Selection of Single-Walled Carbon Nanotubes According to Both Their Diameter and Chirality via Nanotweezers

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Received: 19 January 2010 / Accepted: 12 February 2010

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ABSTRACT

Diameter- and chirality-dependent interactions between aromatic molecule-based nanotweezers and single-walled carbon nanotubes (SWNTs) are revealed by density functional theory calculations. We found that the threshold diameter of selected SWNTs is determined by the end-to-end distance of the nanotweezer. Large-diameter SWNTs are preferred by a nanotweezer with an obtuse folding angle, whereas small-diameter SWNTs are favored by a nanotweezer with an acute folding angle. The adsorption can be further stabilized by the orientational alignment of the hexagonal rings of the nanotweezer and the SWNT sidewall. Therefore, by taking advantage of the supramolecular recognition ability of the aromatic molecule-based nanotweezer, SWNTs can be enriched with both controllable diameter and chirality.

KEYWORDS

Carbon nanotubes, nanotweezer, selective adsorption, density functional theory

1. Introduction

The electronic properties of single-walled carbon nanotubes (SWNTs) depend strongly on their diameters and chiralities, which are defined by the chiral indices n and m : for example, when the difference between n and m is divisible by 3, i.e., $n-m=3k$ (where k is an integer), the SWNTs are metallic, whilst the remainder (i.e., $n-m \neq 3k$) is semiconducting. Also, the band gap of semiconducting SWNTs is approximately inversely proportional to their diameter. SWNTs are

typically grown as mixtures of tubes with various chiralities in a certain diameter distribution. Thus, it is desirable to devise strategies to separate SWNTs according to their electronic type, diameter or chirality for the sake of their broad technological applications.

The early work on separating SWNTs focused mainly on separating metallic nanotubes from semiconducting nanotubes or *vice versa* [1–10]. Recently, Chen et al. found that the diameter of the nanotubes significantly affects the on-current of carbon nanotube field-effect transistors (CNTFETs), and the on-current of the

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CNTFET can differ by up to five orders of magnitude depending on the band gap of SWNTs [11]. Consequently, it is widely accepted that it is important to separate nanotubes with different diameters. Arnold et al. demonstrated a diameter-sensitive separation scheme by means of density gradient ultracentrifugation in combination with appropriate surfactants [12, 13]. Tromp et al. developed an alternate and controllable approach by utilizing the size match between SWNTs and a so-called aromatic molecule-based nanotweezer [14], which is an anchor molecule with two planar arms (as illustrated in Fig. 1). They found that the nanotweezer constructed from a pentacene–maleimide adduct preferred to interact with SWNTs with a diameter smaller than the end-to-end distance of the nanotweezer. In addition, a combined separation of SWNTs according to both electronic type and diameter has also been reported by several groups [15–18].

On the other hand, separating SWNTs according to their chirality is a more difficult task, and little progress has been made until recently [19]. Experimentally, Nicholas et al. and Chen et al. reported that fluorine-based polymers with different structures are capable of preferentially wrapping SWNTs with high chiral angles ($\theta > 24.5^\circ$) or certain diameters [20, 21]. Lu et al. [22, 23] predicted theoretically that certain planar aromatic molecules can selectively interact with armchair ($\theta = 30^\circ$) or zigzag ($\theta = 0^\circ$) SWNTs depending on the structural compatibility between them, by using density functional theory (DFT) calculations. Later Meunier et al. confirmed that a pentacene-based amphiphile can selectively solubilize armchair SWNTs, whereas a quaterrylene-based amphiphile can selectively solubilize zigzag SWNTs as a result of structural compatibility [24]. Furthermore, Komatsu et al. found that left- or right-handed helical SWNTs

Figure 1 Optimized structures of (a) anthracene-, (b) pentacene-, and (c) heptacene-based nanotweezers and hypothetical (d) quaterrylene- and (e) hexarylene-based nanotweezers. Gray ball: C; white ball: H; blue ball: N; red ball: O. The end-to-end distance and the angle between the two arms of the nanotweezers are labeled

can be extracted by using chiral diporphyrin nanotweezer isomers [25, 26]. Simultaneous enrichment of optical purity and abundance of specific indices of SWNTs was achieved by the same group using improved chiral diporphyrin nanotweezer isomers [27]. Very recently, Zheng et al. demonstrated that short DNA sequences enable chromatographic purification of SWNTs with a specific chirality [28].

So far, controlling both the diameter and chirality of separated SWNTs remains a big challenge. In this study, we study the interactions of three real anthracene-, pentacene-, and heptacene-based, and two hypothetical quaterrylene- and hexarylene-based nanotweezers with armchair SWNTs and zigzag SWNTs in a large diameter range, by using the DFT method. We find that the aromatic molecule-based nanotweezers are capable of recognizing not only the diameter but also the chirality of SWNTs. Based on our study, an efficient approach is proposed to separate SWNTs with both controllable diameter and chirality. In conventional separation schemes, the chirality and diameter of the enriched SWNTs are very difficult to predict.

2. Results and discussion

The anthracene-, pentacene-, and heptacene-based nanotweezers we chose to study are Diels–Alder adducts of fused-ring aromatic hydrocarbons and maleimide with chemical formulae $C_{18}H_{13}NO_2$, $C_{26}H_{17}NO_2$, $C_{34}H_{21}NO_2$. They all have the shape of a folded ribbon. Their attraction with SWNTs arises from the π – π stacking interactions between the nanotweezer arms and SWNT sidewalls. We consider the zigzag ($n,0$) ($n = 8$ – 26) and armchair (n,n) ($n = 4$ – 15) SWNTs with diameters $d = 6$ – 20 Å. The periodicities of the zigzag and armchair SWNTs are 4.25 Å and 2.45 Å, respectively. In our supercell model, we construct two supercells with sizes of 60 Å $\times$ 60 Å $\times$ 12.76 Å and 60 Å $\times$ 60 Å $\times$ 12.25 Å for the zigzag SWNTs and armchair SWNTs, respectively. Geometry optimization is performed for atomic positions. The adsorption energy of the molecule-based nanotweezers on SWNTs is defined as

$$E_{\text{ad}} = E(\text{SWNT}) + E(\text{molecule}) - E(\text{SWNT} + \text{molecule}) \quad (1)$$

We show the optimized structures of the three nanotweezers in Figs. 1(a), 1(b), and 1(c), in which the optimized end-to-end outer hydrogen atom distances of the anthracene-, pentacene-, and heptacene-based nanotweezers are 8.42, 12.79, and 17.19 Å, respectively, with optimized folding angles of 124.2° , 126.6° , and 126.9° , respectively. Experimentally, the end-to-end outer carbon atom distance of the pentacene-based nanotweezer determined by X-ray diffraction is 11 Å [14], which is in good agreement with our calculated C–C distance of 11.18 Å, and the measured folding angle is also only 0.1° smaller than the one calculated.

In our model, we set the vertex line of the nanotweezers parallel to the tube axis, and two arms wrap around the SWNTs, so as to maximize the effective contact area between the nanotweezers and SWNTs. Two symmetrical configurations are constructed for the anthracene-based nanotweezer adsorbed on the (5,5) SWNT: the center of the middle hexagon of the nanotweezer lies above (I) the midpoint of a C–C bond that is perpendicular to the tube axis (Fig. 2(a)) and (II) the center of a hexagon on the tube (Fig. 2(b)). Similarly, two symmetrical configurations are constructed for the anthracene-based nanotweezer adsorbed on the (8,0) SWNT: the center of the middle hexagon of the nanotweezer lies above (I) the midpoint of a C–C bond that is parallel to the tube (Fig. 2(c)) and (II) the center of a hexagon on the tube (Fig. 2(d)). The favorable configurations of the anthracene-based nanotweezer on both the (5,5) and (8,0) SWNTs have the center of the middle hexagon of the nanotweezers above the center of a hexagon of the tube, and the unfavorable orientations are 0.07 and 0.02 eV higher in total energy, respectively. The adsorption configurations of the three real nanotweezers on all the other armchair and zigzag SWNTs are taken from the favorable orientations found for the anthracene-based nanotweezer on the (5,5) and (8,0) SWNTs, respectively.

Based on the optimized structures, both the folding angle of the three nanotweezers on the sidewall of SWNTs and the aspect ratio between the major and minor axes of the nanotubes show a general increase with the tube diameter. For example, in the optimized structures of the pentacene-based nanotweezers adsorbed on the (6,6) and (13,13) SWNTs, shown in

Figure 2 Constructed symmetrical adsorption configurations of the anthracene- and quaterrylene-based nanotweezers on the sidewall of the (5,5) and (8,0) SWNTs. The center of the middle hexagon of the anthracene-based nanotweezer lies above (a) the midpoint of a C–C bond that is perpendicular to the (5,5) tube axis, (b) the center of a hexagon on the (5,5) tube, (c) the midpoint of a C–C bond that is parallel to the (8,0) tube, and (d) the center of a hexagon on the (8,0) tube. The center of the middle hexagon of the quaterrylene-based nanotweezer lies above (e) the midpoint of a C–C bond that is perpendicular to the (5,5) tube axis, (f) the center of a hexagon on the (5,5) tube, (g) the midpoint of a C–C bond that is parallel to the (8,0) tube, and (h) the center of a hexagon on the (8,0) tube. Gray ball: C; white ball: H; blue ball: N; red ball: O

Figs. 3(a) and 3(b), respectively, we noticed that the folding angle of the pentacene-based nanotweezer is increased from 124.1° on the (6,6) SWNT to 133.7° on the (13,13) SWNT. The aspect ratio of the SWNT is also increased from 1.00 for the (6,6) SWNT to 1.05 for the (13,13) SWNT.

From the adsorption energies of the anthracene-, pentacene-, and heptacene-based nanotweezers on the sidewall of the SWNTs expressed as a function of the tube diameter shown in Fig. 4(a), we deduced three major features. (1) The larger the size of the nanotweezer, the larger the value of E_{ad} as a result of the increasing contact area. (2) The E_{ad} values of the three nanotweezers for the same chirality SWNTs show a general increase with the diameter (d) and nearly saturate when d reaches the end-to-end distance (d_{end}) of the nanotweezers ($d_{\text{end}} = 8.42 \text{ \AA}$, $12.79 \text{ \AA}$, and $17.19 \text{ \AA}$ for the anthracene-, pentacene-, and heptacene-based nanotweezers, respectively). The reason lies in the fact that the effective contact area scales with increasing d at $d < d_{\text{end}}$. In contrast, when $d_{\text{end}} < d < 20 \text{ \AA}$, the nano-

tweezer folding angle is expanded with increasing d , and hence the two arms of the nanotweezers are approximately parallel to the tube sidewall. As a result, the effective contact area and thus E_{ad} remains unchanged at $d_{\text{end}} < d < 20 \text{ \AA}$. (3) The three aromatic molecule-based nanotweezers show the same clear chirality recognition ability as their planar counterparts [22–24]. When $d > 8 \text{ \AA}$, the E_{ad} values of the nanotweezers on the zigzag SWNTs are always larger than those on the similar-diameter armchair SWNTs by about 0.03–0.10 eV, 0.03–0.13 eV, and 0.04–0.16 eV for the anthracene-, pentacene-, and heptacene-based nanotweezers, respectively.

We noticed an agreement with the experimental result obtained in toluene as a solvent, where the threshold diameter of SWNTs for the pentacene-based nanotweezer supramolecular recognition is about $13 \text{ \AA}$ [14]. Yet instead of $d > 12.79 \text{ \AA}$ as observed theoretically, experimentally it was found that $d < 12.79 \text{ \AA}$. We tentatively ascribe this discrepancy to a toluene solvent effect in the experiment, since a gas phase model is

Figure 3 Optimized structures of (a) the pentacene-based nanotweezer on the (6,6) SWNT, (b) the pentacene-based nanotweezer on the (13,13) SWNT, (c) the hexarylene-based nanotweezer on the (6,6) SWNT, (d) the hexarylene-based nanotweezer on the (8,8) SWNT, and (e) the hexarylene-based nanotweezer on the (12,12) SWNT. Gray ball: C; white ball: H; blue ball: N; red ball: O. The angles between the two arms of the nanotweezers are labeled

Figure 4 Calculated adsorption energies (E_{ad}) of (a) anthracene-, pentacene-, and heptacene-based nanotweezers and (b) quaterylene- and hexarylene-based nanotweezers on the sidewall of the armchair (red circles) and zigzag (blue stars) SWNTs as a function of the tube diameter. The end-to-end distances of the nanotweezers are indicated by vertical dotted lines

used in our calculations. Nicholas et al. reported that different solvents may lead to a reversal of the preference of polymers towards small- and large-diameter SWNTs [29]. For example, the polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEHPPV) shows a preference for larger diameter SWNTs in tetrahydrofuran (THF) as a solvent, but a preference for smaller diameter SWNTs in toluene as a solvent.

The calculated selectivities of the three nanotweezers for the zigzag tubes *versus* the armchair tubes are attributed to the fact that the hexagonal carbon ring of the three nanotweezers is identical with (matches) that on the zigzag tube sidewall. Our previous calculations [22, 23] demonstrate that the alignment between the hexagonal ring of planar aromatic molecules and that of SWNTs can stabilize the adsorption (by atomic correlation effects). Since the hexagonal rings of the anthracene-, pentacene-, and heptacene-based nanotweezers are aligned with those on the sidewall of zigzag SWNTs, these three molecules all prefer to attach to the zigzag SWNTs.

In order to corroborate the atomic correlation between the nanotweezers and SWNTs, we design two nanotweezers, which are Diels–Alder adducts formed by addition reactions of the central hexagonal ring of quaterylene and hexarylene with two maleimide groups. The chemical formulae of the two hypothetical nanotweezers are $C_{48}H_{26}N_2O_4$ and $C_{68}H_{34}N_2O_4$, respectively. The optimized structures of the two nanotweezers are shown in Figs. 1(d) and 1(e), respectively. It turns out that the end-to-end distance of the outer hydrogen atoms of the quaterylene- and hexarylene-based nanotweezers are 9.82 and 14.21 Å, with acute folding angles of 62.8° and 65.1°, respectively. We noticed that the two proposed nanotweezers have identical hexagonal carbon ring configurations to those of armchair SWNTs when their two arms wrap around the SWNTs. In our calculations, two symmetrical configurations are considered for the quaterylene-based nanotweezer adsorbed on the (5,5) SWNT: the center of the nanotweezer middle hexagon is (I) above the midpoint of a C–C bond perpendicular to the tube (Fig. 2(e)) and (II) above the center of a hexagon on the tube (Fig. 2(f)). Likewise, two symmetrical configurations are considered for

the quaterylene-based nanotweezer adsorbed on the (8,0) SWNT: the center of the nanotweezer middle hexagon is (I) above the midpoint of a C–C bond parallel to the tube (Fig. 2(g)) and (II) above the center of a hexagon on the tube (Fig. 2(h)). The favorable configurations of the quaterylene-based nanotweezer on both the (5,5) and (8,0) SWNTs have the center of the nanotweezer middle hexagon lying above the midpoint of a C–C bond of tube, namely Scheme (I), which are lower in total energy by about 0.16 eV and 0.003 eV (within calculation accuracy), respectively, than of the corresponding configurations in Scheme (II). The adsorption configurations of the two proposed nanotweezers on all the examined armchair and zigzag SWNTs are taken from the favorable configurations, Scheme (I).

The folding angle of the two nanotweezers on the sidewall of the SWNTs initially decreases with increasing tube diameter for $d < d_{\text{end}}$ and then increases for $d > d_{\text{end}}$, while the deformation degree of the nanotubes always increases with increasing d . The optimized structures of the quaterylene-based nanotweezers adsorbed on the (6,6), (8,8), and (12,12) SWNTs are shown in Figs. 3(c), 3(d), and 3(e), respectively. The optimized folding angle of the quaterylene-based nanotweezer decreases from 76.7° on the (6,6) SWNT to 60.7° on the (8,8) SWNT, and then increases to 65.9° on the (12,12) SWNT. The aspect ratio of the SWNT increases from 1.01 for the (6,6) SWNT to 1.03 for the (8,8) SWNT, and then to 1.06 for the (12,12) SWNT.

We present the adsorption energies of quaterylene- and hexarylene-based nanotweezers on the sidewall of SWNTs as a function of their tube diameter in Fig. 4(b). Three major features are apparent. (1) The adsorption energy is proportional to the nanotweezer size. (2) In contrast to the nanotweezers with an obtuse angle, the nanotweezers with an acute angle prefer wrapping strongly the smaller-diameter SWNTs, and the adsorption energies initially decrease significantly with d and then change slightly when d approaches d_{end} ($d_{\text{end}} = 9.84$ and 14.21 Å for the quaterylene- and hexarylene-based nanotweezers, respectively). As apparent from Figs. 3(c) and 3(d), in the acute folding angle case, the effective contact area between the two nanotweezers and SWNTs scales down approximately with d when $d < d_{\text{end}}$ and thus results in a reduction

of E_{ad} with increasing d . But, when $d_{\text{end}} < d < 20 \text{ \AA}$, the effective contact area is mainly confined between the SWNTs and the ends of the two arms of the nanotweezers, and hence the effective contact area and thus E_{ad} remains nearly constant. (3) As expected, the two proposed nanotweezers are selectively adsorbed on the armchair SWNTs as a result of the alignment of the hexagonal rings. The adsorption energies on the armchair SWNTs are larger than those on similar-diameter zigzag SWNTs by about 0.11–0.15 eV for the quaterrylene-based nanotweezer at $6 \text{ \AA} < d < 8 \text{ \AA}$ and by about 0.01–0.21 eV for the hexarylene-based at $6 \text{ \AA} < d < 12 \text{ \AA}$. We attribute the absence of recognition towards the chirality of the SWNTs with large diameter to the fact that the effective contact area between the quaterrylene- and hexarylene-based nanotweezers and SWNTs is so small that the nanotweezers are unable to distinguish the chirality of the SWNTs.

Finally, we examined the effects of the adsorption of the nanotweezers on the electronic structure and transport properties of the SWNTs. The calculated electronic band structures of the pure (6,6) and (13,13)

SWNTs and their complexes with the pentacene-based nanotweezer are displayed in Figs. 5(a)–5(d), respectively. The band structures near the Fermi level of the SWNTs are only slightly affected by the adsorption of the pentacene-based nanotweezer. We use the pure SWNT (6,6) and (13,13) as the metal electrodes, which are coupled to their respective complexes with the pentacene-based nanotweezer. The two-probe model of the (6,6) SWNT case is shown in Fig. 6(a). As shown in Figs. 6(b) and 6(c), the quantum conductance of the pure SWNTs is only slightly influenced by the pentacene-based nanotweezer. There are only a few dips 0.5 eV away from the Fermi level caused by the scattering of the adsorbed nanotweezer. For examples, the conductance of the (6,6) SWNT is decreased from $2G_0$ to G_0 ($G_0 = 2e^2/h$) at $E = -0.83 \text{ eV}$ and $E = 0.89 \text{ eV}$, and that of the (13,13) SWNT is decreased from $2G_0$ to G_0 at $E = -0.69 \text{ eV}$ due to adsorption by the pentacene-based nanotweezer. It appears that the electronic and transport properties of the wrapped SWNTs, at least the wrapped armchair SWNTs, are merely slightly affected by the adsorbed nanotweezers.

Figure 5 Electronic structures of (a) the pure (6,6) SWNT, (b) the (6,6) SWNT with the pentacene-based nanotweezer adsorbed on its sidewall, (c) the pure (13,13) SWNT, and (d) the (13,13) SWNT with the pentacene-based nanotweezer adsorbed on its sidewall. The Fermi level is set to zero

Figure 6 (a) Two-probe model of the pentacene-based nanotweezer adsorbed on the sidewall of the (6,6) SWNT. Gray ball: C; white ball: H; blue ball: N; red ball: O. The quantum conductance of the (b) (6,6) and (c) (13,13) SWNTs before and after adsorption of the pentacene-based nanotweezer

3. Conclusions

We have revealed a diameter- and chirality-dependent interaction between aromatic molecule-based nanotweezers and SWNTs in the diameter range 6–20 Å by using density functional theory calculations. We found that the interaction between the aromatic molecule-based nanotweezers and SWNTs depends mainly on three factors: the end-to-end distance, the folding angle of the nanotweezers, and the atomic correlation between the nanotweezers and SWNTs. Nanotweezers with obtuse folding angles selectively interact with SWNTs with diameters greater than their end-to-end distance, whereas nanotweezers with acute folding angles preferentially attract SWNTs with diameter smaller than their end-to-end distance. The atomic correlation, namely the alignment of the hexagonal rings, results in the aromatic molecule-based nanotweezers adsorbing more favorably on SWNTs with an identical configuration of hexagonal carbon rings. Such a supramolecular recognition enables us to perform controllable separation of SWNTs according to both their diameters and chiralities by choosing an appropriate aromatic molecule-based nanotweezer.

4. Computational Methods

The attraction between nanotweezers and SWNTs arises from the π - π stacking interactions between the nanotweezer arms and SWNT sidewalls. A local or even semilocal density functional is in principle not capable of describing the attraction due to dispersion, and one would expect to find little or no binding for the π - π stacking interaction system. The use of more reliable methods, such as many-body perturbation theory is surely desirable, but the extremely high computational cost makes it impossible to apply these methods to systems of large size such as the SWNT–nanotweezer complex. On the other hand, in the minimum energy configuration the charge clouds overlap and it turns out that the local density approximation (LDA) provides an attraction. Namely, the LDA is fortuitously more suitable than the generalized gradient approximation (GGA) for the

study of the π - π stacking interaction system [30, 31]. For example, two parallel benzene molecules are unbounded using the GGA, whereas the LDA results are in good agreement with high level quantum chemistry calculations [31]. A review of the applicability of the LDA for describing dispersion-dominated weak interactions can be found in Ref. [32]. In fact, the LDA has been widely used to study the π - π stacking interaction between molecules and SWNTs [31, 33, 34] and in other large systems [30, 35]. We use the LDA to study the interaction between aromatic molecule-based nanotweezers and SWNTs, inspired by the fact that the our previous LDA calculations [22, 23] correctly predicted the selectivity of planar aromatic molecules towards SWNTs [24].

Geometry optimization is performed for atomic positions by using an all electron double numerical atomic orbital basis set plus polarization (DNP) implemented in DMol³ package [36] with two k points. It is known that the DMol³ package does not implement correction for basis set superimposition error (BSSE), which will consequently cause an overestimate of the adsorption energy. However, we have checked the differences in adsorption energy obtained using the atomic orbital basis set implemented in the DMol³ package and the plane-wave basis set implemented in the CASTEP [37] package in our former studies [38, 39], and found that the adsorption energy differences for both naphthalene and NO₂⁺ on similar-diametered metallic and semiconducting SWNTs calculated using the two different basis sets are similar. Hence, we expect the inclusion of a correction for BSSE in DMol³ will not significantly change our calculated relative adsorption energies of the nanotweezers on SWNTs, and the main conclusions of this paper would not be affected.

We performed the transport calculations based on DFT and nonequilibrium Green's function method combined in the code SMEAGOL [40, 41]. Norm-conserving pseudopotentials of the Troullier-Martins type and a mesh cutoff of 200 Ry are adopted. The single- ζ plus polarization basis set (SZP) and the single- ζ basis set (SZ) are employed for the (6,6) and (13,13) SWNTs, respectively.

Acknowledgements

This work was supported by the the National Natural Science Foundation of China (NSFC) (Nos. 10774003, 10474123, 10434010, 90626223, and 20731162012), the National Basic Research Program of China (973 Program) (Nos. 2002CB613505 and 2007CB936200, MOST of China), the Program for New Century Excellent Talents in University of Ministry of Education of China, National Foundation for Fostering Talents of Basic Science (No. J0630311), and Nebraska Research Initiative of USA (No. 4132050400). We thank R. M. Tromp and A. Afzali for helpful discussions of solvent effects.

Electronic Supplementary Material: Tabulated data of the adsorption energy of the anthracene-, pentacene-, heptacene- quaterrylene-, and hexarylene-based nanotweezers on the sidewalls of the armchair and zigzag SWNTs are available in the online version of this article at <http://dx.doi.org/10.1007/s12274-010-1033-1> and are accessible free of charge.

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