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First-principle simulations on silicon-doped armchair single-walled carbon nanotubes of various diameters

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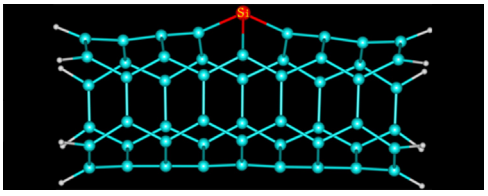
HIGHLIGHTS

- The defect formation energy of Si-doped tubes is linear-scale with tube curvature.
- The hyperpolarizability of carbon nanotubes is enhanced dramatically as silicon doping.
- Aromaticity/anti-aromaticity transition is occurred at selected positions after Si atoms present.

GRAPHICAL ABSTRACT



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ABSTRACT

This work presented theoretical studies of structures, energies and properties of armchair carbon nanotubes (CNTs) upon the silicon substitutional doping by using first-principle calculations. The doping effects on quantitative description from viewpoint of the pi-orbital axis vector theory, relative stability, defect formation energy, electronic structure, nonlinear optical property and aromaticity of the tubes has been addressed systemically and in details. The obtained pyramidalization angles of the silicon are much larger than those of carbon according to the pi-orbital axis vector analysis. The results of defect formation energy suggest that the Si-doping would be contained easier in small CNTs. A quantitative relation about the curvature-dependent defect formation energy is obtained. The silicon atoms exhibit large distributions for the frontier molecular orbital of doped tubes. As for the nonlinear optical property, the hyperpolarizability of the tubes is dramatically enhanced upon silicon defect. The doping effect on the aromaticity is also studied. It is found that the aromaticity/anti-aromaticity transition is even occurred at the selected positions based on the probe of nuclear independent chemical shift.

1. Introduction

Since the discovery in 1991, a great deal of attention has been paid to carbon nanotubes (CNTs), especially the single-walled carbon nanotubes (SWCNTs), due to the state-of-the-art potentials in physics, chemistry, material science and nanotechnology. It is known that the structure and physical property of a SWCNT mainly depend on the diameter as well as chirality. Also the property of CNTs could be modified by various physical or chemical methods, such as electronic field [1–3], vacant defect [4–6], encapsulation [7–9], and physical or chemical adsorptions on the side wall of the tubes [10–13].

On the other hand, if one or more carbon atoms of the tubes are substituted by heteroatoms, the doped CNTs can be obtained. These hybrid CNTs recently have become good candidates with unique structural, electronic and elastic properties, which are much different from those of the pristine ones due to the existence of heteroatoms [14–19]. Therefore, substitutional doping is also one of the important strategies to modulate the structure and property of CNTs. Most recently, Si-doped SWCNTs have been

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synthesized using chemical vapor deposition method for the first time [20]. This new species of doped CNTs should be interesting nano-scaled materials to be expected in the future.

As for the theoretical side, several literatures have pad attentions to the hybrid CNTs containing heteroatoms [21–34]. However, most investigations focus on N- or B-doped CNTs. Furthermore, silicon shares the same column of the Periodic Table with carbon, and doping CNTs with silicon does not alter the valence electrons, which is different from N- and B-substitutions. Thus the electronic structure of the Si-doped CNTs would likely to be similar to that of pristine CNTs from viewpoint of total occupancy of the energy levels. Previous computations on Si-doped CNTs are limited on one or two selected SWCNTs substitutionally doped by silicon atoms. For instance, the zigzag (10, 0), (8, 0) and (5, 5) tubes doped by silicon atoms were calculated by Fagan, Bian and Jiang as well as their co-workers and Zardoost et al., pay attention to Si-doped doped (6, 3) tube [29–34]. Thus further investigation is still necessary to get more understanding about the Si-doped CNTs. Up to date, only a few theoretical studies are available on this issue according to our best knowledge, and the following topics still need to be addressed: (a) the quantitative description of silicon doping on CNTs deformation from viewpoint of the pi-orbital axis vector (POAV) theory; (b) the roles of silicon doping on molecular orbital, electronic structure and functional property of CNTs; (c) the diameter-dependent or -independent effects on structures, relative stabilities and properties of Si-doped CNTs.

In this paper, we carried out theoretical studies on silicon substitutionally doped armchair SWCNTs with various diameters by means of self-consistent field molecular orbital (SCF–MO) method under the framework of density functional theory (DFT). The structure, stability, electronic property hyperpolarizability and aromaticity of the hybrid CNTs are calculated and compared with those of pure ones. We hope the studies would be helpful for promotion of this state-of-the-art research subject.

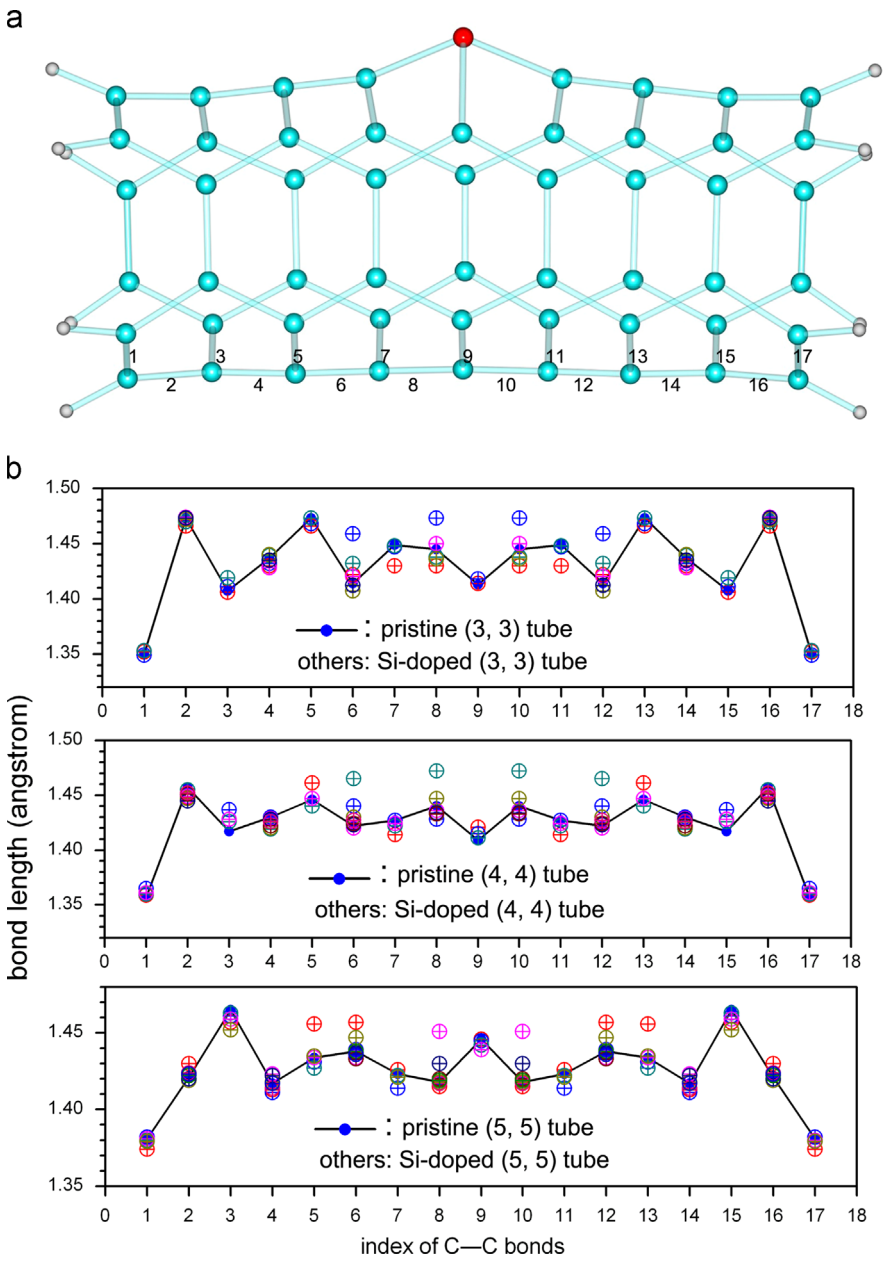

Fig. 1. Structure (a) and bond lengths (b) of Si-doped tubes. The number in figure (a) is the index of C–C bonds.