



# A reasonable criterion of nitrogen-doped single-walled carbon nanotubes with pyridine-like configurations

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## ABSTRACT

Bond curvature  $K_D$  as a universal criterion is used to identify structures and reactivities of  $N_2$ -doped single-walled carbon nanotubes. Calculations of adjacent  $N_2$ -dopings show that, as  $K_D$  is large, a pyridine-like structure is formed and the formation energies  $E_f$  linearly decrease with increasing  $K_D$ , whereas as  $K_D$  is small, the doping N–N bond cannot be broken. A boundary of  $K_D$  between generating broken and unbroken N–N bond structures is about  $1.6 \text{ nm}^{-1}$ . For the  $(n,0)$  tubes, the  $E_f$  of products with the pyridine-like configurations have an odd–even oscillation rule with  $n$  values, and display a decreasing trend with increasing  $K_D$ . As the largest value  $K_{\text{largest}}$  among all  $K_D$  in a given tube is small, two N atoms are inclined to disperse in the tube and its product has a perfect  $sp^2$  hexagonal network configuration. The approximate border value of  $K_{\text{largest}}$  for the adjacent and disperse substitutions is  $2.3 \text{ nm}^{-1}$ .

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## 1. Introduction

Carbon nanotubes (CNTs) exhibit interesting electronic, mechanical, and structural properties [1]. However, in the experimental synthesis of CNTs, the properties mentioned above can be hardly tailored. Defects and impurities are often incorporated to control these properties. Due to the small difference in the atomic radius compared with carbon, nitrogen is the most widely used to modify the electronic and chemical properties of CNTs by substituting carbon in the hexagonal graphitic structures of CNTs for certain applications, such as catalyst supports [2], sensors [3,4] and carbon electrodes [5,6].

Nitrogen-doped CNTs have been investigated experimentally and theoretically since 1993 [7–22]. With respect to the nitrogen-doped single-walled CNTs (SWCNTs), their syntheses are more difficult than those of doped multi-walled CNTs. Now, some groups have used arc-discharge [8] and ion implantation [9] methods to successfully obtain them. The local doping structures are always concerned [9–15]. In experiment, scientists have found products with all kinds of structures such as the perfect  $sp^2$  hexagonal network and pyridine-like configurations at the doping areas. In the  $N_2^+$  ion implantation, Xu et al. [9] thought that the  $N_2^+$  particles first produced carbon atomic vacancies in the SWCNT, then these high active vacancies trapped nitrogen, forming the nitrogen-doped SWCNT. In theory, Yu et al. [10] found that the formation energies of one-nitrogen-doped SWCNTs had  $3n$  oscillation rule with  $n$  values of the  $(n,0)$  tubes, due to the same oscillation character of their HOMO (highest occupied molecular orbital) energy

levels. Kang and Jeong's study [11] showed that two N atoms tended to disperse in the (10,0) tube, however, they were favorably adjacent to each other in the (5,5) tube along the tube circumference, forming the product with the pyridine-like configuration. Based on tight binding and ab initio theoretical calculations, Czerw et al. [12] also pointed out that the product with the pyridine-like configuration at the doping area was stable. In the nitrogen-doped SWCNT with the pyridine-like configuration, it seems that two N atoms directly substitute two adjacent C ones, and the N–N bond with the C–C bond length of the SWCNT is broken, resulting in two pyridine rings and a 10-membered ring at the doping site. Kang and Jeong [11] conjectured that the aromaticity attainment of these rings after breaking the N–N bond stabilized the unstable lone-pair–lone-pair repulsion from two adjacent N atoms and the product structure with the pyridine-like configuration. Although the pyridine-like configuration at the nitrogen-doping site has been found using the spectroscopic technique [9,13–15], further theoretical studies and experimental confirmations are still expected, just as Ayala et al. [15] said in the review, and the theoretical criterion that these local configurations take on at the doping areas is almost absent.

Up to now, there is still a lack of systemic and critical theoretical investigations for nitrogen-doping of SWCNTs with different types and sizes, especially for the chiral SWCNTs that possess the most common SWCNT structures [23]. Therefore, in this paper, we study one- or two-nitrogen dopings of various SWCNTs including the chiral, arm-chair and zigzag tubes. The presence of some local configurations at the doping areas, such as the pyridine-like and the perfect  $sp^2$  hexagonal network configurations, is explained using Directional Curvature Theory (DCT) we earlier proposed [24–26]. DCT has succeeded in predicting reactivities and adduct structures of the [2 + 1] cycloadditions on CNTs [24–26], BN nanotubes [27,28] and fullerene [25], and

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can well estimate the activation energies of the [2 + 1] cycloaddition on CNTs from the experimental data [29].

## 2. Computational models and directional curvature theory

The optimized structures and formation energies were obtained by the hybrid density functional theory (DFT), namely Becke's three parameter hybrid functional [30], B3LYP method was employed in this work. For all atoms considered, the standard 6–31 G\* basis set was used. The method has successfully applied to other calculations of SWCNTs [18,24–26,31]. All the calculations were performed with the Gaussian 03 package [32]. On the basis of the method mentioned above, we obtain structures and energies of a series of nitrogen-doped SWCNTs. In these tubes, one carbon atom is substituted by one N atom, named as N<sub>1</sub>-doped tubes (or N<sub>1</sub>-dopings), and two carbon atoms which are adjacent or disperse are substituted by two N atoms, named as adjacent or disperse N<sub>2</sub>-doped tubes (or adjacent or disperse N<sub>2</sub>-dopings). The adjacent N<sub>2</sub>-doping can be understood in which the N–N bond with the C–C bond length substitutes the C–C bond of the perfect tube. During the calculations, a SWCNT is simulated by a section of the tube, and the dangling C–C bonds at two ends of the tube are saturated by H atoms. For chiral SWCNTs, one unit cell is selected except for the (6,5) tube, for which a fragment with 100 carbon atoms is chosen because there are too many carbon atoms in the unit cell. In a chiral tube, there are three types of the C–C bonds (bonds a, b and c), seen Fig. 1a, so we consider three adjacent N<sub>2</sub>-doping models. In an armchair or zigzag tube, two adjacent N<sub>2</sub>-doping models for substituting two types of the C–C bonds (bonds a and b) are studied, as seen in Fig. 1b and c, respectively. The adjacent substitutions are used to explain the local doping structures with the pyridine-like configurations. For the products with the perfect sp<sup>2</sup> hexagonal network structures, N<sub>1</sub>-doping and disperse N<sub>2</sub>-doping models are explored.

Formation energies  $E_f$  of the nitrogen-doped SWCNTs can be calculated according to the following expression

$$E_f = [E_{\text{dope}} - E_{\text{perfect}} - (nE_N - nE_C)]/n \quad (1)$$

where  $E_{\text{dope}}$  and  $E_{\text{perfect}}$  are the energies of the N-doped and perfect SWCNTs, respectively,  $E_N$  and  $E_C$  are the energies of an isolated N and C atoms, respectively, and  $n$  is the doping atomic number. As  $E_f < 0$ , the N-doping reaction is exothermic, and as  $E_f > 0$ , it is endothermic. Here, the calculated results indicate that this reaction is endothermic, consistent with results from other studies [10–12].

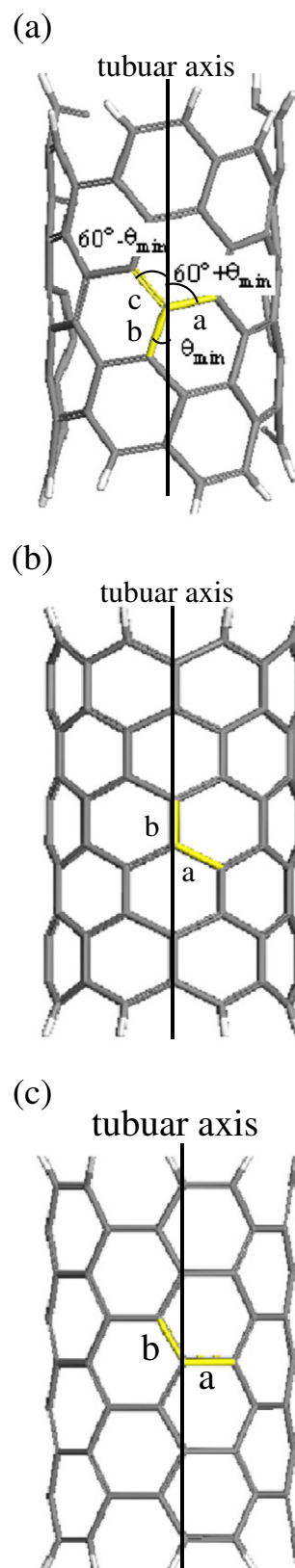
Directional Curvature Theory (DCT) involves the bond curvature ( $K_D$ ) and atomic one ( $K_M$ ).  $K_D$  is defined as the average curvature of the corresponding arc of a C–C bond in the SWCNT [25], expressed as

$$K_D = \frac{\sin^2 \theta}{R} \quad (2)$$

and the  $K_M$  values for the vertices of the SWCNT can be obtained from the average of the  $K_D$  values for the various bonds [25], written as

$$K_M = \frac{1}{2R} \quad (3)$$

where  $\theta$  is an acute angle between the tubular axis and the C–C bond on the plane of the unfolded SWCNT, defined as the C–C bond obliquity angle or the bond angle [24–26], and  $R$  is the tubular radius. From formula (2), it can be seen that  $K_D$  is related to the  $\theta$  and  $R$  values. For the C–C bonds of a given SWCNT, the  $K_D$  values change only with  $\theta$ , and for the bonds of different SWCNTs with the same  $\theta$ , the  $K_D$  values change only with  $R$ . In a word,  $K_D$  relates only to a given C–C bond in a SWCNT. From formula (2), it can also be seen that  $K_D$  is the geometric expression, which allows its use as the curvature



**Fig. 1.** The nonequivalent C–C bonds in the chiral (a), zigzag (b) and armchair (c) SWCNTs. The minimum  $\theta_{\text{min}}$  of the obliquity angles is just the chiral angle of a SWCNT, and other C–C bond angles are equal to  $60^\circ - \theta_{\text{min}}$  and  $60^\circ + \theta_{\text{min}}$  respectively.

of the N–N bond substituting the C–C bond of the SWCNT. Similarly, the strain energy ( $E_s$ ) of the C–C bond that  $K_D$  can express by using the continual elastic model [25,33] in our previous studies [24–26],

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