Derivation of the linear relationship between SWCNTs functionalization energies and sidewall curvature

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Abstract A simple linear relationship between the functionalization reaction energies for the exohedral monovalent addition on the surface of an ideal, infinitely long, single-walled carbon nanotube (SWCNT) and the reciprocal SWCNT radius has been derived employing the hard-soft acid basis principle and the tight binding model. The slope of the derived linear relationship is a function of the effective number of valence electrons involved in the functionalization reaction. The intercept of the derived linear relationship, equal to the reaction energies on a planar graphite surface, is a function of the electrophilicity of the monovalent addend and of the condensed Fukui function of its reacting atom. The theoretical predictions of this simple formula are coherent with the computational density functional theory data reported in the literature.

Keywords SWCNT · Functionalization energies · Hardness · Radius of a nanotube

Introduction

The great interest in carbon nanotubes has been in large due to their unique electronic properties, predicted to be either metallic or semiconducting depending upon the diameter and helicity of the tubes [1, 2]. These remarkable mechanical, electronic and structural properties make carbon nanotubes the most promising candidates for the building blocks of molecular-scale machines and nanoelectronic devices [3–6].

A single-walled carbon nanotube (SWCNT) is usually described as rolled graphene, where the hexagonal, two-dimensional lattice is mapped on a cylinder of radius R with various helicities characterized by a set of two integers (n, m) . The electronic structure of SWCNTs can be either metallic or semiconducting depending upon the chiral vector (n, m) [7]. Therefore, electronic properties of SWCNTs can, at first order, be deduced from that of graphene by mapping the band structure of a two-dimensional hexagonal lattice on a cylinder [2, 8–12]. Such analysis indicates that the (n, n) armchair nanotubes are always metallic and exhibit one-dimensional quantum conduction [13, 14]. The $(n, 0)$ zigzag nanotubes are generally semiconductors; but, if n is an integer multiple of three, they are metallic.

One of the problems that synthetic chemistry faces is the solubility of nanotubes. Solubility can be obtained by functionalization of these materials through attachment of oxidized, polar groups to the graphene surfaces.

The functionalization reaction energy ΔE (equivalent to the negative binding energy of the reactants A) is defined as

$$\Delta E(A\text{-SWNT}) = E(A\text{-SWNT}) - E(\text{SWNT}) - E(A). \quad (1)$$

The functionalization reaction energy versus the reciprocal SWCNT radius ($1/R$, measuring sidewall curvature) was found to fit the linear equation

$$\Delta E = \Delta E_0 + C/R. \quad (2)$$

This is shown in calculations by Gulseren et al. [7] where $A = \text{H, Al}$; Zhao et al. [15] where $A = \text{NH}_2$; Park et al. [16] where $A = \text{F, OH, H, NH}_2, \text{CH}_3, \text{COOH}$; and Zheng et al. [17] and Wang et al. [18] where $A = \text{CH}_2, \text{NH, O}$.

It has been suggested [7, 15] that ΔE_0 is a quantity related solely to the adatom/electrophilic agent and corresponds to its reaction energy on a planar graphite surface ($1/R = 0$) and that C is apparently related to the tube chirality [7, 15].

This paper is devoted to Professor Malgorzata Witko.

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Zheng et al. and Wang et al. [17, 18] also suggested that the C term in the linear relationship depends not only on the nature of the binding interaction and tube chirality, but also on the isomer type (for divalent addends).

The aim of this paper is to derive the linear relationship described in Eq. 2 starting from the HSAB principle and the tight binding model.

Theoretical background

Hardness, softness and Fukui function

Hardness, softness and Fukui function are powerful tools to predict the reactivity site of a molecule [19]. Fukui function $f(\underline{r})$ [19–21] is defined as a derivative of electronic density $\rho(\underline{r})$ versus the total number of electrons N at constant external potential v generated by the nuclei. Thus,

$$f(\underline{r}) = \left(\frac{\partial \rho(\underline{r})}{\partial N} \right)_v. \quad (3)$$

According to the density functional theory (DFT) [22], the chemical potential μ [23], electronegativity χ [23, 24], hardness η [23, 25] and softness S [20, 23] of a chemical species can be represented by

$$\mu = -\chi = \left(\frac{\partial E}{\partial N} \right)_v, \quad (4)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_v = \left(\frac{\partial \mu}{\partial N} \right)_v, \quad (5)$$

and

$$S = \left(\frac{\partial N}{\partial \mu} \right)_v = \frac{1}{\eta}, \quad (6)$$

where E is the total electronic energy (the factor of 1/2 in the original definition of the global hardness has been omitted here for convenience). The Fukui condensed function f_i is obtained by integrating the Fukui function over the atomic volume of the i th atom [23], such that

$$\begin{aligned} f_i &= \iiint_{V_i} f(\underline{r}) d^3 \underline{r} = \iiint_{V_i} \left(\frac{\partial \rho(\underline{r})}{\partial N} \right)_v d^3 \underline{r} \\ &= \left(\frac{\partial \int_{V_i} \rho(\underline{r}) d^3 \underline{r}}{\partial N} \right)_v = \left(\frac{\partial q_i}{\partial N} \right)_v. \end{aligned} \quad (7)$$

As a result, the Fukui condensed function for the i th atom is equal to the derivative of the charge q_i of the i th atom with respect to the number of electrons.

Considering the variation in energy in frozen molecular orbitals (MOs) by the Koopmans theorem [23], in a finite difference approximation, we have the approximate expressions of Eqs. 4, 5 and 6, respectively:

$$\chi = -\mu \approx \frac{I + EA}{2}, \quad (8)$$

$$\eta \approx I - EA \quad (9)$$

and

$$S \approx \frac{1}{I - EA}, \quad (10)$$

where I and EA are the vertical ionization energy and the electroaffinity, respectively [23].

Local quantities

The site selectivity of a chemical system cannot, however, be studied by means of the global descriptors of reactivity (i.e. η and S). For this, appropriate local descriptors need to be defined. Local softness $s(\underline{r})$ is defined by [23]

$$s(\underline{r}) = \left(\frac{\partial \rho(\underline{r})}{\partial \mu} \right)_v = \left(\frac{\partial \rho(\underline{r})}{\partial N} \right)_v \cdot \left(\frac{\partial N}{\partial \mu} \right)_v = f(\underline{r}) \cdot S. \quad (11)$$

The condensed local s_i softness for the i th atom is defined as

$$\begin{aligned} s_i &= \iiint_{V_i} s(\underline{r}) d^3 \underline{r} = \iiint_{V_i} f(\underline{r}) \cdot S \cdot d^3 \underline{r} = S \iiint_{V_i} f(\underline{r}) d^3 \underline{r} \\ &= S \cdot f_i. \end{aligned} \quad (12)$$

Slope discontinuities occur because $\rho(\underline{r})$ is a function of N , thus, Eq. 3 provides the following three reaction indices [24]

$$f^-(\underline{r}) = \left(\frac{\partial \rho(\underline{r})}{\partial N} \right)_v^- \text{ (electrophilic attack)} \quad (13)$$

$$f^+(\underline{r}) = \left(\frac{\partial \rho(\underline{r})}{\partial N} \right)_v^+ \text{ (nucleophilic attack)} \quad (14)$$

and

$$f^\bullet(\underline{r}) = \frac{f^-(\underline{r}) + f^+(\underline{r})}{2} \text{ (radical attack)}. \quad (15)$$

The condensed local softness (Eq. 12) of atom, i , in a molecule is therefore defined as [25]

$$s_i^- = S \cdot f_i^- \text{ (electrophilic attack)} \quad (16)$$

$$s_i^+ = S \cdot f_i^+ \text{ (nucleophilic attack)} \quad (17)$$

and

$$s_i^\bullet = S \cdot f_i^\bullet \text{ (radical attack)}. \quad (18)$$

The local HSAB principle

The interaction energy between two chemical species A and B with the number of electrons N_A and N_B can be written within the framework of DFT [22] as

$$\Delta E_{\text{int}} = E[\rho_{\text{AB}}] - E[\rho_{\text{A}}] - E[\rho_{\text{B}}], \quad (19)$$

where ρ_{AB} , ρ_{A} and ρ_{B} are the electron densities of the systems AB at equilibrium and of the isolated systems A and B, respectively.

It has been shown by Gazquez and Mendez [26] that the interaction between A and B is assumed to take place in two steps. Initially, interaction will take place through the equalization of chemical potential at constant external potential. As A and B approach the equilibrium state through changes in the electron density of the global system, changes will be generated in the external potential at constant chemical potential. This step is actually a manifestation of the principle of maximum hardness [26]. Thus, the total interaction energy between A and B becomes [27]

$$\Delta E_{\text{int}} = \Delta E_{\text{v}} + \Delta E_{\mu}. \quad (20)$$

Following Gazquez and Mendez [27, 28], the expressions for each term in Eq. 20 can be written as

$$\Delta E_{\text{v}} \approx -\frac{1}{2} \frac{(\mu_{\text{A}} - \mu_{\text{B}})^2 S_{\text{A}} S_{\text{B}}}{S_{\text{A}} + S_{\text{B}}} \quad (21)$$

and

$$\Delta E_{\mu} \approx -\frac{1}{2} \frac{N_{\text{AB}}^2 k}{S_{\text{A}} + S_{\text{B}}} = -\frac{1}{2} \frac{N_{\text{e}}^2}{S_{\text{A}} + S_{\text{B}}} = -\frac{1}{2} \frac{\lambda}{S_{\text{A}} + S_{\text{B}}}, \quad (22)$$

where S_{A} and S_{B} are the values of the softness of the isolated systems A and B, respectively. N_{AB} is the total number of electrons of the system AB and k is the proportionality constant between S_{AB} (softness of the system AB at equilibrium) and $S_{\text{A}} + S_{\text{B}}$.

The product of the terms N_{AB}^2 and k is known as λ [26, 27] and can be interpreted as the effective number of valence electrons N_{e} [29] participating in the interaction between A and B ($\lambda = N_{\text{e}}^2$).

From a local point of view, if the interaction between two chemical systems A and B occurs through the i th atom of A, one can express the interaction by replacing the softness of A with the local softness of the site i in A [25, 27], thus

$$(\Delta E_{\text{int}})_{\text{Ai}} \approx -\frac{1}{2} \frac{(\mu_{\text{A}} - \mu_{\text{B}})^2 S_{\text{A}} f_{\text{Ai}} S_{\text{B}} + \lambda}{S_{\text{A}} f_{\text{Ai}} + S_{\text{B}}}, \quad (23)$$

where f_{Ai} is the condensed Fukui function of the site i in A.

Reaction energies for SWCNTs

In order to evaluate the reaction energy (Eq. 1) between a monovalent addend A (radical and electrophilic agent) and a SWCNT, we assume that the reaction energy $\Delta E(\text{A-SWNT})$ can be approximated by the interaction energy (Eq. 23). Where the chemical system B is a SWNT, it follows that

$$\Delta E(\text{A-SWNT})_{\text{Ai}} \approx -\frac{1}{2} \frac{(\mu_{\text{A}} - \mu_{\text{SWNT}})^2 S_{\text{A}} f_{\text{Ai}} S_{\text{SWNT}} + \lambda}{S_{\text{A}} f_{\text{Ai}} + S_{\text{SWNT}}}. \quad (24)$$

The length of the (n, m) SWCNTs is supposed to be infinite. The chemical potential, μ_{SWNT} , of an undoped, ideal, infinitely long SWCNT is zero [30, 31], as is that of undoped intrinsic graphene [32]. From Eq. 24, it follows

$$\Delta E(\text{A-SWNT})_{\text{Ai}} \approx -\frac{1}{2} \frac{\mu_{\text{A}}^2 S_{\text{A}} f_{\text{Ai}} S_{\text{SWNT}} + \lambda}{S_{\text{A}} f_{\text{Ai}} + S_{\text{SWNT}}}. \quad (25)$$

Replacing the variables softness (S_{A} , S_{SWNT}) with the multiplicative inverse of hardness (Eq. 6) it follows

$$\Delta E(\text{A-SWNT})_{\text{Ai}} \approx -\frac{1}{2} \frac{\mu_{\text{A}}^2 \frac{f_{\text{Ai}}}{\eta_{\text{A}}} + \lambda \eta_{\text{SWNT}}}{\frac{f_{\text{Ai}}}{\eta_{\text{A}}} \eta_{\text{SWNT}} + 1}, \quad (26)$$

where η_{A} and η_{SWNT} are the values of the hardness of the isolated systems A and SWCNT, respectively.

Semiconducting SWCNTs

The $(n, 0)$ zigzag nanotubes (where n is not a multiple of 3) are semiconductors [8, 33, 34]; their highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and energy band gap (E_{gap}) can be approximated in a tight binding model by the expression [8, 34]

$$E_{\text{gap}} = \frac{|V_{\text{pp}\pi}| a_{\text{cc}}}{R}. \quad (27)$$

This expression is also valid for chiral SWCNTs (n, m) with $n \neq m$ and $n - m \neq 3q$, where q is an integer not equal to zero [34], the carbon-carbon bond length $a_{\text{cc}} = 1.42 \text{ \AA}$ [35] and a Slater-Koster parameter [34] (hopping matrix element) $V_{\text{pp}\pi} \approx -2.7$ to -3 eV . According to Koopmans theorem [36], ionization energy is simply the negative HOMO energy. In molecules with coupled spins, such as SWCNTs, electron affinity is equal to the negative LUMO energy.

From Eqs. 9 and 27 it follows $\eta_{\text{SWNT}} \approx \frac{|V_{\text{pp}\pi}| a_{\text{cc}}}{R}$ with

$$|V_{\text{pp}\pi}| a_{\text{cc}} = 4.1 \pm 0.3 \text{ eV} \cdot \text{\AA}. \quad (28)$$

This is also valid when R tends to infinity, such as for graphene [37].

Inserting η_{SWNT} of Eq. 28 into Eq. 26 it follows

$$\Delta E(\text{A-SWNT})_{\text{Ai}} \approx -\frac{1}{2} \frac{\mu_{\text{A}}^2 \frac{f_{\text{Ai}}}{\eta_{\text{A}}} + \lambda \frac{|V_{\text{pp}\pi}| a_{\text{cc}}}{R}}{\frac{f_{\text{Ai}}}{\eta_{\text{A}}} \frac{|V_{\text{pp}\pi}| a_{\text{cc}}}{R} + 1} \quad (29)$$

Assuming $\frac{|V_{\text{pp}\pi}| a_{\text{cc}} f_{\text{Ai}}}{\eta_{\text{A}} R} < 1$, one can expand Eq. 29 into an asymptotic series in powers of $1/R$. Thus,

$$\Delta E(A\text{-SWNT})_{Ai} \approx -\frac{1}{2} \frac{\mu_A^2}{\eta_A} f_{Ai} - \frac{\left(\lambda - \left(\frac{\mu_A}{\eta_A}\right)^2 f_{Ai}^2\right) |V_{pp\pi}| a_{cc}}{2} \frac{1}{R} \sum_{j=0}^{\infty} \left(-\frac{|V_{pp\pi}| a_{cc} f_{Ai}}{\eta_A R}\right)^j. \quad (30)$$

In the case of $R \gg \frac{|V_{pp\pi}| a_{cc} f_{Ai}}{\eta_A}$, Eq. 30 can be approximated by the expression

$$\Delta E(A\text{-SWNT})_{Ai} \approx -\frac{1}{2} \frac{\mu_A^2}{\eta_A} f_{Ai} - \frac{\left(\lambda - \left(\frac{\mu_A}{\eta_A}\right)^2 f_{Ai}^2\right) |V_{pp\pi}| a_{cc}}{2} \frac{1}{R}. \quad (31)$$

Metallic SCWNTs

The (n, n) armchair nanotubes are metallic [8, 33, 34, 38] and the $(3n, 0)$ zigzag nanotubes are quasi-metallic [8, 32] due to a small band gap. The chemical hardness generally measures the energy required for the tube to store charge. For molecules such as nanotubes, this is dominated by the band gap (zero for metallic and negligible for quasi-metallic SWCNTs) and the charging energy, whilst the reorganization energy is minor [39]. In this approximation, by the cluster charging model, the hardness is proportional to $1/R$ [39, 40]. In our approximation model, we assume that the hardness of a metallic or quasi-metallic SWCNT can be expressed by the relationship

$$\eta_{\text{SWNT}} \approx \frac{\Theta}{R} \quad \eta_{\text{SWNT}} \approx \frac{\Theta}{R}, \quad (32)$$

where Θ is a constant to be derived. By means of the DFT data of hardness [39] for a finite section of the (5,5) metallic SWCNT with hydrogen termination at open ends and molecular formula $C_{10L}H_{20}$, where L is proportional to the length of the SWCNT section, the constant Θ has been evaluated. Fitting the data of hardness [39] with the exponential equation versus L gives

$$\eta(C_{10L}H_{20}) = \eta_{(5,5)\text{SWNT}} + B e^{-L/t}, \quad (33)$$

with B , t and $\eta_{(5,5)\text{SWNT}}$ fitting parameters (Fig. 1).

The radius of a (n, m) SWCNT can be calculated by the relationship [34]

$$R = \frac{a_{cc}\sqrt{3}}{2\pi} \sqrt{n^2 + m^2 + nm}. \quad (34)$$

The constant Θ has been estimated by Eqs. 32 and 34. Thus, by means of the value of the fitting parameter $\eta_{(5,5)\text{SWNT}} = 2.1 \pm 0.3$ eV it follows

$$\Theta \approx 7 \pm 1 \text{ eV} \cdot \text{\AA}. \quad (35)$$

Fig. 1 The DFT hardness, $\eta(C_{10L}H_{20})$, [39] for molecular models $C_{10L}H_{20}$ of SWCNTs, versus L fitted with the exponential equation: $\eta(C_{10L}H_{20}) = \eta_{(5,5)\text{SWNT}} + B e^{-L/t}$; $\eta_{(5,5)\text{SWNT}} = 2.1 \pm 0.3$ eV, $R = 0.93$ (the correlation coefficient.)

Utilizing Eq. 31 for metallic and quasi-metallic SWCNTs and the analogy between Eqs. 28 and 32, whilst assuming $R \gg \frac{\Theta f_{Ai}}{\eta_A}$, one can obtain

$$\Delta E(A\text{-SWNT})_{Ai} \approx -\frac{1}{2} \frac{\mu_A^2}{\eta_A} f_{Ai} - \frac{\left(\lambda - \left(\frac{\mu_A}{\eta_A}\right)^2 f_{Ai}^2\right) \Theta}{2} \frac{1}{R}. \quad (36)$$

It is known [41] that the hardness of molecules, atoms and radicals is proportional to its chemical potential. The constant of proportionality calculated for many atoms and molecules and [41] give rise to

$$\left|\frac{\eta_A}{\mu_A}\right| = \gamma = 1.6 \pm 0.3. \quad (37)$$

The condensed Fukui function $f_{Ai} \in [0, 1]$ (Eq. 7) follows that $\left(\frac{\mu_A}{\eta_A}\right)^2 f_{Ai}^2$ in Eqs. 31 and 36 can be replaced by K . Thus,

$$K = \left(\frac{\mu_A}{\eta_A}\right)^2 f_{Ai}^2 = \left(\frac{f_{Ai}}{\gamma}\right)^2 = 0.3 \pm 0.3. \quad (38)$$

Many chemical interactions involve fractional charge transfer processes. In this context, an electrophilicity index has been defined, which measures the energy change of an electrophile when it becomes saturated with electrons [42]. For this purpose, a chemical species immersed in an idealized bath of electrons with zero chemical potential is considered. Thus, the species will accept electrons until the point at which its chemical potential becomes equal to that of the bath [43].

The electrophilicity ω_A of a monovalent neutral addend A is defined as [42, 43]

$$\omega_A = \frac{1}{2} \frac{\mu_A^2}{\eta_A}. \quad (39)$$

Using Eqs. 31, 36, 38 and 39, where $\lambda = N_e^2$ [29], if $R \gg \frac{|V_{pp\pi}|a_{cc}f_{Ai}}{\eta_A}$ it follows for $(n, 0)$ zigzag SWCNTs and in general chiral SWCNTs (n, m) with $n \neq m$ and $n - m \neq 3q$ where q is an integer

$$\Delta E(A\text{-SWNT})_{Ai} \approx -\omega_A f_{Ai} - \frac{(N_e^2 - K)|V_{pp\pi}|a_{cc}}{2} \frac{1}{R}. \quad (40)$$

For (n, n) armchair SWCNTs and in general chiral SWCNTs (n, m) with $n - m = 3q$ where q is an integer.

If $R \gg \frac{\Theta f_{Ai}}{\eta_A}$ then

$$\Delta E(A\text{-SWNT})_{Ai} \approx -\omega_A f_{Ai} - \frac{(N_e^2 - K)\Theta}{2} \frac{1}{R}. \quad (41)$$

Equations 40 and 41, in our simplified model, are the expressions of the functionalization reaction energies for the semiconducting and metallic SWCNTs, respectively.

Computational methods

The only calculations performed in this paper are the condensed Fukui function for the monovalent addend A_i (OH, NH₂, CH₃ and COOH). In the case of a single atom (e.g. F and H), the condensed Fukui function is one by definition.

In order to calculate the condensed Fukui function, f_{Ai} , for reacting atom i of different monovalent addends A_i , we used a quantum mechanical approach. In particular, the hybrid density functional B3LYP method with a split valence basis set and d polarization function 6-31G(d) [44]. All calculations were performed by means of a Gaussian 03 software [45].

The condensed Fukui's function for radical attack was estimated by a finite difference approximation as shown by [46]

$$f_{Ai} = \left(\frac{\partial q_i}{\partial N} \right)_v \approx \frac{q_i(N+1) - q_i(N-1)}{2}. \quad (42)$$

The 'natural population analysis' (NPA) [47] charges q_i on the atom i of the monovalent addends A was calculated by adding or subtracting an electron ($N+1$, $N-1$) to the N electrons system the geometry of which was optimized by the DFT:B3LYP/6-31G(d) method. The NPA scheme for calculating the condensed Fukui's function has been found to be more appropriate than the 'atoms in molecules' (AIM) and Mulliken schemes [46].

Results

Linear relationship

A linear relationship between the functionalization reaction energies, ΔE , of SWCNTs (equivalent to the negative binding energy of the reactants) for monovalent addends A versus $1/R$ has been reported as fitting the equation of the calculations (this was not derived) by Gulseren et al. [7] for $A_i = \text{H}$, Al; Zhao et al. [15] for $A_i = \text{NH}_2$; and Park et al. [16] for $A_i = \text{F}$, OH, H, NH₂, CH₃, COOH. In these papers, the smallest radius SWCNTs used were (5,5) and (7,0).

In order to validate Eqs. 40 and 41, we verified the validity conditions of the equations such as

$$\begin{aligned} R_{(7,0)} = 2.7 \text{ \AA} &\gg \frac{|V_{pp\pi}|a_{cc}f_{Ai}}{\eta_A} \leq \frac{|V_{pp\pi}|a_{cc}}{\eta_{\min(\text{H,NH}_2,\text{F,OH,H,CH}_3,\text{COOH})}} \\ &= \frac{|V_{pp\pi}|a_{cc}}{\eta_{\text{COOH}}} = 0.5 \text{ \AA} \end{aligned} \quad (43)$$

and

$$\begin{aligned} R_{(5,5)} = 3.4 \text{ \AA} &\gg \frac{\Theta f_{Ai}}{\eta_A} \leq \frac{\Theta}{\eta_{\min(\text{H,NH}_2,\text{F,OH,H,CH}_3,\text{COOH})}} \\ &= \frac{\Theta}{\eta_{\text{COOH}}} = 0.7 \text{ \AA}, \end{aligned} \quad (44)$$

where $\eta_{\min(\text{H,NH}_2,\text{F,OH,H,CH}_3,\text{COOH})}$ is the minimum value of the hardness between the different addends A , which corresponds to the hardness of the COOH addend (9.42 eV Table II of [48]). In this table, the value reported is half of that expected due to a different definition of the hardness (Eq. 5). The values of hardness for the other addends A are calculated from Table 1 of [45] and from Table IV of [49], where $R_{(7,0)}$ and $R_{(5,5)}$ are the radii of the (5,5) and (7,0) SWCNTs.

It follows from Eqs. 2, 40 and 41 that

$$\Delta E_0 = -\omega_A f_{Ai}. \quad (45)$$

For $(n, 0)$ zigzag SWCNTs and in general chiral SWCNTs (n, m) with $n \neq m$ and $n - m \neq 3q$ where q is an integer,

$$C_{\text{semiconducting}} = -\frac{(N_e^2 - K)|V_{pp\pi}|a_{cc}}{2}. \quad (46)$$

For (n, n) armchair SWCNTs and in general chiral SWCNTs (n, m) with $n - m = 3q$ where q is an integer,

$$C_{\text{metallic}} = -\frac{(N_e^2 - K)\Theta}{2}. \quad (47)$$

Equation 45, in our simplified model, is the approximate expression of the functionalization reaction energies for planar graphene.

Table 1 The reaction (=negative binding) energy, ΔE_0 , on a planar graphite surface (eV) for different monovalent addends A_i = (F, OH, H, NH₂, CH₃ and COOH) [16], H* [7] and NH₂* [15, 16]

A	ΔE_0 (eV)	ω_A (eV electrophilicity)	f_{A_i} condensed Fukui function	$-\omega_A f_{A_i}$ (eV)
F	−1.92	3.86 ^a	1	−3.86
OH	−1.03	2.48 ^b	0.87/O	−2.16
H	−1.59	2.01 ^a	1	−2.01
H*	−1.49	2.01 ^a	1	−2.01
NH ₂	−0.67	1.71 ^a	0.82/N	−1.40
NH ₂ *	−1.39	1.71 ^a	0.82/N	−1.40
CH ₃	−0.59	1.26 ^a	0.82/C	−1.03
COOH	−0.45	1.82 ^c	0.42/C	−0.77

The condensed Fukui function f_{A_i} (calculated from Eq. 42) is calculated for the monovalent addend A with reacting atom i

The electrophilicity, ω_A (eV): ^afrom Table 1 of [42]

^b Calculated by Eq. 39 and data from Table IV of [49] with the factor of 1/2 in the original definition of the global hardness omitted in this paper for convenience

^c By Eq. 39 and data from Table II of [48]

Equations 46 and 47 express the linear fit slopes of the functionalization reaction energies for the semiconducting and metallic SWCNTs, respectively, versus the inverse of the SWCNTs radius.

Linear fit slopes

Linear fit slopes have been reported for the functionalization reaction energies versus the inverse of the SWCNTs radius with values of C of -4.3 and -3.2 eV Å [16] and -3.14 eV Å [7] for metallic and semiconducting SWCNTs, respectively. These slopes are found to be constant, independent of the addend, the tube size and the chirality.

From Eqs. 46 and 47, it follows

$$\frac{C_{\text{metallic}}}{C_{\text{semiconducting}}} = \frac{-4.3}{-3.2} = 1.3 \approx \frac{\Theta}{|V_{\text{pp}\pi}|a_{\text{cc}}} = 1.7 \pm 0.4. \quad (48)$$

The ratio between the linear fit slope of the metallic and the semiconducting SWCNTs is calculated from the DFT data [16]. The resulting value of 1.3 is in agreement with the value obtained from our simplified model (1.7 ± 0.4).

Effective number of valence electrons

The constancy of the slopes of the linear fits, independent of the addend, the tube size and the chirality, can be explained from Eqs. 46 and 47. In the radical reactions, the effective number of valence electrons involved, N_e , is independent of the addend, the tube size and the chirality.

From Eq. 46 and [17] it follows

$$N_e \approx \sqrt{\frac{-2C_{\text{semiconducting}}}{|V_{\text{pp}\pi}|a_{\text{cc}}}} + K = 1.4 \pm 0.2. \quad (49)$$

From Eq. 47 it follows

$$N_e \approx \sqrt{\frac{-2C_{\text{metallic}}}{\Theta}} + K = 1.0 \pm 0.2. \quad (50)$$

Equations 49 and 50 are the expressions of the effective number of valence electrons involved in the radical reaction between the semiconducting and metallic SWCNTs, respectively. The obtained value is close to one electron, which is the expected value for a radical reaction.

Reaction energy on a planar graphite surface

The reaction energy, ΔE_0 , on a planar graphite surface is reported in Table 1 [7, 15, 16]. The ΔE_0 on a planar graphite surface for the monovalent addend A_i (where A_i = F, OH, H, NH₂, CH₃, COOH) is extrapolated from the binding energies, ΔE , of the (5,5) SWCNTs (from Table 1 of [16]) by Eq. 2, the value of $C_{\text{metallic}} = -4.3$ eV · Å [16] and the radius of a (5,5) SWCNT (Eq. 44). The monovalent addends A_i (where A_i = F, OH, H, NH₂, CH₃, COOH) are calculated by means of a supercell length of 7.38, 7.5 Å for H* and 12.6 Å for NH₂*. H and H* (Table 1) have similar supercell lengths and similar ΔE_0 .

The ΔE_0 on a planar graphite surface (Table 1) was plotted versus $\omega_A f_{A_i}$ (Fig. 2). The ratio between ΔE_0 of NH₂ (supercell length 7.38 Å) and NH₂* (supercell length 12.6 Å) is $\frac{\Delta E_0(\text{NH}_2)}{\Delta E_0(\text{NH}_2^*)} = 0.48 \approx a$.

Fig. 2 Plot of binding (=negative reaction) energies, $-\Delta E_0$, on a planar graphite surface versus $\omega_A f_{A_i}$ (Table 1). The resulting linear fitting parameters are: slope $a = 0.48 \pm 0.02$, intercept $b = 0.05 \pm 0.05$, $R = 0.99$ (the correlation coefficient.). NH₂*, H* and H (Table 1) are not included in this fitting

From the linear fit of ΔE_0 (Fig. 2) on a planar graphite surface of the monovalent addends A_i (where $A_i = \text{F, OH, NH}_2, \text{CH}_3, \text{COOH}$), we deduce that $\Delta E_0 = -a \cdot \omega_{\text{AF}A_i}$, which is approximately minus one half of our theoretical prediction (Eq. 45, $a = 0.48 \pm 0.02$). The ratio between ΔE_0 of NH_2 and NH_2^* is $\frac{\Delta E_0(\text{NH}_2)}{\Delta E_0(\text{NH}_2^*)} = 0.48 \approx a$. We can therefore hypothesize that with a supercell length of 7.38 Å, for the monovalent addends $A_i = (\text{F, OH, NH}_2, \text{CH}_3, \text{COOH})$, ΔE_0 is reduced by a factor of 0.48 ± 0.02 due to the interaction between the neighbouring supercell. In fact, for the monovalent addend NH_2^* with supercell length 12.6 Å (Table 1), ΔE_0 on a planar graphite surface is very close to our theoretical prediction (Eq. 45). The interaction between neighbouring supercells for the monovalent addends (H and H*) with similar supercell lengths (7.38 and 7.5 Å, respectively) have less intensity ($\frac{\Delta E_0(\text{H})}{\omega_{\text{H}}} = 0.79$) compared with the monovalent addends $A_i = (\text{F, OH, NH}_2, \text{CH}_3, \text{COOH})$, ($\frac{\Delta E_0(A)}{\omega_{\text{AF}A_i}} = 0.48 = a$). This can be explained for two reasons, the small dimension of the hydrogen atom compared to the other monovalent addends A and the difference of electronegativity (Pauling) between the hydrogen atom and the carbon atom. For hydrogen, this is 0.4; whilst for the fluorine atom, it is 2.9. This fact can influence the intensity of the interaction between neighbouring supercells.

Conclusions

A simple linear relationship between the functionalization reaction energies for the exohedral monovalent addition on the surface of an ideal, infinitely long SWCNT and the reciprocal SWCNT radius has been derived from the HSAB principle and the tight binding model.

The slope of the derived linear relationship is a function of the effective number of valence electrons involved in the functionalization reaction. The intercept of the derived linear relationship, equal to the reaction energies on a planar graphite surface, is a function of the electrophilicity of the monovalent addend and of the condensed Fukui function of its reacting atom.

The theoretical predictions of this simple formula are coherent with the computational DFT data reported in the literature.

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