electron tunneling through the CNT. As such, the encaging of \(C_{60}\) by the CNT should enhance the electronic conducton of the CNT, consistent with a previous experimental measurement. For the \(C_{60}@BNNT\) peapod, the top valence band and bottom conduction band are contributed solely by the \(C_{60}\) \(h_u\) and \(t_{1u}\) states, respectively, suggesting that the transport would be primarily through the \(C_{60}\). The \(C_{60}@BNNT\) peapod is predicted to be a semiconductor with a band gap ~1.35 eV, close to the reported value of 1.2 eV.†

Next, for the V-containing systems 1a, 2a, 1b, and 2b, marked changes in electronic structures can be seen from Fig. 2 and 3. For the non-H systems 1a and 2a, the coupling between the 3d state of the V atom and the \(\pi\) states of the fullerene leads to the splitting of the \(h_u\), \(t_{1u}\), and \(t_{1g}\) states (Fig. 2). A new band originated from the hybridization of the V 3d state and the \(\eta^5\) fullerene \(h_u\) state appears just below the Fermi level (Fig. 3), indicating that the doping of V atoms increase the number of quantum channels. This new band also enhances the \(\pi\) state coupling between the \(C_{60}\) and the CNT in \((\eta^5-C_{60}-V)@CNT\) near \(E_F\) but has little influence on the \(\pi\) interaction between the \(C_{60}\) and the BNNT in \((\eta^5-C_{60}-V)@BNNT\). The \((\eta^5-C_{60}-V)@CNT\) peapod is a metal with characters of multiple carriers stemming from the CNT, \(C_{60}\)\(S\), and V atoms. The plotted Kohn–Sham orbitals in Fig. 3 demonstrate a feature of multiple carriers for the \((\eta^5-C_{60}-V)@CNT\) peapod. For the \((\eta^5-C_{60}-V)@BNNT\) peapod, the coupling between the \(C_{60}\) and the V atom results in a remarkable downshift of the fullerene \(t_{1u}\) conduction band closer to the Fermi level, and a narrow band gap (0.43 eV). The charge carriers are distributed on both fullerene and V atom (Fig. 2 and 3).

For the H-substituted peapods 1b and 2b, the H-fullerene chain also shows \(h_u\), \(t_{1u}\), and \(t_{1g}\)-like states near the Fermi level. From Fig. 2 and 3, it is found that the \(t_{1u}\) like states of the \(C_{60}\) in the \(C_{60}@CNT\) are downshifted to the top of the valence band and coupled with the 3d states for both \((\eta^5-C_{60}H_{10-V})@CNT\) and \((\eta^5-C_{60}H_{10-V})@BNNT\) peapods, suggesting more electron carriers than the multidecker chain. However, the \((\eta^5-C_{60}H_{10-V})@BNNT\) system has a larger band gap (1.53 eV) than the non-H substituted system (1.35 eV), due to the weakening of the \(\pi\) delocalization of the fullerene by the –H attachment.

To confirm the predication of the transport property based on the electronic structures, we have also computed transport properties of finite-sized 1a, 2a, 1b, and 2b between two electrodes. Three transport behaviors are seen from Fig. 4 and 5: (1) the \(C_{60}@CNT\) peapod shows a metal character while the \(C_{60}@BNNT\) peapod shows an insulating one, proving that the metallic CNT severs as the main transport channel for \(C_{60}@CNT\), and the \(C_{60}\) chain is the main channel for \(C_{60}@BNNT\). (2) The current in the case of V-containing peapods is greater than that of the corresponding non-V system \((\eta^5-C_{60}-V)@CNT\) vs. \(C_{60}@CNT\) and \((\eta^5-C_{60}-V)@BNNT\) vs. \(C_{60}@BNNT\), indicating that the incorporation of V atoms can enhance the conductivity. The V atoms clearly contribute to the transport of the \((\eta^5-C_{60}-V)@CNT\) and \((\eta^5-C_{60}-V)@BNNT\) peapods. (3) The
attachment of H atoms to the C$_{60}$ indeed weakens the electron transport \([\langle n^{6}\text{C}_{60}V\rangle@\text{CNT} \text{ vs. } \langle n^{4}\text{C}_{60}\text{H}_{10}V\rangle@\text{CNT} \text{ and } \langle n^{6}\text{C}_{60}V\rangle@\text{BNNT} \text{ vs. } \langle n^{4}\text{C}_{60}\text{H}_{10}V\rangle@\text{BNNT}\)]\). The transmission around the Fermi level for \(\langle n^{6}\text{C}_{60}\text{H}_{10}V\rangle@\text{CNT}\) arises only from the CNT, that is, no contribution from the C$_{60}$H$_{10}$V chain owing to the weakening of the C$_{60}$ $\pi$ channel by the H attachment. All these transport characteristics are consistent with those derived from band structure analysis.

**Conclusions**

We have investigated the electronic and transport properties of a novel form of V–C$_{60}$ peapods by means of density functional theory methods. It is found that the dopant V atoms tend to be located between neighboring fullerene cages along the axial direction. The spins in \(\langle n^{6}\text{C}_{60}V\rangle@\text{CNT}\) and \(\langle n^{4}\text{C}_{60}V\rangle@\text{BNNT}\) are coupled via antiferromagnetic exchange interactions, and the C$_{60}$V chain in \(\langle n^{6}\text{C}_{60}V\rangle@\text{BNNT}\) provides a well-defined spin qubit. The \(\langle n^{6}\text{C}_{60}V\rangle@\text{CNT}\) peapod is a metal with characters of multiple carriers due to the nanotube, enclosed fullerene and V atoms. The \(\langle n^{6}\text{C}_{60}V\rangle@\text{BNNT}\) possesses a narrow band gap (0.43 eV) with charge carriers distributed on fullerene and V atoms. With the V atoms located sandwiched between C$_{60}$s, the electron transport of the peapod can be enhanced. Binding hydrogen atoms to the $\alpha$ position with respect to the pentagons of C$_{60}$ can strengthen the V–fullerene interaction. The AFM and FM states of the H-substituted systems, \(\langle n^{5}\text{C}_{60}\text{H}_{10}V\rangle@\text{CNT}\) and \(\langle n^{3}\text{C}_{60}\text{H}_{10}V\rangle@\text{BNNT}\), are nearly iso-energetic. The FM state shows a total magnetic moment higher than that of the V$_x$ chains in \(\langle n^{x}\text{C}_{60}$V$_c$chain\rangle@\text{CNT} and \(\langle n^{x}\text{C}_{60}$V$_c$chain\rangle@\text{BNNT}\) respectively. The electronic conduction of peapods \(\langle n^{x}\text{C}_{60}$V$_c$chain\rangle@\text{CNT}\) is set to be 3. The plane-wave basis set cutoff is 400 eV. Spin-polarized calculations are performed for all peapod structures. Only the $\Gamma$ point is chosen for the $k$-point sampling. As shown in the ESI Table S1, the predicted chemical stabilities based on the reaction energies for various structures are consistent with the SIESTA calculations.

**Acknowledgements**

GLZ is supported by grants from the NSFC (51073048), the NSF of Heilongjiang Province of China (B201102), the science foundation for leaders in academy of Harbin City of China (2010RFJGG016, 2013RXJXJ024), and the science foundation for Outstanding Scientists of Harbin University of Science and Technology. XCZ is supported by grants from the NSF (EPS-1010674) and ARL (W911NF1020099), and by the University of Nebraska’s Holland Computing Center.

**References**


Carbon nanotube and boron nitride nanotube hosted C\textsubscript{60}-V nanopeapods

Guiling Zhang\textsuperscript{1,3}, Rulong Zhou\textsuperscript{2,3}, Xiao Cheng Zeng\textsuperscript{3,*}

\textsuperscript{1}Key Laboratory of Green Chemical Engineering and Technology of College of Heilongjiang Province, College of Chemical and Environmental Engineering, Harbin University of Science and Technology, Harbin 150040, China

\textsuperscript{2}School of Science and Engineering of Materials, Hefei University of Technology, Hefei, Anhui, 230009, China

\textsuperscript{3}Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588
**Table S1.** Calculation Results Per Supercell of 1a-1h and 2a-2h Peapods in the Antiferromagnetic (AFM) and Ferromagnetic (FM) States: Total energy \((E)\), Energy Difference between the FM and AFM States \((\Delta E_{\text{FM-AFM}})\), Total Magnetic Moment \((S)\), and Reaction Energy \((\Delta E_r)\). The Data for V-free C\(_{60}\@CNT and C\(_{60}\@BNNT are Listed for Comparison. Abbreviation: hfh refers to hexagon-facing-hexagon, and pfh refers to pentagon-facing-hexagon.

<table>
<thead>
<tr>
<th>Peapods</th>
<th>(E_{\text{AFM}}) (eV)</th>
<th>(E_{\text{FM}}) (eV)</th>
<th>(\Delta E_{\text{FM-AFM}}) (meV)</th>
<th>(S_{\text{AFM}}/S_{\text{FM}}) ((\mu)B)</th>
<th>(\Delta E_r,\text{AFM}/\Delta E_r,\text{FM}) (eV)</th>
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<td>Multi-Pod Structures</td>
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<tr>
<td>1a ((\eta^6)-C(_{60})@CNT)</td>
<td>-68839.00998</td>
<td>-68838.90292</td>
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<td>2a ((\eta^6)-C(_{60})@BNNT)</td>
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<td>-18.44/-18.36</td>
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<td>1b ((\eta^5)-C(<em>{60}H</em>{10})@CNT)</td>
<td>-69170.70640</td>
<td>-69170.70278</td>
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<td>0.0/6.0</td>
<td>-26.68/-26.68</td>
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<td>1c ((\eta^5)-C(_{60})@CNT)</td>
<td>-68837.31546</td>
<td>-68837.13664</td>
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<td>0.0/6.8</td>
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<td>2c ((\eta^5)-C(_{60})@BNNT)</td>
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<td>0.0/2.0</td>
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<td>V-Side-Binding Structures</td>
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<td>1e ((\eta^6)-C(_{60})@CNT(hfh) cis</td>
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<td>C(_{60})@CNT (pfp)</td>
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<td>C(_{60})@CNT (hfh)</td>
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<td>C(_{60})@BNNT(pfp)</td>
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<td>VASP Calculation Results</td>
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<td>1a ((\eta^6)-C(_{60})@CNT)</td>
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<td>1d ((\eta^6)-C(<em>{60}H</em>{12})@CNT)</td>
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<td>-3964.2896</td>
<td>7.4</td>
<td>0.0/2.0.</td>
<td>-</td>
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</table>
Figure S1. Optimized side-V-binding structures of 1e-1h and 2e-2h peapods. We denote a pVh structure if the C\textsubscript{60} uses the pentagon and the tube uses the pentagon to coordinate with the V atom and a HH structure if both C\textsubscript{60} and tube use the hexagon.
Figure S2. Computed band structures of C$_{60}$@CNT and C$_{60}$@BNNT peapods.