

Formation energy of Stone–Wales defects in carbon nanotubes

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A Stone–Wales (SW) defect is a dipole of 5–7 ring pair in a hexagonal network, which is one of the most important defective structures in carbon nanotubes (CNTs) that will affect mechanical, chemical, and electronic properties of CNTs. Using the extended Hückel method, we calculated the formation energy of SW defects in carbon nanotubes. The formation energy of SW defects was then fitted to a simple formula as a function of the tube radius and the orientation of a SW defect in the tube. This result provides a convenient tool for the study of thermodynamics and kinetics of SW defects, as well as the interaction of SW defects with other types of defects in CNTs. © 2003 American Institute of Physics. [DOI: 10.1063/1.1599961]

A carbon nanotube (CNT) was first thought of as a perfect graphene sheet wrapped up into a cylinder. However, as more experimental results became available and theoretical investigations went deeper, CNT was found to be not as perfect as it seems. Defects such as the 5–7 rings, kinks, junctions, and impurities may be presented in as-prepared CNTs. These defects can significantly change the electrical, chemical, and mechanical properties of CNTs.^{1–3} Therefore, it is highly desirable to gain an understanding on the energetic condition for the formation and thermodynamic behavior of defects in CNT for applications such as nanoelectronic devices, composite reinforcement, and energy storage. Unlike bulk materials, the structure of CNT has two degrees of freedom: one is the radius (r) of the tube and the other is the chiral angle (χ). The (r, χ) notation of CNT can be easily translated from the normal (n, m) notation as follows:⁴

$$r = \sqrt{3}a(m^2 + n^2 + mn)^{1/2}/2\pi,$$

$$\chi = \tan^{-1}[\sqrt{3}n/(2m + n)], \quad (1)$$

where a is the C–C bond length, and χ is limited to being $0 \leq \chi \leq \pi/6$ due to the geometrical symmetry of the hexagon network. Such two degrees of freedom introduce a complexity in the description of the formation energy of a defect: with the change of radius and chiral angle of a CNT, the formation energy of a defect may also change. In addition, the orientation of the defect itself in relation to the CNT may cause variations in formation energy.

The Stone–Wales (SW) defect is one of most important defective structures in CNTs. It is formed by rotating a C–C bond in the hexagonal network by 90° (the so-called Stone–Wales transformation),⁵ resulting in the creation of a dipole of a 5–7 ring pair [see Fig. 1(a)]. Murry and co-workers⁶ examined the kinetics of the SW transformation as an essential part of fullerene annealing and fragmentation. Beyond a critical level of tension, CNT releases its excessive strain via a spontaneous formation of topological defects. It was proposed that at high temperatures, a plastic response could oc-

cur due to the separation and gliding of SW defects, whereas at lower temperatures the result could be fractures.⁷ The formation energy of the SW defect is sensitive to the applied strain along the axial direction of CNT.^{8,9} Samsonidze *et al.*¹⁰ presented an analytic expression of the formation energy (E_{sw}) for SW defects under an applied strain ε . There are some calculations of E_{sw} without applied strain in the literature,¹¹ mostly on a specific configuration of CNT (i.e., the fixed radius and chiral angle). This letter will report a systematic investigation to develop an expression for E_{sw} as a function of tube geometry and orientation of SW defects in CNT.

A perfect wall of CNT consists of a hexagonal network of carbon–carbon bonds. SW transformation may take place at each of the three sets of generally nonequivalent carbon–carbon bonds. Therefore, SW defects may have three possible orientations as the one shown in Fig. 1(a). To simplify the description, we distinguish different SW defects by using a pair of variables, r and θ . Here, r is the radius of the tube, and θ is the orientation of a SW defect that is defined as the angle between the direction of the short axis of a SW defect and the rolling direction of the graphene sheet; i.e., direction **R** in Fig. 1 (a direction vertical to **R** and within the plane of the graphene sheet is the axial direction of the tube, **A**). The angle θ ranges from $-\pi/2$ to $\pi/2$. If r and χ are fixed, three possible orientations of a SW defect would be $\pi/3 - \chi$, χ , and $\pi/3 + \chi$ according to our definition. For a zigzag tube, $\chi = 0$, two out of three orientations of SW defects are equivalent. A similar situation is found for armchair tubes with $\chi = \pi/6$.

Using a semiempirical *ab initio* method (extended Hückel)^{12,13} and an amber force field,¹⁴ we calculated the formation energy of SW defects at different rolling radii and orientations. The procedure of calculations is as follows: (1) embed a SW defect in a flat graphene sheet such as the one shown in Fig. 1(b), rotate the sheet to an angle θ in relation to the rolling direction **R**, and then roll the sheet by a radius r to mimic a part of the CNT wall, Fig. 1(c); (2) relax the structure using an amber force field until the maximum force in the cluster is less than 1.0×10^{-4} eV/Å and those atoms far from the center (in a gray color) are fixed in this process; (3) calculate the total energy (E_{def}) of the cluster with a SW

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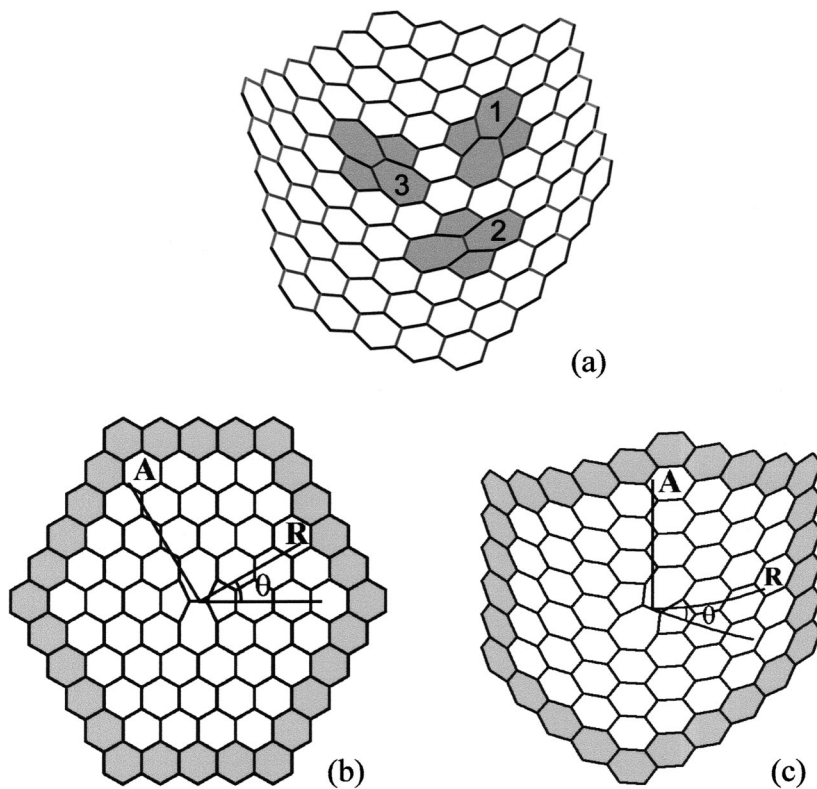


FIG. 1. An illustration of three possible orientations of SW defects in CNT, (a); and the clusters used in calculation: (b) a SW defect is embedded in a graphene sheet, and (c) the sheet is rolled in the **R** direction by a radius *r*. The direction **A** is the axial direction of the nanotube. It has been tested that this cluster is large enough to eliminate the edge effect on the center SW defect.

defect embedded using the extended Hückel method and also calculate the total energy (E_{perf}) of a cluster without the SW defect embedded, then find the difference that gives the formation energy (E_{sw}) of a SW defect; i.e., $E_{\text{sw}} = E_{\text{def}} - E_{\text{perf}}$; and (4) repeat the procedure by varying the rolling radius and the rotation angle, respectively, at small steps. The result is shown in Fig. 2 as an energy contour for E_{sw} . For any rotation angle θ , if the radius of the tube is large enough, the formation energy of a SW defect will converge to that for a flat graphene sheet (E_{sw}^0). However, this tendency is not always monotonic. For those SW defects with an absolute rotation angle θ smaller than about $\pi/6$, E_{sw} increases monotonically with r to E_{sw}^0 . For those that have larger absolute rotation angles, E_{sw} first increases with r to a maximum, then decreases to E_{sw}^0 . For a given radius of the CNT, the smaller

the absolute rotation angle θ is, the lower the formation energy E_{sw} will be. The smallest and largest formation energies of SW defects are found in zigzag tubes with $\theta = 0$ and in armchair tubes with $\theta = \pm \pi/2$, respectively.

In developing an analytical expression for E_{sw} that is relatively simple, we noticed the fact¹⁵ that the strain energy of a perfect CNT is inversely proportional to the square of the CNT radius. The introduction of a SW defect will inevitably cause a change in local CNT radius. Therefore, a term in the form of $1/r^2$ should be included in the expression for E_{sw} . On the other hand, when the radius of CNT approaches infinity, E_{sw} must converge to E_{sw}^0 . By fitting to the theoretical result at a given rotation angle θ , we found that the formation energy of a SW defect, E_{sw} , can be best described by a first order exponential decay function of the tube radius, plus a term similar to the strain energy of CNT; i.e.,

$$E_{\text{sw}} = E_{\text{sw}}^0 + ae^{-br} + \frac{c}{r^2}, \quad (2)$$

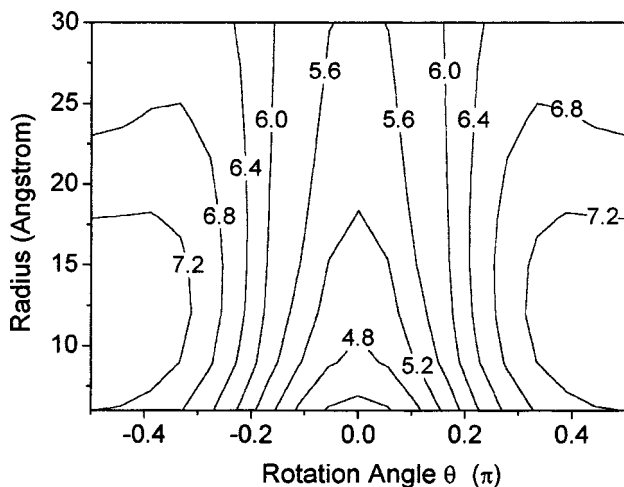


FIG. 2. Formation energy of the Stone–Wales defect, E_{sw} (eV) as a function of r and θ .

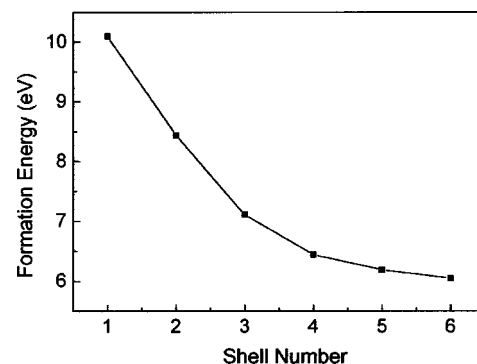


FIG. 3. Formation energy (E_{sw}^0) of a SW defect in a flat graphene sheet as a function of relaxation area.

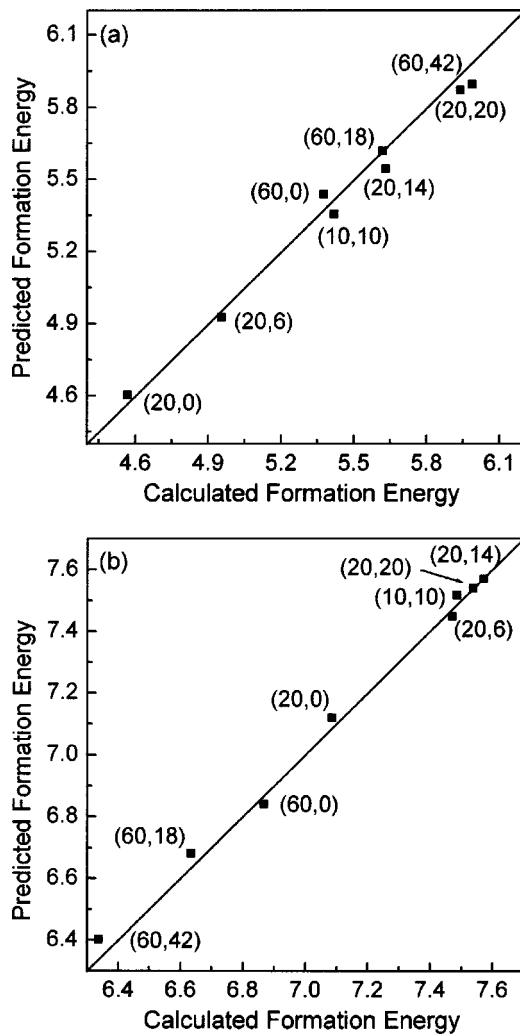


FIG. 4. Comparison of E_{sw} calculated for selected CNTs and the predictions from Eq. (2). (a) $\theta = \chi$ and (b) $\theta = \pi/3 + \chi$.

where E_{sw}^0 is the formation energy of a SW defect in a flat graphene sheet, given in the unit of eV; r is the radius of CNT in the unit of \AA ; and a , b , and c are the fitting parameters related only to the orientation angle θ and have the units of eV, \AA^{-1} , and eV \AA^2 , respectively. Using the least-square method, we found the best fit

$$\begin{aligned} a(\theta) &= -3.25 \cos(2\theta) + 1.67, \\ b(\theta) &= -0.0123 \cos(2\theta) + 0.006396 \cos(4\theta) + 0.051, \\ c(\theta) &= 26.72 \cos(2\theta) - 45.46, \end{aligned} \quad (3)$$

where $\theta = \pi/3 - \chi$, χ , and $\pi/3 + \chi$, respectively, and χ is the chiral angle of the CNT. The maximum fitting errors for a , b , and c are 0.089 eV, 0.00076 \AA^{-1} and 0.55 eV \AA^2 , respectively, determined by assuming that the cosines take a value of 1 or -1 . Note that $c(\theta)$ is always negative.

In 1988, Kaxiras *et al.*¹⁶ determined the value of E_{sw}^0 , reporting it to be 10.4 eV. However, this value is disputable because, in their calculations, Kaxiras *et al.* only allowed the two center atoms of a SW defect to relax. Using the extended Hückel method, we enlarged the region for relaxation. The

relaxation area is defined by a shell concept. The first "shell" is defined as the two center atoms of a SW defect, the second shell is the whole 5-7-7-5 ring, and the third shell refers to those adjacent atoms that enclose the second shell, and so on. It can be found from Fig. 3 that, with the enlarged relaxation area, the formation energy of a SW defect decreases considerably. E_{sw}^0 in Eq. (2) is determined to be 6.02 eV for a flat graphene sheet. This result was also verified by using an independent *ab initio* pseudopotential package developed by CAMP at the Technical University of Denmark.

Since the Eq. (2) was obtained from a piece of curved graphene sheet shown in Fig. 1 rather than a complete section of CNT, a group of CNTs covering a wide range of geometry was selected as real cases to verify Eq. (2). They include one set of armchair tubes, one set of zigzag tubes, and two sets of other chiral tubes. Each set of tubes includes two tubes that have the same chiral angle but different radii. The formation energy of SW defects in these tubes was calculated using the extended Hückel method, and compared to the predictions of Eq. (2). The results are given in Fig. 4, showing a good agreement. The formation energies for the (10,10) armchair tube are 5.4 eV ($\theta = \pi/6$) and 7.5 eV ($\theta = \pi/2$), respectively. The lower one agrees very well with that obtained by Rubio *et al.*¹¹

Equation (2) might be universal to other localized topological defects on CNT walls, although the fitting parameters may be different from the values given in this letter.

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