Communication

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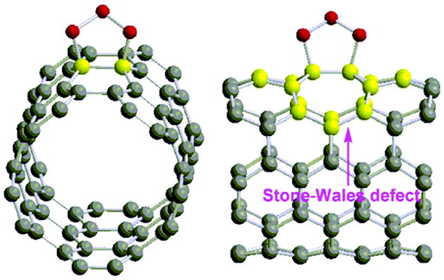

B3LYP/6-31G* Prediction

	Reaction Energy (kcal/mol)
Addition of O_3 on a perfect (5,5) tube	-20.2
Addition of O_3 on a defective (5,5) tube	-4.4

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Are Stone−Wales Defect Sites Always More Reactive Than Perfect Sites in the Sidewalls of Single-Wall Carbon Nanotubes?

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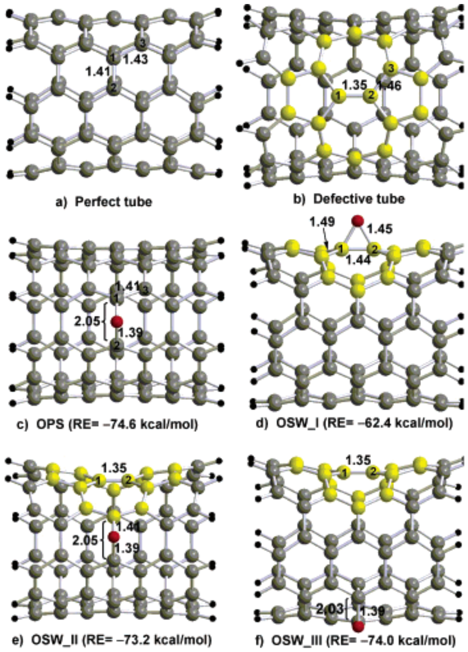
Perfect graphene sheets and carbon nanotubes are known to have high chemical stability and unique physical properties resulting from the strong π-interactions of their hexagonal networks.[1,2] However, unavoidable imperfections, such as vacancies, Stone−Wales (SW) defects, pentagons, heptagons, and dopants, are believed to have a pivotal role in tailoring the physical and chemical properties of graphenes and carbon nanotubes.[2−4] It is generally accepted that these defective sites are chemically more reactive than the perfect sites (PS) in graphenes and carbon nanotubes.[5−8] Indeed, a number of recent theoretical investigations revealed the higher chemical reactivity of Stone−Wales defects than that of PS in the sidewalls of zigzag (n,0) single-wall carbon nanotubes (SWNTs) and planar graphenes (polycyclic graphite fragments).[5−8] However, the chemical reactivity of Stone−Wales defects in the sidewalls of armchair (n,n) SWNTs has not been examined theoretically before now. The present study shows, in contrast to the general belief, that the central C−C bond of Stone−Wales defects in an armchair (5,5) SWNT is chemically *less reactive* than that in perfect sites.

A finite model, $C_{70}H_{20}$, was used to represent a defect-free (5,5) SWNT (Figure 1a; the hydrogen atoms were added at the open ends to avoid dangling bonds). As shown in Figure 1b, a Stone−Wales defect can be generated topologically by rotating one of the C−C bonds (i.e., the C1−C2 bond in Figure 1a) by 90°.[9] This results in a 5−7−7−5 ring fusion. Geometry optimizations were performed at the B3LYP/6-31G* DFT level[10] using Gaussian 98.[11] The optimized C1−C2 bond length (∼1.35 Å) at the 7−7 ring fusion of the Stone−Wales defect, much shorter than the C−C bonds in the defect-free tube model, implies a rather localized C═C double bond. More significantly, the local carbon skeleton at the 5−7−7−5 ring fusion of the Stone−Wales defect, i.e., >C1═C2<, is nearly planar. Hence, the local curvature at the Stone−Wales defect is far less severe than that at a perfect site. The curvature-induced pyramidalization angle (PA)[1h,12] of ∼5.3° at the C1 and C2 atoms of the defect-free tube is much larger than the PA of only ∼0.3° at the corresponding atoms of the Stone−Wales defect model. Such an intriguing structural feature should decrease the reactivity of the Stone−Wales defect, since the sidewall reactivity of armchair (n,n) SWNTs depends largely on the sidewall curvature.[13]



a) Perfect tube b) Defective tube

c) OPS (RE= −74.6 kcal/mol) d) OSW_I (RE= −62.4 kcal/mol)

e) OSW_II (RE= −73.2 kcal/mol) f) OSW_III (RE= −74.0 kcal/mol)

Figure 1. (a) Seven-layer defect-free (5,5) tube model ($C_{70}H_{20}$); (b) 7-layer defective (5,5) tube model containing a Stone−Wales defect (colored yellow); (c) optimized O adduct of a defect-free (5,5) tube model; (d) optimized O adduct at the Stone−Wales defect of defective (5,5) tube model; (e) optimized O adduct at a 6−6 ring fusion near the Stone−Wales defect of defective (5,5) tube model; (f) optimized O adduct on a 6−6 ring fusion far away from the Stone−Wales defect of defective (5,5) tube model. (Bond lengths in angstroms.)

The optimized geometries of O atom adducts at the sidewalls of defect-free and defective (5,5) tube models are depicted in Figure 1c−f. In agreement with the previous theoretical finding,[14a] the addition of O to the defect-free tube model (Figure 1c) leads to the cleavage of the C1−C2 bond; the computed exothermicity is 74.6 kcal/mol. The C−C bond cleavage can be ascribed both to the release of strain of the curved structure and to homoconjugation.[14] In contrast, an epoxy species (Figure 1d) is formed upon O addition to the Stone−Wales defect (i.e., the 7−7 ring fusion). Consistent with the lower reactivity of the Stone−Wales defect than the perfect site, the exothermicity of the reaction at the defect is much (12.2 kcal/mol) lower in energy. In contrast, the computed exothermicities of two other types of O additions at the 6−6 ring fusions of the defective (5,5) tube model (see Figure 1e,f) were 73.2 kcal/mol for **1e** and 74.0 kcal/mol for **1f**. Both energies are comparable to that of the defect-free tube (74.6 kcal/mol). Thus, the Stone−Wales defect is less reactive than all the other sites, even in the defective tube.

Longer tube models give similar results. Figure 2 depicts the 13-layer defect-free (5,5) tube (model I) and the corresponding defective tube (model II). The geometries of these larger models were optimized at B3LYP/3-21G; final energies were then computed at B3LYP/6-31G*. At this B3LYP/6-31G*//B3LYP/3-21G level, the exothermicities of the O atom additions to the perfect site (Figure 3a) and to the Stone−Wales defect (Figure 3b) are 76.2 and 57.9 kcal/mol, respectively (Table 1). Hence, the predictions based on the longer 13-layer tube models agree well with those based on the 7-layer tube.

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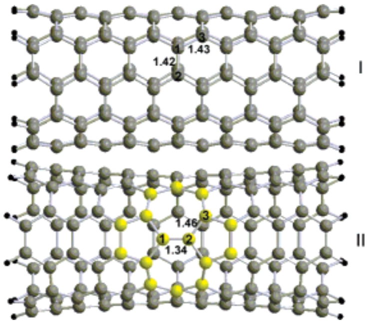

Figure 2. (I) Thirteen-layer defect-free (5,5) tube model; (II) 13-layer defective (5,5) tube model with a Stone−Wales defect (colored yellow).

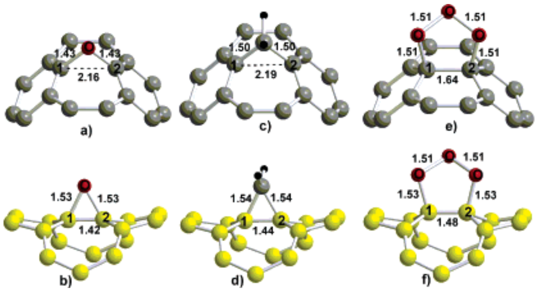

Figure 3. Optimized geometries (bond lengths in angstroms) for the addition products of (a) O on the perfect site, (b) O on the Stone−Wales defect, (c) CH_2 on the perfect site, (d) CH_2 on the Stone−Wales defect, (e) O_3 on the perfect site, and (f) O_3 on the Stone−Wales defect.

Table 1. Predicted Reaction Energies[a] (RE, kcal/mol) for the Additions of O, CH_2, and O_3 onto the Perfect Site (PS) and Stone−Wales (SW) Defect of a 13-Layer (5,5) Tube Model

	RE (PS)	RE (SW)	ΔRE[c]
O[b]	−76.2	−57.9	−18.3
CH_2[b]	−89.9	−55.5	−34.4
O_3	−25.9 (−20.2)[d]	−13.1 (−4.4)[d]	−12.8 (−15.8)[d]

[a] Negative REs denote exothermic reactions. [b] RE refers to the triplet states of O or of CH_2. [c] ΔRE = RE(PS) − RE(SW). [d] Data in parentheses are predicted using the B3LYP/6-31G* geometry.

Two additional types of sidewall reactions, the addition of CH_2[14] and the 1,3-cycloaddition of ozone (O_3),[8,13b,15] on the 13-layer tube models led to similar conclusions. The reaction energies computed at the B3LYP/6-31G*//B3LYP/3-21G level are listed in Table 1. The optimized geometries for the addition products are depicted in Figure 3.

Like the reaction with O, the addition of CH_2 to the perfect site of model I is highly exothermic and leads to cleavage of the substrate C1−C2 bond (Figure 3c). In contrast, CH_2 addition to the Stone−Wales defect results in an intact cyclopropane ring (Figure 3d). This defect-involving reaction is 34.4 kcal/mol less exothermic than the defect-free process.

The 1,3-cycloadditions of O_3 to the perfect site and to the Stone−Wales defect site both form primary ozonide species (Figure 3e,f). The B3LYP/6-31G* exothermicity of the defect-free process is 15.8 kcal/mol greater than that involving the defect site. The activation energies for the defect-free and defect-involving processes are 2.9 and 17.8 kcal/mol, respectively.

Thus far we have shown that the central 7−7 ring fusion at the Stone−Wales defect in the (5,5) SWNT sidewall is less reactive than the defect-free sites. As the local curvature of the Stone−Wales defect is far less severe than that of a perfect site, the much lower chemical reactivity at the defect site can be ascribed to the constraints of its planar local structure. Since the sidewall reactivity of perfect armchair SWNTs decreases monotonically with an increase in tube diameter,[13] we infer that the reactivity difference between perfect and Stone−Wales defect sites in the sidewalls of larger armchair SWNTs also should decrease.[16] Further density functional calculations using periodic boundary conditions have been performed for an infinite (5,5) single-wall carbon nanotube without/with a Stone−Wales defect. The results (described in the Supporting Information) coincide with our cluster model calculations and reveal that the peripheral 5−6 and 6−7 ring fusions at the Stone−Wales defect site are much more reactive.

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Supporting Information Available: Results of periodic boundary conditions calculations on the addition of O_3 to an infinite (5,5) tube with and without a Stone−Wales defect. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Preliminary B3LYP/6-31G* calculations reveal that for O addition to 7-layer (8,8) tube models, the defect-free process (RE = −58.1 kcal/mol) is by only 2.6 kcal/mol more exothermic than the defect-involving one.

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