Supporting Information

Metal-semiconductor transition like behavior of naphthalene-doped single wall carbon nanotube bundles

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1. Molecular simulation of partial intercalation model of DNN molecules

Six (12,10) semiconductive SWCNTs of tube diameter D of 1.495 nm were used. The simulation cell of L_x = L_y = 5.86284 nm and L_z = 4.06378 nm was used, as shown in Fig S1. Here SWCNTs are arranged in parallel to the zx plane and the tube axis is parallel to z-axis. (12,10) SWCNTs of tube diameter of 1.495 nm were used. We used the intertube distances of 0.364 nm and 0.65 nm for the original bundle and for a pried interstice for a DNN molecule. Here, 0.364 nm was adopted from the X-ray diffraction result. The interaction between a carbon atom in SWCNT and a DNN molecule was modeled by Lennard-Jones potential. The interaction parameters were obtained from universal force field[1]. Geometric optimization of a DNN molecule was performed by DFT calculation using generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional and double-numerical pluspolarization (DNP) basis set with DMol^3 software package[2,3]. The interaction between DNN molecules treated as rigid bodies was evaluated by summation of Lennard-Jones potential and Coulombic potential using atomic partial charges from Mulliken population analysis of the DFT calculation results. GCMC simulation was carried out at T = 298.15 K and μ/k = −13986 K. The step numbers for equilibration and ensemble averaging were 1 × 10^7 MC and 1 × 10^7 MC steps, respectively. The snapshot was obtained after 2 × 10^7 MC steps.

References

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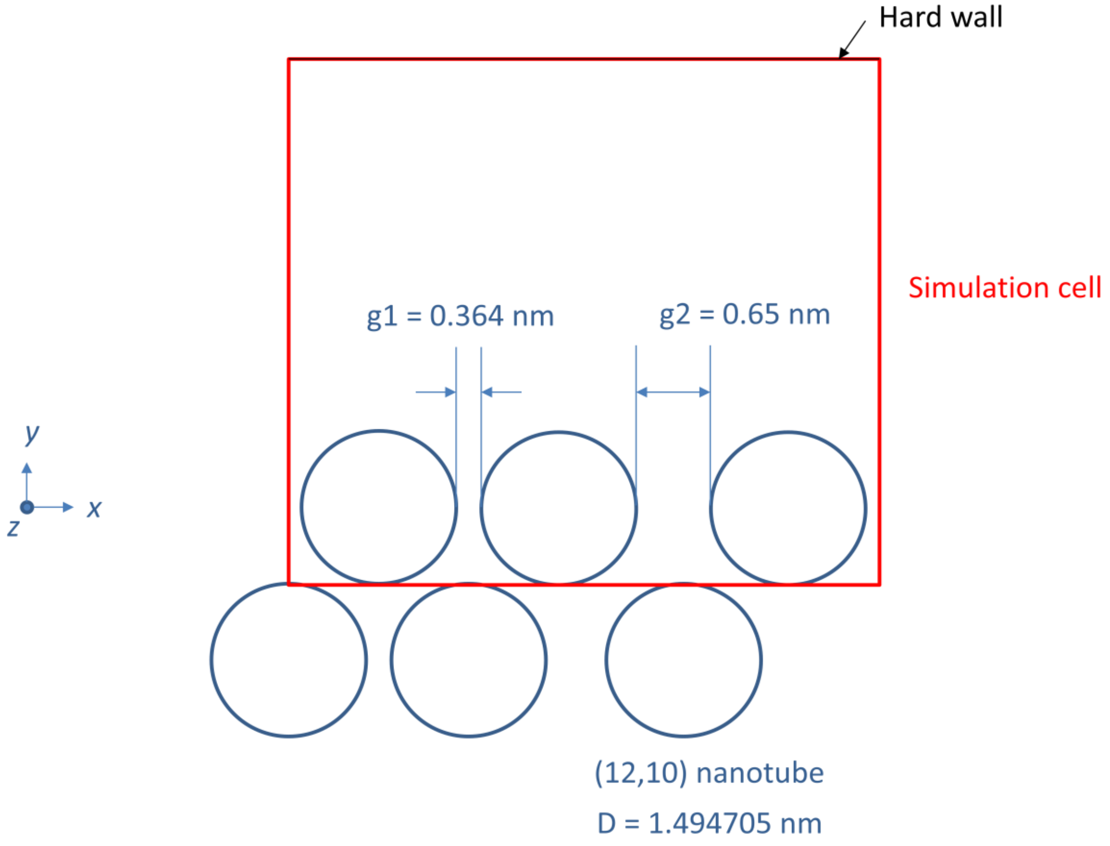

Fig. 1S Simulation cell. The periodic boundary conditions were employed to the directions of x and z-axes. The upper wall along y-axis is a hard wall. We used the diameter of SWCNT and intertube distances from the experimental structural data.

2. Raman Spectroscopic Data

Fig 2S shows RBM and G bands determined by excitation with 532 nm and 785 nm. The frequency shift of RBM and G-bands by the adsorption treatment is not remarkable; the higher frequency shifts of RBM by 532 nm and 785 nm are in the range of 2 – 6 cm^{-1} and 1-8 cm^{-1}, respectively. On the other hand, the higher frequency shift of the G^+-band by 532 nm is only 1.6 cm-1 for N- and DHN-SWCNT, whereas no shift of the G^+-band by 785 nm is found.

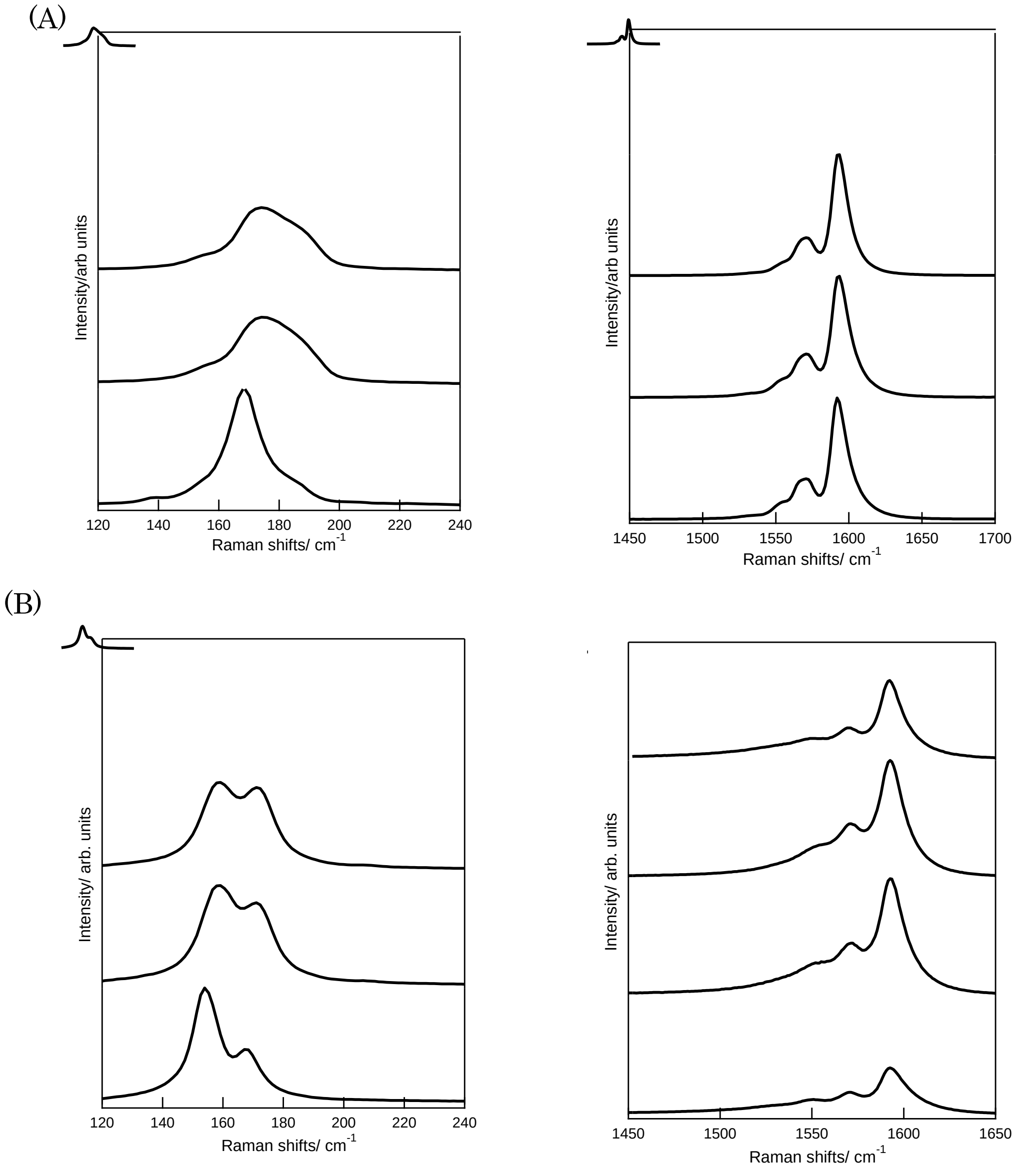

Fig. 2S The RBM and G-bands obtained by excitation with 532 nm (A) and 785 nm (B) for SWCNT, N-SWCNT, DHN-SWCNT and DNN-SWCNT.

3. Computation of the density of state of SWCNT and the energy diagram of naphthalene and ND molecules.

The preliminary computation of the density of the state (DOS) of the semiconductive (17,0) SWCNT and the electronic structure of naphthalene, DNN, and DHN molecules were carried out, as shown in Fig. 3S. The computation of the (12,10) chiral SWCNT needs more calculation time than that of the (17,0) SWCNT and the DOS is not sensitive to the slight change in the tube diameter for semiconductive SWCNTs from the general theory.[1] Accordingly the obtained results can be helpful to understand the electrical conductivity of the naphthalene- or ND-adsorption treated SWCNTs.

The DOS of the SWCNT and electronic structure of naphthalene and ND molecules were computed using *ab initio* density functional theory, as implemented in the SIESTA code[2]. We used the Perdew-Burke-Ernzerhof exchange-correlation functional[3] with norm-conserving Troullier-Martins pseudopotentials[4] and a double-ζ basis including polarization orbitals. We used a mesh cutoff energy of 180 Ry to determine the self-consistent charge density. We used a mesh cutoff energy of 180 Ry to determine

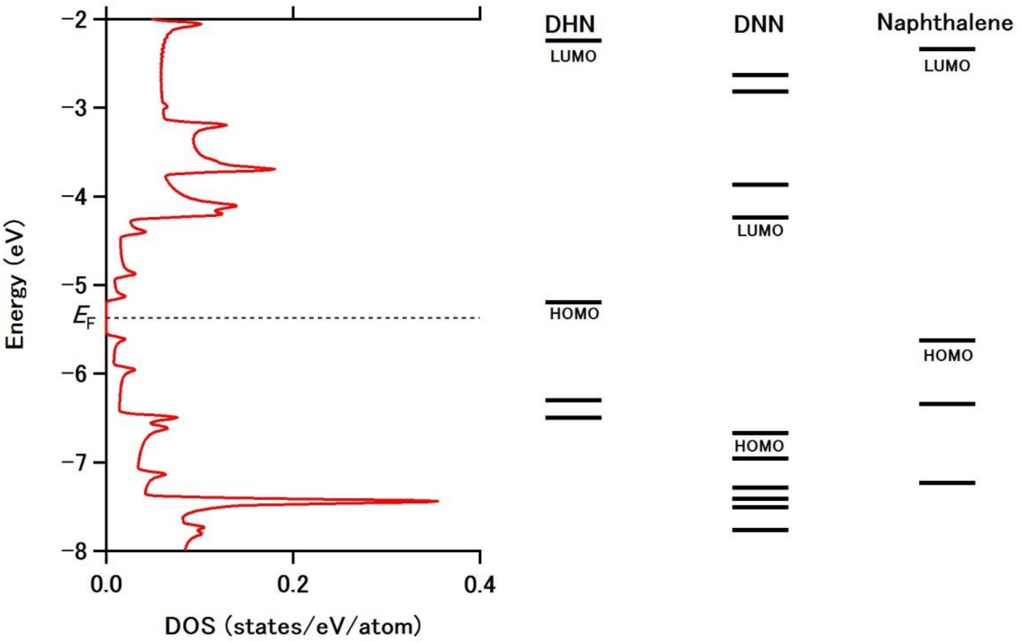

Fig. 3S The density of state of (17,0) SWCNT and energy diagram of naphthalene, DNN, and DHN molecules. Here HOMO and LOMO are the highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively.

the self-consistent charge density. We used periodic boundary conditions in all directions and separate the structures by 1 nm to prevent them for interacting with each other. The Brillouin zone of (17,0) SWCNT was sampled by 100-k points and that of the molecules by a 1×1×1 k-point grid.

According to Fig. 3S, the HOMO level of DHN is slightly higher than the Fermi level of the SWCNT, whereas the HOMO levels of naphthalene and DNN are lower than the Fermi level. This indicates that DHN can work as an electron donor to the SWCNT, while naphthalene and DNN should be electron acceptors against the SWCNT. The LUMO level of DNN is closer to the Fermi level of the SWCNT than that of naphthalene and DNN can work as a stronger acceptor for the SWCNT than naphthalene, although we cannot conclude this precisely without evaluation of the orbital overlapping.

References

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