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# A metallic peanut-shaped carbon nanotube and its potential for CO<sub>2</sub> capture

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# ABSTRACTS

One of the greatest challenges in greenhouse gas reduction is to develop low-cost materials capable of efficient CO<sub>2</sub> capture. Carbon, due to its flexible bonding characteristics, numerous allotropic forms, and lightweight, is an attractive material for such investigation. Inspired by the experimental synthesis of C<sub>50</sub>Cl<sub>10</sub> in milligram quantities and recent works on peanut-shaped carbon nanotubes (PSNT), using state-of-the-art first-principles theory and molecular dynamics simulation, we have discovered a new form of C<sub>50</sub> fullerene-based PSNT,  $\alpha$ -PSNT. which is not only dynamically and thermally stable, but also energetically more stable than previously identified PSNTs composed of C<sub>50</sub> cages, and can withstand temperatures to 1000 K. Due to its unique atomic configuration,  $\alpha$ -PSNT exhibits interesting physical properties including a high heat capacity, ultra-soft mechanical property with Young's modulus being a quarter of single-walled carbon nanotube (SWNT), and chirality independent metallicity. A systematical study of the adsorption properties reveals that both pristine and N-doped  $\alpha$ -PSNTs have better CO<sub>2</sub> as well as other gases because of the high density of electronic states at the Fermi level.

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# 1. Introduction

Carbon-based fuels are the main cause for the increasing level of  $CO_2$  in the atmosphere. Being a greenhouse gas,  $CO_2$  is linked to global warming. To mitigate this effect, there is increasing interest in developing materials for the sequestration of  $CO_2$  [1,2]. Since 2008, Department of Energy has been actively pursuing the  $CO_2$  sequestration program [3], which promotes the studies on noble metal-based alloys [4–6], transition metal chalcogenides [7], porous carbon monoliths [8], and enzymatic electrocatalytic systems [9] for  $CO_2$  capture and/or conversion. However, the complex synthetic procedure and the excessive cost of the noble metals [10] preclude their potential for industrial applications. To date, it remains a daunting task to find  $CO_2$  capture materials that have high surface area, good stability, low cost, and easy synthesis route.

Carbon-based materials are promising, as carbon is one of the most versatile elements and forms a number of allotropes from zero dimension (0D) to one (1D), two (2D) and three dimensions (3D) [11–13]. To this end, 1D armchair/zigzag single-walled carbon nanotubes (SWNTs) [14] have been tested for CO<sub>2</sub> adsorption. However, it is not a suitable material as CO<sub>2</sub> prefers to adsorb in the interior of the tube and binds weakly. There is experimental evidence that CO<sub>2</sub> can be adsorbed on charged fullerenes [15], but technical and stability issues prevent their practical use due to electron ionization and carbon clustering [16].

Following the discovery and bulk-synthesis of  $C_{60}$  [17],  $C_{50}$  fullerenes [18] have been synthesized in macroscopic quantities in the form of  $C_{50}Cl_{10}$  [19]. Theoretical studies of the dimers and oligomers [20] of  $C_{50}$  have been carried out and their stability has been confirmed [21].  $C_{60}$ -based PSNT has been synthesized using electron-beam (EB) irradiation method [22]. Unlike  $C_{60}$  that has  $I_h$  symmetry and isolated pentagons, the ground state isomer of  $C_{50}$  has  $D_3$  symmetry and adjacent pentagons. With higher curvature than  $C_{60}$ ,  $C_{50}$  fullerenes are more reactive [23] and, hence, may bind more strongly with each other during assembly [23] as compared to





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that of C<sub>60</sub> fullerenes. Using density functional theory (DFT), Bai et al. [24] have studied the structure and stability of D<sub>5h</sub> C<sub>50</sub>-based dimers by allowing the pentagon (hexagon) on one to interact with the pentagon (hexagon) of the other. In addition, they have also studied the structure and stability of different forms of C<sub>50</sub>-based PSNT materials. All of these materials are found to be semiconductors. No studies, thus far, have found C<sub>50</sub>-based PSNT to be metallic.

In this paper we have explored the possibility of finding a metallic C<sub>50</sub> fullerene-based PSNT, and examined the role of impurities. Moreover, we have studied the potential of this new class of materials as a possible candidate for CO<sub>2</sub> sequestration since their geometries contain the features of both 0D and 1D carbon morphology. We note that there is a growing interest in considering clusters as building blocks of cluster-assembled materials [25–28]. In the past, C<sub>60</sub> fullerenes [17] have been assembled [29] to produce such materials. Recently, instead of C<sub>60</sub> linked by [2 + 2] cyclo-additional bond [29], C<sub>60</sub>-based peanut-shaped carbon nanotubes (PSNTs) have been synthesized by electron beam irradiation [22,30], exhibiting the morphologies with both cage and tubular characteristics.

In our study of a new metallic C<sub>50</sub> fullerene-based PSNT,  $\alpha$ -PSNT, we address the following questions: Can  $\alpha$ -PSNT be stable at high temperature? If so, does its stability exceed those of already known C<sub>50</sub>-based PSNTs? What are the electronic, mechanical and thermal properties of  $\alpha$ -PSNT? Would N doping affect the properties of pristine  $\alpha$ -PSNT? Do these  $\alpha$ -PSNTs offer advantages over other carbon nanotubes for the adsorption of CO<sub>2</sub> and other gases?

#### 2. Computational methods

Calculations were carried out using density functional theory (DFT) and generalized gradient approximation (GGA) [31]. We used projector augmented wave method implemented in the Vienna Abinitio Simulation Package (VASP) [32] with the exchangecorrelation functional formulated by Perdew-Burke-Ernzerhof (PBE). The energy cutoff is 500 eV, and the convergence criteria of total energy and force components are set to be 0.0001 eV and 0.01 eV/Å. A vacuum space of 25 Å in the radial directions (y and z) is used to avoid mirror interactions. A  $7 \times 1 \times 1$  Monkhorst-Pack [33] K point mesh is adopted. Knowing that the conventional exchange-correlation functional cannot account for van der Waals (vdW) interaction, we optimized the structure with two different methods: PBE functional [31] without vdW corrections and PBE with vdW-D2 corrections [34]. We find those two different methods give same lattice parameter. Therefore, the subsequent calculations of O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, CO, and CO<sub>2</sub> adsorption are based on PBE with vdW-D2 corrections [34]. AIMD simulations are performed using the canonical ensemble with the Nosé thermostat [35] to examine thermal stability. Bader charge analysis [36] is carried out to calculate charge transfer.

## 3. Results and discussion

#### 3.1. Pristine $\alpha$ -PSNT

#### 3.1.1. Geometry

In a previous study of C<sub>50</sub>-based PSNTs, Bai et al. [24] predicted four different configurations, named T1-T4, as shown in Fig. S1 in the Supporting Information (SI). The common feature of these structures is that they all are composed of C<sub>50</sub> cages with D<sub>5h</sub> symmetry. However, the C<sub>50</sub> cage structure with D<sub>3</sub> symmetry (as shown in Fig. 1A) is 0.30 eV lower in energy than that with D<sub>5h</sub> symmetry. Thus, we constructed a PSNT structure by fusing two C<sub>50</sub> cages having D<sub>3</sub> symmetry in a unit cell. We name it as  $\alpha$ -PSNT. After full geometry optimization the lattice constant ( $l_0$ ) of  $\alpha$ -PSNT is found to be 13.81 Å, as given in Fig. 1B. The  $\alpha$ -PSNT structure has  $D_{2h}^5$  symmetry with space group *Pmma*, where the pentagons are isolate rather than fused [18]. The unit cell contains 100 carbon atoms with three chemically nonequivalent atomic Wyckoff positions: type- $\alpha$  is at the edge of 8-8 rings marked in blue, type- $\beta$  is at the edge of 5–6 rings marked in green, and type- $\gamma$  is at the edge of a 6–8 ring marked in red. When viewed along the axial direction, there are three circular structures (Fig. 1B) with diameters of 5.73 Å, 6.08 Å, and 6.78 Å, which are comparable to that of the armchair (5,5) SWNT (5.57 Å) [37] and zigzag (9,0) SWNT (7.13 Å). The bond lengths between  $\alpha$ - $\alpha$ ,  $\beta$ - $\beta$ , and  $\gamma$ - $\gamma$  carbon atoms are 1.37 Å, 1.43 Å, and 1.40 Å, respectively. The distances between  $\alpha$ - $\gamma$  and  $\beta$ - $\gamma$  carbon atoms are, respectively, 1.48 Å and 1.45 Å, which are comparable to the carbon-carbon distance in SWNT (1.42 Å) [38].

In Fig. 1C, we compare the energies per atom of  $\alpha$ -PSNT with other theoretically predicted C<sub>50</sub> PSNT [24], experimentally found C<sub>60</sub> PSNT [22,30], and C<sub>50</sub> [39,40] and C<sub>60</sub> [17] clusters. The binding energy of  $\alpha$ -PSNT is 8.92 eV per C<sub>50</sub> cluster, which that for the PSNT structures constructed by using two C<sub>50</sub> clusters assembly [25–27,41] is 8.75–8.88 eV, indicating that the  $\alpha$ -PSNT structure is energetically more stable than T1 and T3 C<sub>50</sub> PSNT structures [24]. This enhanced stability results from the isolated pentagons, which reduce the strain-related instability [18]. We plotted the XRD spectra in Fig. S2, which could be used to compare with the data of future experiments.

#### 3.1.2. Stability

In order to confirm the thermal stability of the  $\alpha$ -PSNT structure, we performed *ab initio* molecular dynamics (AIMD) simulation at 1000 K with a 3 × 1 × 1 supercell containing 300 atoms for 10 *ps* with a time step of 1 *fs*.  $\alpha$ -PSNT is found to be thermally stable as the geometry remains nearly intact without any obvious distortion and the total potential energy only fluctuates around a constant value during the simulation, as shown in Fig. 2A. Details are presented in text S1, SI. We also calculated the phonon spectra of  $\alpha$ -PSNT to study its dynamical stability. As shown in Fig. 2B, there are no any imaginary modes in the phonon spectra, confirming that  $\alpha$ -PSNT is dynamically stable.

#### 3.1.3. Mechanical properties

Having confirmed the thermal and dynamical stability of  $\alpha$ -PSNT, we then studied its mechanical property. We applied external strain from -5% to 5% along the axial direction, as shown in Fig. S3. Young's modulus was calculated using the equation,  $Y = \Delta E/(A \cdot \Delta l \cdot (\Delta l/l_0))$ , where  $\Delta E$  is the increment of the potential energy, A is the average cross-sectional area,  $\Delta l$  is the increment of the length, and  $l_0$  is the lattice parameter. The Young's modulus Y along the axial direction is calculated to be 0.273 TPa, which is about a one-fourth of that of the carbon nanotube (1.029 TPa) [42]. This suggests that  $\alpha$ -PSNT is an ultra-soft material, resulting from the combination of  $sp^2$  and  $sp^3$  bonds.

#### 3.1.4. Electronic properties

The electronic properties of  $\alpha$ -PSNT are investigated by calculating its electronic band structure, and the total and partial density of states (DOS). As shown in Fig. 3A. We note that  $\alpha$ -PSNT is metallic as the partially occupied bands cross the Fermi lever. Such phenomenal has been found in carbon structures in previous studies [43]. The band structure is very different from that of T1-T4 PSNTs [24] as they all are semiconductors. An analysis of the partial DOS reveals that the electronic states at the Fermi level are mainly contributed by the  $p_x$  orbitals of type- $\alpha$  carbon atoms. This is further confirmed by calculating the band decomposed charge density, as shown in Fig. 2B, which suggests that the highest



**Fig. 1.** (A) The most stable  $C_{50}$  isomer having  $D_3$  symmetry. (B) Top and side views of the optimized geometry of  $\alpha$ -PSNT with its lattice parameters.  $\alpha$ ,  $\beta$ , and  $\gamma$  are chemically nonequivalent carbon atoms in the unit cell. (C) Average total energy per atom of  $\alpha$ -PSNT compared to other 1D nanotubes composed of  $C_{50}/C_{60}$  clusters. (A colour version of this figure can be viewed online.)



**Fig. 2.** (A) Thermal stability examined by using *ab initio* molecular dynamics simulation at 1000 K. (B) Phonon dispersion and density of states of  $\alpha$ -PSNT. (A colour version of this figure can be viewed online.)

occupied band is contributed by the electron lone pairs on the type- $\alpha$  carbon atoms, while the lowest unoccupied band is dominated by the antibonding states of type- $\alpha$  and type- $\gamma$  carbon atoms. Besides,  $\alpha$ -PSNT could be considered as several Stone-Wales (S-W) defects rotated operations on armchair (5,5) SWNT, as presented in text S2 and Schemes S1 and SI. Because Crespi et al. [44] found that the S-W rotation in (5,5) SWNT not only keeps the system metallic, but

also increases the DOS at the Fermi level. In  $\alpha$ -PSNT, bonds formed by type- $\alpha$  atoms can be regarded as S-W defects rotated bonds, and the DOS at the Fermi level is contributed significantly by type- $\alpha$ atoms. These results are consistent with those of the TB model [44]. In addition, by employing 1D Tomonaga-Luttinger liquid (TLL) model [45], as described in text S3 and shown in Figs. S4 and SI, we find that the band with the large velocity  $v_1$  is not degenerate, whereas that with smaller velocity  $v_2$  is degenerate. According to the  $\alpha$ -PSNT band structure, the TLL ratio of  $v_2/v_1$  is 0.46, which is comparable with ratios of other 1D materials (0.36–0.62) [45]. In addition, with electron doping of 0.1 electrons per unit cell, the Fermi level can be shifted up crossing the band, as shown in Figs. S5 and SI.

We also calculated the electron localization function (ELF) [46] to further study the metallicity of  $\alpha$ -PSNT. The slices parallel and perpendicular to the axis, crossing the five pairs of type- $\alpha$  carbon, are plotted in Fig. 3C, showing that the type- $\alpha$  and type- $\gamma$  carbon atoms are surrounded by the delocalized electrons. The type- $\alpha$  carbon could be regarded as S-W defect, as mentioned above. In fact, the S-W defect leads to charge delocalization, which gives rise to metallic properties.

#### 3.1.5. Thermal properties

We then calculated heat capacity and the weighted phonon DOS (W-P-DOS) [47] to study the thermal properties of  $\alpha$ -PSNT. As phonons are subjected to Bose-Einstein distribution, the weighted phonon DOS  $g(\nu)W(h\nu/k_BT)$  describes the contribution of vibrational modes with a certain frequency to the heat capacity. The frequency and temperature dependence of the weighted phonon DOS (W-P-DOS) are plotted in Fig. 3D. The computational details are given in text S4, SI. At 50 K, more than 99% W-P-DOS exists in the region below  $350 \,\mathrm{cm}^{-1}$ , showing that, at low temperature, the low-frequency modes contribute to the heat capacity. At 300 K, nearly 20% W-P-DOS exists in the frequency region over 1200  $\text{cm}^{-1}$ suggesting that mainly frequency modes contribute to the heat capacity at room temperature. At 600 K, nearly all frequency modes are excited. The calculated results are plotted in Fig. 3E, showing the variation of the W-P-DOS with respect to the frequency at different temperatures. The calculated phonon heat capacity with respect to temperature is given in Fig. S6.



**Fig. 3.** (A) Electronic band structure and total and partial DOS, (B) band-decomposed charge density distribution of the highest occupied and lowest unoccupied bands, (C) slices of ELF from the side and top views. (D) 3D plot of W-P-DOS as a function of frequency and temperature, and (E) cross-sections of the W-P-DOS of α-PSNT. (A colour version of this figure can be viewed online.)

## 3.2. N-doped $\alpha$ -PSNT

N-doped carbon-based materials have received increased attention both experimentally [48–50] and theoretically [51,52], because of their applications in the environment and energy fields [10,53–59]. We extended the current study by substituting one C atom with one N atom in  $\alpha$ -PSNT to explore the role of the impurity. We substituted all the three nonequivalent sites,  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively, and calculated the total energies by fully optimizing the defected systems. The substitution energy  $E_s$  is calculated as follows:

$$E_s = E_{N-PSNT} - E_{PSNT} + \mu_C - \frac{1}{2}\mu_N \tag{1}$$

where  $E_{N-PNST}$  and  $E_{PSNT}$  are the total energies of N-doped and pristine  $\alpha$ -PSNT,  $\mu_C$  and  $\mu_N$  are the cohesive energy of graphene and binding energy of molecular N<sub>2</sub>, respectively. The relative energies measured with respect to the most favorable site, are given in Fig. 4A. We find that N prefers to substitute the type- $\beta$  carbon site, which lies 0.16, and 0.23 eV lower in energy than the other two configurations, respectively. The substitution energy  $E_s$  is 0.02 eV at



**Fig. 4.** (A) Three optimized configurations and their relative energies with respect to the most stable configuration, (B) strain energy curve with respect to the lattice constant, (C) slices of ELF (side and top views), and (D) band-decomposed charge density distributions of the highest occupied and lowest unoccupied bands, electronic band structure, and total and partial DOS of the N-doped α-PSNT structure. (A colour version of this figure can be viewed online.)

the nitrogen concentration of 1%, which is comparable with that in single wall carbon nanotube (0.25% atom) [60].

Next we study the mechanical property of N-doped  $\alpha$ -PSNT under external strain, as shown in Fig. 4B. The Young's modulus is calculated to be 0.271 TPa along the axial direction, which is close to that of pristine  $\alpha$ -PSNT. We find that at low N- concentration, the mechanical property of  $\alpha$ -PSNT does not change.

In order to study the charge gained by the N from its neighboring carbon atoms, we used Bader charge analysis. We found that each N atom accepts 2.71 electrons from other C atoms and remains in the system as a negative ion. The band structure, banddecomposed charge density distributions of the highest occupied and lowest unoccupied bands, and the total and partial DOS of the N-doped  $\alpha$ -PSNT are calculated and plotted in Fig. 4D, which shows that the N-doped  $\alpha$ -PSNT structure remains the feature of metallicity, while the band dispersion changes from that of pristine  $\alpha$ -PSNT. With N-doping, one extra electron is introduced into the system, consequently, it opens a gap between the original metallic bands in pristine α-PSNT and introduces one new band crossing at the Fermi level. This metallic band is mainly contributed by N  $2-p_x$ orbital as shown in the partial DOS. The ELF analysis, as shown in Fig. 4C, confirms that the delocalized charges originate from the carbon atoms surrounding the N atom. N atom has more electrons than the rest of the C atoms, indicating the ionic nature of the C-N bonds. We find that even in such low concentration (1%) limit, N doping changes the charge distribution of the system, which is caused by the donation of electrons from C p orbitals to the N lone pair *p* orbital [61].

#### 3.3. CO<sub>2</sub> adsorption

Due to their interesting electronic and physical properties, metallic carbon-based materials have been studied in great detail in recent years [11,62]. These studies have illustrated novel properties

dealing with magnetism [63], strong phonon-plasmon coupling [64], superconductivity [65], and anode materials for lithium battery [66]. Metallic carbon materials may also be useful for  $CO_2$ storage application, as the latter could be activated by electron donation, leading to stronger binding. However, only semi-metallic armchair SWNT has been used to study the adsorption of  $CO_2$  [14], which is found to adsorb  $CO_2$  on the inside surface of the tube. Here, we have studied the potential of both pristine and N-doped metallic  $\alpha$ -PSNTs to adsorb  $CO_2$ , and compared the results with those of SWNTs.

It is known that enhanced charge transfer can lead to a stronger binding of CO<sub>2</sub> molecule. We used an electrostatic potential model to predict possible adsorption sites of CO<sub>2</sub>. The details are given in text S5, SI. To find the energetically most favorable adsorbed configuration of CO<sub>2</sub>, we studied five typical adsorption sites on  $-\alpha$ .  $-\beta$ , and  $-\gamma$  carbon atoms with different vertical or parallel orientations of CO<sub>2</sub>. The fully optimized configurations and the corresponding adsorption energies are given in Figs. S8 and SI. In the lowest energy configuration, as shown in Fig. 4A, CO<sub>2</sub> molecule prefers to adsorb on the type- $\alpha$  carbon atom with an adsorption energy of 0.29 eV. Recall that the electrons are mostly delocalized around the type- $\alpha$  carbon atoms, and thus, can be easily transferred to CO<sub>2</sub>. According to Bader charge analysis, each adsorbed CO<sub>2</sub> molecular accepts 0.04 electrons from the neighboring atoms, indicating that the bonding is mainly physisorption. The total adsorbed amount of CO<sub>2</sub> on  $\alpha$ -PSNT is 0.83 mmol/g, which is larger than the 3D SWNT bundles (0.8 mmol/g) [67]. The ELF distribution, as shown in Fig. 5B, there is no indication of an ionic bond with CO<sub>2</sub>.

Besides pure carbon, N-doped carbon materials have also been studied as  $CO_2$  conversion and storage materials [48–50]. Here, we have studied  $CO_2$  adsorption on N-doped  $\alpha$ -PSNT to see if N doping offers any advantages. We note that the electronic properties of pristine  $\alpha$ -PSNT are changed due to N doping, which could influence the adsorption properties of  $CO_2$ . Nine possible configurations



Fig. 5. (A) and (B) Geometry and a slice of ELF of CO<sub>2</sub> adsorbed on  $\alpha$ -PSNT. (C) and (D) Geometry and a slice of ELF of CO<sub>2</sub> adsorbed on the N-doped  $\alpha$ -PSNT structure. (A colour version of this figure can be viewed online.)

for CO<sub>2</sub> adsorption were explored, and the corresponding adsorption energies were calculated with respect to the most stable configuration (see Figs. S10 and SI). It is found that CO<sub>2</sub> molecule prefers to adsorb near the type- $\alpha$  carbon site, adjacent to the N atom (see Fig. 5C). The adsorption energy is 0.27 eV (26.1 kJ/mol), which is slightly smaller than that of pristine  $\alpha$ -PSNT. The equilibrium distance between CO<sub>2</sub> and adsorption site is 3.29 Å. Each adsorbed CO<sub>2</sub> molecule accepts 0.06 electrons from the neighboring atoms. In Fig. 5D, the ELF slice shows a similar feature to that of CO<sub>2</sub> on the pristine  $\alpha$ -PSNT structure. The amount of adsorbed CO<sub>2</sub> on N-doped  $\alpha$ -PSNT is equal to that of pristine  $\alpha$ -PSNT, namely, 0.83 mmol/g. By comparing the adsorption sites, binding energies, charge transfers, and the ELF analysis of pristine *vs* N-doped  $\alpha$ -PSNTs, we conclude that N-doped  $\alpha$ -PSNT is a better candidate for CO<sub>2</sub> adsorption than pristine  $\alpha$ -PSNT.

In addition, we extended this study to examine the adsorption of a series of other gases (H<sub>2</sub>, CO, N<sub>2</sub>, and O<sub>2</sub>) on the pristine and Ndoped  $\alpha$ -PSNT structures. Following the same procedure used in the study of CO<sub>2</sub> adsorption, we calculated the adsorption energies and the equilibrium distances between the gas molecules and adsorption sites, respectively. The energetically most favorable adsorbed configurations are given in Figs. S10 and SI, where all the gas molecules (O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, and CO) are adsorbed on the hollow site of the type- $\beta$  carbon atoms ring, respectively. Their corresponding adsorption energies are calculated to be 29.03, 3.29, 19.85, and 32.63 kJ/mol, with the equilibrium distances of 2.280, 3.347, 2.806, and 3.229 Å for O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, and CO, respectively. While when the gas molecules are absorbed on N-doped  $\alpha$ -PSNT, the adsorption energies of O<sub>2</sub> and N<sub>2</sub> molecules are larger than those on the pristine  $\alpha$ -PSNT. The adsorption energies and the equilibrium distances for  $O_2,\ N_2,\ H_2,\ and\ CO$  are 76.42, 21.62, 17.05, and 22.19 kJ/mol, and 2.538, 3.165, 2.804, and 3.208 Å, respectively.

To study on the effect of temperature and pressure on  $CO_2$  adsorption on both the pristine and N-doped  $\alpha$ -PSNTs, we further carried out the grand canonical Monte Carlo (GCMC) calculations to provide a qualitative understanding by using the MUSIC program [68]. The computational details are presented in text S6, and the calculated results are plotted in Figs. S11 and SI. We found that at 298 K and 5000 kPa, for both the pristine and N-doped  $\alpha$ -PSNTs, the amount of CO<sub>2</sub> adsorbed is 4.15 mmol/g, while at 298 K and 10000 kPa, the corresponding amount is 8.30 mmol/g. This is comparable to that of a (5,5) SWNT. At 77 K, both for the pristine and N-doped  $\alpha$ -PSNTs, the adsorption amount of CO<sub>2</sub> is larger than that of the SWNT structure.

# 4. Conclusions

In summary, using state of the art theoretical calculations, we have systematically studied the structure and properties of a new metallic  $\alpha$ -PSNT composed of C<sub>50</sub> fullerenes with D<sub>3</sub> symmetry. The potential of this carbon allotrope in sequestering gases, including CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, and CO, has also been analyzed in its pristine form as well as the one doped with N atoms. Following are our main results: (1)  $\alpha$ -PSNT prefers isolated rather than fused pentagon structures, and is energetically more stable than the PSNTs structures composed of C<sub>50</sub> fullerenes having D<sub>5h</sub> symmetry because its structural unit, C<sub>50</sub> fullerene with D<sub>3</sub> symmetry, is lower in energy than that with D<sub>5h</sub> symmetry. (2)  $\alpha$ -PSNT possesses a high heat capacity, and is metallic. Its Young's modulus is only a quarter of that of carbon nanotubes, exhibiting an ultra-soft mechanical

property. (3) N doping does not change the lattice parameter, mechanical property, and the metallicity. The energy cost for substituting a C atom with N is only 0.016 eV, thus, making it easy to synthesize N-doped  $\alpha$ -PSNTs. (4) Both pristine and N-doped  $\alpha$ -PSNTs have better CO<sub>2</sub> adsorption properties as compared to SWNTs. We hope that these results will motivate experimentalists to synthesize  $\alpha$ -PSNT and N-doped  $\alpha$ -PSNT materials, and study their potential for gas storage.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.carbon.2018.02.061.

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