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Silicon doping of defect sites in Stone–Wales defective carbon nanotubes: A density functional theory study

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ABSTRACT

Using density-functional theory calculations, we investigate how the stabilities and electronic properties of Stone Wales (SW) defective armchair (4,4) and (5,5) nanotubes are modified via Si atom doping at eight selected symmetric positions of SW defect sites with two different orientations, parallel and diagonal. A quasi-tetrahedral bonding configurations of silicon atoms based on sp^3 hybridization are formed, which leads to puckered silicon doped rings. Our results indicate that tube diameter affects the doping reactions so that the doping single-walled carbon nanotubes (SWCNTs) with high curvature (small diameter) might be more favorable, based on both energetic and structural considerations. Density of state (DOS) obtained for the systems indicate that the doping of the defect sites causes the redistribution of electronic states of the SW defective SWCNTs. An average charge of 0.5e is also transferred from silicon atoms to first neighboring carbon atoms on the SWCNT, which indicates that charge redistributions after doping process mostly take place to a relatively small number of carbons at the zone of doped atoms.

1. Introduction

The structures of single-walled carbon nanotubes (SWCNTs) could be described as a perfect graphene sheet wrapped up into a cylinder. However, the experimentally available SWCNTs are not perfect. Topological defects such as vacancies, pentagons, heptagons, dopants, and Stone–Wales defects [1–5]

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formed inevitably during the growth of carbon nanotubes or introduced during workup (e.g., oxidative cleaning, ultrasonication) [6,7] can significantly change the electronic structure [8–10], chemical reactivity [11–13], mechanical [14] and transport [15,16] properties of the systems. Stone–Wales (SW) defect which is a very important topological one in SWCNTs is comprised of two pairs of pentagons and heptagons (5-7-7-5) formed by rotating one bond of the traditional hexagon by 90° [1]. A number of theoretical investigations revealed that these defective sites are chemically more reactive than the perfect sites in the sidewalls of carbon nanotubes [17–20]. Indeed they could act as nucleation centers for the formation of dislocations in the originally ideal network. Therefore, it is expected that with a local deformation, the nanotube containing SW defects might be more favorable for subsequent reactions. For example, the adsorption of small molecules such as H_2 [21], O_2 and O_3 [12], N_2 [22], NH_3 [23,24], NO_2 [24,25], H_2O [26], CO and CO_2 [22,27], Ar [28], Ne and Xe [29–31], and some relevant addends like O, SiH_2, NH, and CH_2 [32] on defective SWCNTs has been reported; it is demonstrated that the adsorption of atoms and molecules on defects is more stable than that on the smooth sidewall, and the chemical and physical properties induced are obviously different. On the other hand, doping of carbon nanotubes by introducing heteroatoms on the sidewall is a significant way to modify their electronic structures and transport properties, making carbon nanotubes more amenable for various potential applications, such as improving the sensitivities of chemical sensors, and opening hollow cavities for gas storage [33] or lithium intercalation [34]. However, the doping of Stone–Wales defects on the surfaces of defective SWCNTs has hardly been investigated before now, to the best of our knowledge, doping of perfect SWCNTs has been the subject of many theoretical and experimental studies. Using first principles calculations, Zeng et al. [35] studied the effect of N doping on the electronic properties of defective zigzag-edged graphene nanoribbons with SW defects. Qin et al. [36] investigated the adsorption of formaldehyde (H_2CO) on the Al-doped SW defective graphene, showing that Al-doped SW graphene is more suitable for H_2CO gas detection. Therefore, the insight into the effect of defect–dopant combination on the carbon nanotube properties is vital for finding their potential applications.

With this initial thought in mind, in the present investigation, we systematically evaluate the doping effect of SW defective armchair SWCNTs with different diameters, (4,4) and (5,5), by replacing carbon atoms on the SW defects with silicon ones, exploring possible atomic arrangements and the resulted electronic properties. For all SWCNTs, a rotation about a C—C bond diagonal (D) or parallel (P) to the tube axis gives rise to two different systems which are labeled P-SW and D-SW, respectively, as illustrated in Fig. 1. For each configuration, eight substitution sites (as shown in Fig1) are considered according to the symmetry of the SW defect. Silicon is selected as a dopant because it is the next group IV element in the periodic table after carbon, and although they share several similarities in their

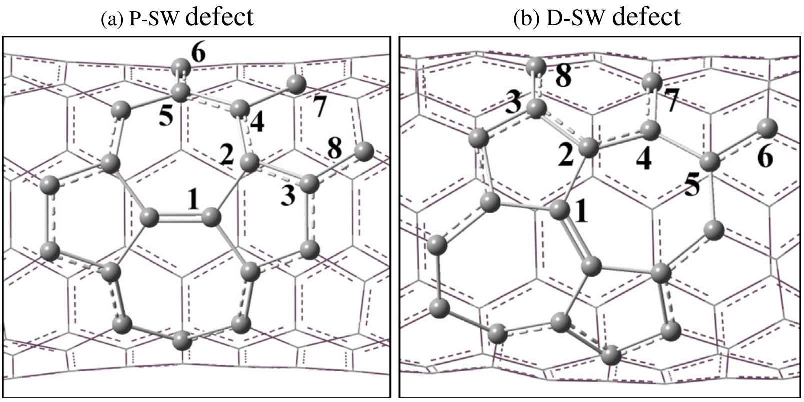
(a) P-SW defect
(b) D-SW defect

Fig. 1. Two configurations of the Stone–Wales defects on the tube sidewall: (a) parallel (P-SW) and (b) diagonal (D-SW). Five different doping positions at the defective sites of SWCNTs according to the symmetry of the SW defects, C1–C5, and three different positions adjoining the defect sites, C6–C8, are shown.