Chemical Physics Letters 658 (2016) 162–167

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Strong adsorption of Al-doped carbon nanotubes toward cisplatin

Wei Li, Guo-Qing Li *, Xiao-Min Lu, Juan-Juan Ma, Peng-Yu Zeng, Qin-Yu He, Yin-Zhen Wang

School of Physics and Telecommunication Engineering, South China Normal University, Guangzhou 510006, PR China

ARTICLE INFO

Article history:
Received 9 April 2016
In final form 16 June 2016
Available online 17 June 2016

Keywords:
Al-doped CNTs
Adsorption
Cisplatin
Symmetry

ABSTRACT

The adsorption of cisplatin molecule on Al-doped CNTs is investigated using density functional theory. The obtained results indicate that Al-doped carbon nanotubes can strongly absorb cisplatin. After absorbing cisplatin, the symmetry of CNTs has some changes. We innovatively defined a parameter of symmetry variation which relates to the adsorption. By analyzing the electronic structure, it can be concluded that under the circumstance that cisplatin was absorbed by Al-doped CNTs through aluminum atom of Al-doped CNTs. In conclusion, Al-doped CNTs is a kind of potential delivery carrier with high quality for anticancer drug cisplatin.

1. Introduction

Iijima found the carbon nanotubes (CNTs) in1991 [1]. With their unique physical and chemical properties as well as with its one-dimensional structure, CNTs has been widely used in many different fields, such as physics, and chemical materials [2–6]. What deserves to be mentioned the most is that CNTs, especially single wall CNTs, has good adsorption properties with a large surface area, stable physical and chemical properties [3–5]. Therefore, CNTs has shown great prospects in applying to biomedical, environmental areas [7–9].

The antitumor properties of cisplatin were accidentally discovered by Rosenberg while examining the influence of electric current on the growth of bacteria [10–12]. Cisplatin can slow down the DNA transcription and replication by managing the cancer cells apoptosis [13]. Cisplatin has been used as an anticancer drug since it was discovered. Due to the fact that chemotherapy drugs for cancer cannot identify differences between cancer cells and normal cells, cisplatin may act on both cancerous and normal cells. And this may lead to the destruction or impairment of vital organs [14]. Apart from the wide use in anticancer, the therapeutic efficacy is somewhat compromised by the occurrence of serious side effects such as nausea, vomiting, nephrotoxicity as well as the resistance to chemotherapy drugs [15–17]. Anticancer drug molecules with the optimization of drug dosage and delivery process of cisplatin anticancer drugs could be precisely delivered to tumor sites for maximum treatment efficacy which can also minimize side effects to normal organs [18,19]. So the investigation of advanced drug delivery systems indicates great promise for improving cancer therapy outcomes [20–23].

The researches showed that the CNTs was able to deliver drugs directly to cancer cells [24,25]. However, the adsorption ability of pristine CNTs is weak [26,27]. But, adsorption performance can be improved by replacing one carbon atom of pristine CNTs with another atom [26–29]. Currently, it is quite rare to adopt the first-principle to analyze the adsorption properties of cisplatin on pristine CNTs and doped CNTs. Therefore, we studied the adsorption performance of cisplatin on Al-doped (7, 7) CNTs by using the first-principle. A new insight to the nanomedicine field was considered with the obtained results.

2. Computational details

The pristine (7, 7) CNTs and Al-doped (7, 7) CNTs with diameter (9.49 Å) were studied in this paper. In order to make the carbon atoms of both ends of the nanotubes reach the saturation state, both ends of nanotubes were added with hydrogen atoms. In this study, all the structures investigated were optimized using DMOL^3 software package based on density functional theory (DFT) calculations in the present study [30–32]. The description the electron exchange-correlation term was done within the generalized gradient approximation (GGA) in form of Perdew–Burke–Ernzerhof (PBE) [33]correction. The electronic wave functions were expanded in double-numeric polarization basis sets (DNP) with an orbital cutoff of 4.5 Å. Along the tubes, $1 \times 1 \times 6$ k-point mesh with Gamma centered Monkhorst–Pack scheme was used for all investigated configurations [34,35]. In order to avoid interaction between adjacent cells, a $30 \times 30 \times 30$ Å supercell with periodic bounding conditions was constructed. Structural optimization

* Corresponding author.
E-mail address: 250198767@qq.com (G.-Q. Li).

http://dx.doi.org/10.1016/j.cplett.2016.06.040
0009-2614/

was carried out on all systems with a convergence criterion for energy of 10^{-5} Ha/atom. The forces and displacements on each atom were converged to less than 2×10^{-3} Ha/Å and 5×10^{-3} Ha/Å. Here, the adsorption energy (E_{ads}) of a cisplatin molecule onto nanotubes was defined to be:

$$E_{ads} = E(A) - E(B) - E(C) \quad (1)$$

where $E(A)$ is the total energy of pristine CNTs or Al-doped CNTs with a cisplatin molecule per supercell, $E(B)$ and $E(C)$ are the total energy of optimized pristine CNTs or Al-doped-CNTs per supercell and the total energy of isolated cisplatin molecule, respectively. Additionally, a negative of value E_{ads} indicates a favorable adsorption. That is to say, the reaction is exothermic and spontaneous without passing through any barrier. Furthermore, the more negative adsorption energy, the more stable the configuration is. On the other hand, a positive of value E_{ads} indicates a difficult adsorption.

3. Results and discussion

3.1. Adsorption of cisplatin molecule on pristine (7, 7) CNTs

In this part, the adsorption properties of cisplatin molecule on pristine (7, 7) CNTs were studied. To find out the most stable adsorption configuration, we consider several kinds of the initial structures which include the Cl, Pt and N atoms of cisplatin molecule close to the outer surface of pristine (7, 7) CNTs and the encapsulation of cisplatin molecule into the pristine (7, 7) CNTs. In the initial configurations, we have tried all kinds of atoms of cisplatin molecule to get close to the pristine (7, 7) CNTs. The selected initial configurations are representative enough. After geometry optimization, the obtained structures were showed in Fig. 1. The adsorption energy and the shortest intermolecular interaction distance were calculated (see Table 1).

It is obvious that the configuration of cisplatin molecule adsorbed inside the pristine (7, 7) CNTs has the largest adsorption energy ($E_{ads} = -0.24$ eV) compared with others. The reason can be that when cisplatin molecule was adsorbed inside the tubes, there are more weak interaction between the molecule and approaching C atoms of the pristine (7, 7) CNTs. The adsorption energy is larger and the configuration is more stable due to the effect of these weak interactions. Even though, the adsorption energy of each model in Fig. 1 is less than 0.24 eV, and the intermolecular distance of each model in Fig. 1 is greater than 3 Å which indicate the weak electron interaction between cisplatin molecule and pristine (7, 7) CNTs. According to the previous reports [36]. We can know that the adsorption process can be regarded as physisorption when the value of adsorption energy is smaller than 0.25 eV. In 1b, 1c, 1d configurations, the bond length (C-C) still is 1.42 Å. The obtained results suggest that the adsorption of cisplatin molecule on pristine (7, 7) CNTs is unstable physisorption. To sum up, it is invalid for cisplatin molecule absorbing on pristine (7, 7) CNTs. Hence, It was necessary to increase the adsorption energy by making some modifications on the surface of pristine (7, 7) CNTs.

Table 1
The obtained adsorption energies (E_{ads}) and intermolecular distances for the configurations of cisplatin molecule with pristine (7, 7) CNTs.

Configuration	E_{ads} (eV)	D (Å)
1a	−0.24	–
1b	−0.12	3.58
1c	−0.23	3.68
1d	−0.20	3.98

3.2. Adsorption of cisplatin molecule on Al-doped (7, 7) CNTs

In this part, we mainly studied the adsorption of cisplatin molecule on Al-doped (7, 7) CNTs. To construct the Al-doped (7, 7) CNTs model, one carbon atom of pristine (7, 7) CNTs was substituted by an aluminum atom. After optimization, there is a large deformation which lead to the fact that the bond length of $l_{C\text{-}C}$ = 1.42 Å turned out to be $l_{Al\text{-}C}$ = 1.87 Å. This is because the radius of Al atom is much larger than that of C atom. For the adsorption of cisplatin molecule on Al-doped (7, 7) CNTs, several possible initial structures were considered. In the initial configurations, we have tried all kinds of atoms of cisplatin molecule to get close to the Al-doped (7, 7) CNTs. The selected initial configurations are representative enough. After optimization, six configurations, such as N, Pt or Cl atom of cisplatin molecule was linked to Al atom of Al-doped (7, 7) CNTs as well as cisplatin molecule adsorbed into Al-doped (7, 7) CNTs, were obtained (see 2a, 2b, 2c, 2d, 2e, 2f of Fig. 2). We found the number of sensitive adsorption sites increase. The adsorption energy and the shortest interaction distances of these configurations are all presented in Table 2.

Ehsan studied the adsorption of Al-doped boron nitride nanotubes toward cisplatin molecule [37]. From Table 2, we can see that the adsorption energies of 2e and 2f are greater than the value of 1.5 eV in the Ehsan's research. In addition, after doping Al atom, the CNTs becomes more sensitive to cisplatin molecule which is not so much at first. And the adsorption energies of all most configurations are greater than those of the configurations of Fig. 1. But the results are quite different in the cases of pristine (7, 7) CNTs. In the 2a, 2b and 2c configurations, cisplatin molecule are adsorbed into Al-doped (7, 7) CNTs. The adsorption energy of 2b (−0.08 eV) is small. Moreover, the adsorption energies of 2a and 2c are much larger than that of 2b. In 2d, 2e and 2f configurations, cisplatin are adsorbed on Al-doped (7, 7) CNTs. And the adsorption energy of 2d is much smaller than that of 2e and 2f. That shows adsorption energy is not relative to the situation that whether cis-

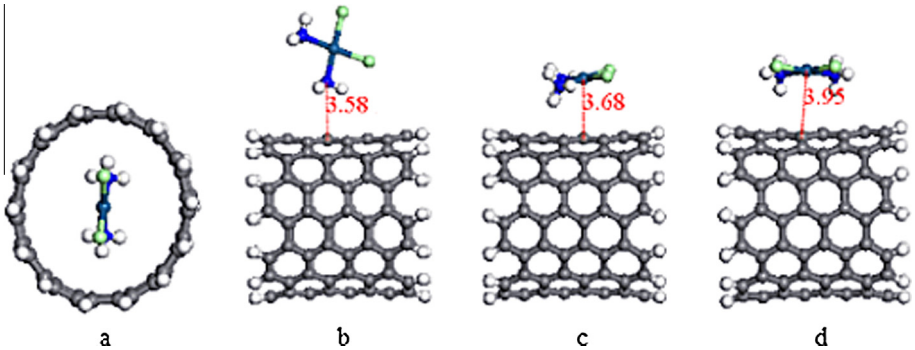

Fig. 1. The obtained different configurations for the adsorption of cisplatin on pristine (7, 7) CNTs.