Chemical Physics Letters 691 (2018) 172–177

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

A catalyst-free achieving of N-doped carbon nanotubes: The healing of single-vacancy defects by NO molecule

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ARTICLE INFO

Article history:
Received 21 September 2017
In final form 12 November 2017
Available online 13 November 2017

Keywords:
Carbon nanotube
Healing
Nitrogen oxide
DFT
Vacancy

ABSTRACT

Density functional theory calculations are performed to study the healing mechanism of single-vacancy defects in zigzag (n,0) CNTs by NO molecule (n = 6,8,10). The results indicate that the healing process proceeds through a two-step mechanism. First, NO molecule adsorbs over the defective site. Then, the extra oxygen atom (O_{ads}) is eliminated by three different ways: (i) NO + O_{ads} → NO_2, (ii) CO + O_{ads} → CO_2, or (iii) SO_2 + O_{ads} → SO_3. The dependency of the healing process on the tube diameter is studied in detail. The results of this work suggest a novel approach to achieve N-doped CNTs.

1. Introduction

Today, carbon nanotubes (CNTs) are very prevalent in the world of research owing to their unique properties, reactivity and potential applications in various areas, such as biosensors, molecular devices, and medicinal chemistry [1–5]. Due to their cylindrical shape, CNTs exhibit novel properties that are not present in the chemically inert graphite, such as their ability to adsorb small molecules [6–8] or H_2 storage [9,10]. In addition, the doping of CNTs with appropriate heteroatom offers a practical way to alter their properties by introducing new states that modify their electronic and chemical properties [11–14]. Among the numerous potential dopants, nitrogen is proven to be an exceptional element to regulate chemical and electronical properties of CNTs [14–18]. This is most likely associated with the electronic configuration as well as the triple-coordination characteristic of nitrogen atom, which seems to be effective in regulating the electrical and chemical properties of CNTs. The large electronegativity of nitrogen atom can also induce charge redistribution over the surface, which results in a significant improvement in the interaction between CNTs and foreign molecules. For example, N-doping of CNTs can facilitate the oxygen reduction reaction (ORR) process by effectively weakening of the O—O bonding of the adsorbed O_2 molecule [19–21].

It is well-known that due to the many limitations during purification, sonication, or due to electron beam induced reactions, a variety of defects can be unavoidably introduced into CNTs. Meanwhile, the mode of CNT synthesis seems to play a critical role in distribution and determining the nature of defects in CNTs [22,23]. These include single carbon vacancy [24–26], divacancy [27,28], Stone–Wales [29,30], topological [31,32] and rehybridization [33,34] defects. Among these, the single-vacancy defect is the simplest one. It can be either introduced into CNT during its growth and by electron or ion-beam irradiation. Earlier studies have shown that this defect can greatly influence properties of CNTs in many ways, e.g. growth behavior, surface reactivity and electrical properties [35–38]. Single-vacancy defects in CNTs have been widely studied in many fields like native electronic properties [39–41] and H_2 storage [42,43] or designing metal-free magnetic materials [37]. Though the presence of these defects can be useful in some applications of CNTs, however, they can undesirably affect the performance and reliability of CNT-based devices. For example, single-vacancy defects can adversely reduce the failure stresses in CNTs [25,44]. Furthermore, the single-vacancy defects in CNTs can easily migrate in various directions and may lead to the formation of bigger vacancy defects [45]. In addition, these defects can considerably shift the band gap of the CNTs which may cause an under- or over-binding between the adsorbed molecule and the CNT [39,46]. In this regard, defects are destructive and the healing of single-vacancy defects is very important in order to benefit from the outstanding properties of perfect CNTs.

In the present study, the possibility of healing single-vacancy defective CNTs (SV-CNTs) by means of NO molecules is investigated. The results of this study are not only important for the understanding of the CNT growth mechanism, but also propose a

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https://doi.org/10.1016/j.cplett.2017.11.017
0009-2614/

new catalyst-free approach for the achieving of nitrogen-doped CNTs (NCNTs). Also, considering the healing process happens without using a metal catalyst, thus, no any purification is required to remove the catalyst. To the best of our knowledge, there is no prior study about the healing of SV-CNTs by a NO molecule.

2. Computational details

The structural optimizations were carried out within the framework of the density functional theory (DFT) using the Gaussian 09 [47] suite of programs. All-electron DFT calculations were performed with the M06-2X [48] density functional and 6-31G** standard basis set. The corresponding harmonic frequency calculations were performed at the same computational level to characterize the nature of stationary points (as a minimum or transition state structure). The connection of the eventually located transition state was checked by the imaginary harmonic vibrational frequency as well as intrinsic reaction coordinate (IRC) calculations. The perfect (6,0) CNT was modeled using 72 carbon atoms. The SV-defective zigzag (6,0) CNT was then built by removing a carbon atom from the pristine CNT, as shown in Fig. 1. To consider the effects of tube diameter, the (8,0) and (10,0) zigzag CNTs with the almost same length were also constructed. Carbon atoms on the edge of the CNTs were terminated by hydrogen atoms. The adsorption energy of the NO molecule over the defective CNTs was calculated by the following equation:

$$E_{ads} = E_{dG\text{-}NO} - E_{dG} - E_{NO} \quad (1)$$

where $E_{dG\text{-}NO}$, E_{dG}, and E_{NO} are the total energies of the NO-defective CNT, the energy of defective CNT, and a single NO molecule, respectively. A negative E_{ads} value indicates that the NO molecule would be energetically favorable to be adsorbed to the surface. The density of state (DOS) plots were obtained by means of Multiwfn [49] program.

3. Results and discussion

3.1. Geometry and electronic structure of SV-CNTs

The optimized structure of pristine and (6,0) SV-CNTs are depicted in Fig. 1. One can see that the removal of a carbon atom from the CNT induces a bond rearrangement around the vacancy

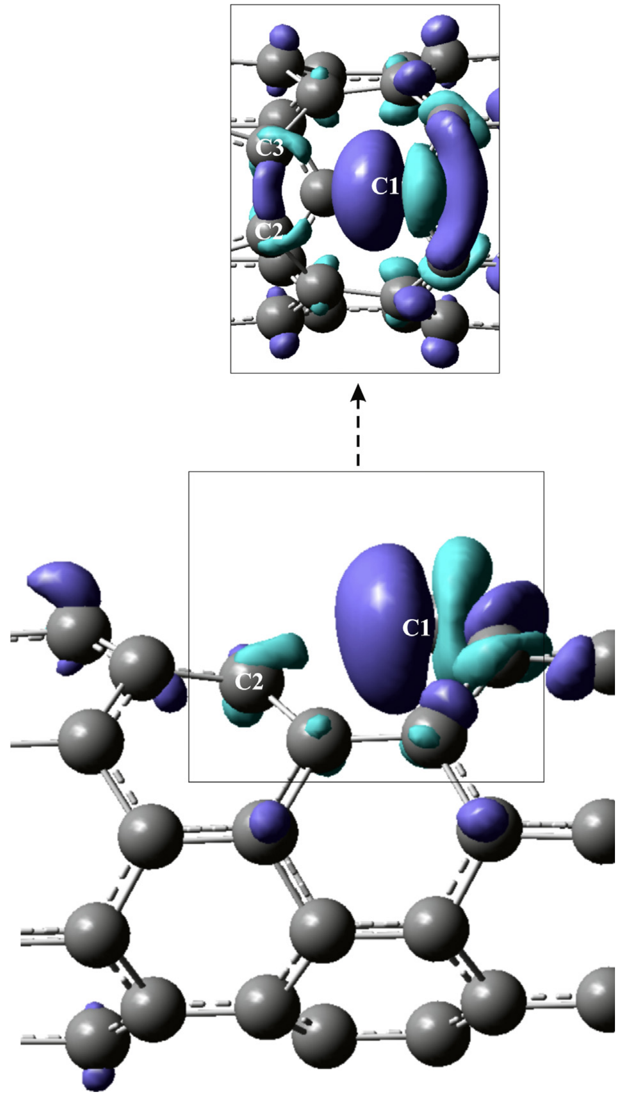

Fig. 2. The nucleophilic Fukui function (isovalue = 0.002 au) of the SV-defective (6,0) CNT.

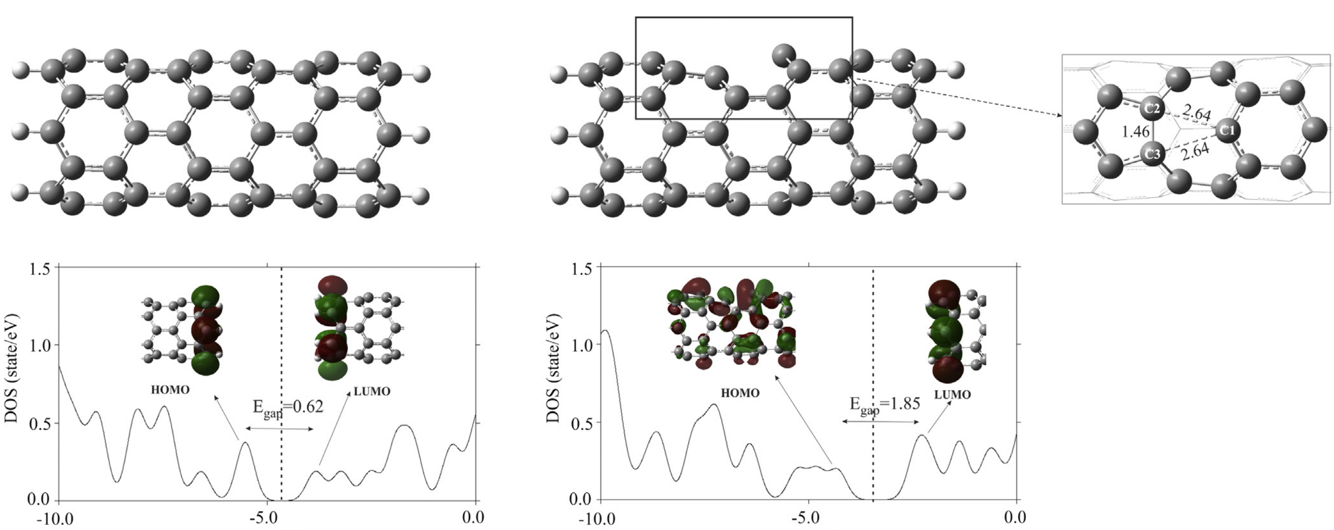

Fig. 1. The optimized structure, the corresponding DOS plot and frontier molecular orbitals of the pristine and SV-defective (6,0) CNTs. All bond lengths are in Å. The dashed line in the DOS plots indicates the Femi level.