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NITROGEN ADSORPTION ON DOUBLE-WALLED CARBON NANOTUBE AT DIFFERENT TEMPERATURES: MECHANISTIC INSIGHTS FROM MOLECULAR DYNAMICS SIMULATIONS

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Nitrogen-adsorbing carbon nanotubes have received considerable attention in the field of materials science due to their unique properties and potential applications. In particular, nitrogen-adsorbed double-walled carbon nanotubes (DWNTs) can exhibit a wide range of tunable electronic and optoelectronic properties. In this study, the effect of different temperatures (i.e., 300, 600, and 900 K) of DWNT on nitrogen adsorption is investigated through molecular dynamics simulations using the ReaxFF potential. The simulation results show a good nitrogen storage capacity of DWNT, particularly at 600 K, reaching a maximum gravimetric density of 12.4 wt%. This study contributes to a better understanding of the mechanisms governing nitrogen adsorption onto DWNTs at different temperatures.
Keywords: *Double-walled carbon nanotube, Nitrogen adsorption, Reactive molecular dynamics*
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INTRODUCTION

Carbon nanotubes (CNTs) have garnered broad interest across physics, chemistry, and materials science [1], showcasing promise in diverse applications including electronic devices [2], sensors [3], material reinforcement [4], adsorbents [5], and numerous other areas [7]. Among them, double-walled carbon nanotubes (DWNTs) have gained significant attention due to their improved stability and mechanical properties [8],[9]. The interactions of DWNTs with other atoms and molecules, particularly boron (B) [10], nitrogen (N) [11], calcium (Ca) [12], palladium (Pd) [13] and platinum (Pt) [14] have been intensively studied in recent years.

Among them, nitrogen (N) atoms adsorption (i.e., chemisorption) on carbon nanotubes has gained much attention in recent years due to its applications in various fields such as energy storage and catalysis [5], [6]. N atom chemisorption and doping on DWNTs are being explored as promising strategies to modify their electrical and chemical properties for various applications. Several studies have investigated the chemisorption mechanism of N atoms on the outer and inner walls of DWNTs, as well as the effect of N doping on their electronic and optical properties [15]. Chemisorption of N atoms on DWNTs depends on various factors, such as tube diameter and chirality, which in turn affect the strength and type of interaction with the adsorbate [11]. In this respect, understanding the chemisorption processes of N atoms on DWNTs is essential for the design of efficient nanomaterials for gas detection and separation [16], [17], [18]. Although nitrogen (N) atoms have been introduced into CNTs by various methods (e.g., CVD, ALD), controlling their amount in the structure is still one of the pressing problems [19], [20].

In this study, we investigate the chemisorption mechanisms of N atoms on DWNT at different temperatures using molecular dynamics (MD) simulations.

COMPUTATIONAL DETAILS

The process of nitrogen adsorption onto DWNTs is investigated using reactive MD simulations [21] using the LAMMPS package [22]. The ReaxFF potential is used to describe the interatomic interactions in the system [23]. This potential is chosen to describe the breaking and joining of bonds between atoms. A neat (5,5@10,10) nanotube was chosen as a DWNT model (DWNT(5,5)@(10,10)) in MD simulations (Fig.1). The diameter of DWNTs is 6.78 and 13.57Å (Fig. 1) which is in the range of experimentally obtained nanotube diameters (6.3Å–7.9Å) and (13Å–16Å) [24]. Periodic boundary conditions are applied along the z-axis, which represents the length of the DWNT (28.12 Å), allowing the simulation of infinitely long DWNTs.

Initially, the energy of all model systems is minimized by the conjugated gradient method. Subsequently, the temperature and pressure of the systems are equilibrated to the desired values (300 K, 600, 900K and 0 Pa) in the NpT ensemble using a Berendsen thermostat and barostat [25] with coupling constants of 100 fs and 5000 fs, respectively. The chosen heating rate (i.e., 1 K/ps) corresponds to a previously reported range of values (0.1–10.0 K/ps) [26] and indicates that the deviations in the thermodynamic equilibrium of the model systems are insignificant during the temperature increase. In the case of the chemisorbtion of N atoms on DWNT, the system's temperature is kept at 300 K, 600 K and 900 K for 100 ps using a Bussi thermostat [27] with a coupling constant of 100 fs in the canonical NVT ensemble.

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In the simulations, the pressure of N atoms in the system is calculated as $p = J\sqrt{2\pi MRT}/N_A$, [28] (1), where J is the impingement flux ($nm^{-2}\cdot ns^{-1}$), N_A is Avagadro's number, R is the universal gas constant, M is the molar mass of the N atom ($kg\cdot mol^{-1}$) and T is the temperature of the system (K). In this work, the impingement flux of the incident N atoms (i.e.,100 N) is 78.74 $nm^{-2}\cdot ns^{-1}$, and its corresponding pressure is approximately 1.94 MPa. The simulation is done under *NVT* conditions with N atoms added to the environment surrounding the surface of the nanotube at a 10 ps interval, and with a minimum distance of 10 Å (i.e., the cutoff radius of the interaction potential) between each N atoms and the model system.

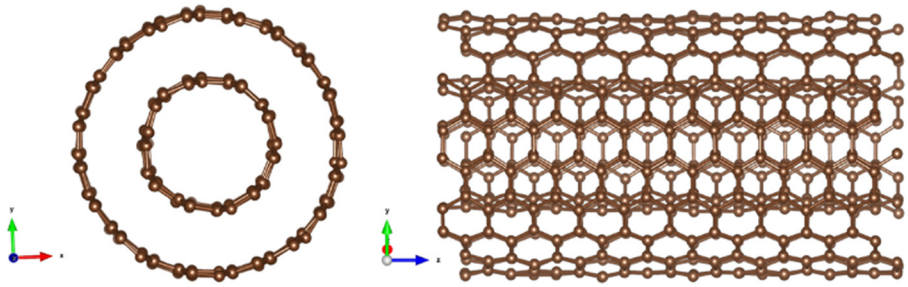

Figure 1. Top and side views of the DWNT(5,5)@(10,10) model system

The gravimetric density of nitrogen (N) atoms remaining on the surface of pure DWNTs under the influence of different temperatures (300 K, 600 K, 900 k) was calculated as follows:

$$wt\% = (1 + m_C N/m_N n)^{-1} \times 100\% \qquad (1)$$

where m_C and N are the mass and number of carbon atoms in DWNT, m_N and n are the mass and number of adsorbed N atoms.

In all MD simulations, a time step of 0.1 fs is used. The simulations are repeated 5 times for each study case, and the final results are obtained by averaging the individual physical quantities.

RESULTS AND DISCUSSION

It can be seen from the results that N atoms adsorbed on the DWNT(5,5)@(10,10) surface for systems with different temperatures (i.e. 300, 600, 900 K) number adsorption N (%) atoms (or adsorption index, ($N_{adsorption}/N_{total}$,%) also varied. Specifically, with an increase in the number of adsorbed N atoms at a temperature of 300 K, the number of adsorbed N atoms was in the range of 2-48% (Fig.2*a*). Temperature of 600 K and 900 K, it is in the range of 2-77% and 10-61%, respectively.

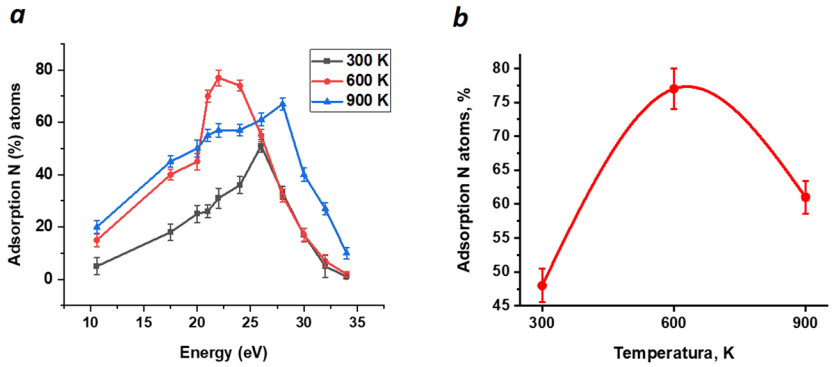

Figure 2. (a) Dependence of the number of adsorbed nitrogen (N) atoms on their kinetic energy, (b) The temperature dependence of the maximum adsorption index of nitrogen atoms.

That is, at temperatures of 300 K, 600 K and 900 K, the maximum adsorption index was equal to 48%, 77% and 61% (Fig.2*b*). The largest adsorption index is at 600 K, which is 1.52 and 1.19 times greater than at 300 K and 900 K. It can be seen from the results that the adsorption index did not increase linearly with increasing temperature. From the results, it is known that the temperature also affects the N adsorption process. As the velocity (i.e., kinetic energy) of N atoms falling on the DWNT(5,5)@(10,10) surface increased, the adsorption level also increased (from 0 eV to 22.50 eV), further increasing the velocity of N atoms led to a decrease in the amount of adsorption (about, 26.24 eV for 300 K, 22.50 eV for 600 K and 28.74 eV for 900 K). The results indicate that an additional elevation in energy (i.e., 33.15 eV) led to a decrease in the adsorption index to a value approaching 0% (Fig.2*a*).

The chemisorption of N atoms on DWNT relies on multiple factors, such as the curvature of the nanotube surface, the arrangement of the six-membered carbon rings, among others [29],[30]. Furthermore, the adsorption index of DWNT varies at different temperatures. Depending on their position (para, ortho, meta) within the hexagon cell of the CNT,

N atoms on the surface of CNT can depart from the surface due to the influence of temperature [31]. N atoms adsorbed on the DWNT surface are influenced by the arrival of other N atoms on the surface, leading to the formation of molecules through the Langmuir-Hinshelwood recombination mechanism (where two N atoms on the surface covalently bond to form a nitrogen molecule) or Eley-Rideal desorption mechanism on the surface due to the impact of incoming N atoms on the adsorbed N atom [32], [33]. The temperature range (i.e., 300–900 K) employed in this study altered the quantity of N atoms adsorbed on the surface.

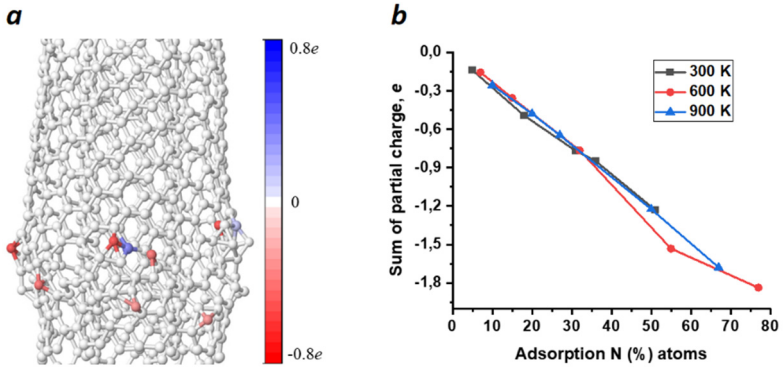

Figure 3. (a) N atoms chemisorbed onto DWNT(5,5)@(10,10) are introduced, and system atoms exhibit partial charges from -0.8e to +0.8e, which range from red to blue is depicted by the color spectrum, which shows the transition from electron-rich regions to electron-poor regions, respectively, (b) The alteration in the partial charge of adsorbed N atoms in relation to temperature

In addition to these effects, in CNT, the carbon atom has a higher electronegativity value (χ=2.55) compared to the N atom (χ = 3.04). Figure *3a* shows the chemisorption process of N atoms on DWNT(5,5)@(10,10). Atoms in the system are depicted in blue with a positive charge and red with a negative charge, while uncharged (*0*) atoms are depicted in white. This difference in electronegativity results in interactions such as Coulomb forces between the CNT surface and N atoms. This, in turn, results in a relatively stronger interaction between N atoms and C atoms on the DWNT(5,5)@(10,10) surface, thereby leading to higher adsorption of N atoms on DWNT(5,5)@(10,10). Figure 3b illustrates that the partial charge increases with the rise in the adsorption index (%) of chemisorbed N atoms on DWNT(5,5)@(10,10).

Table 1. The variation in the partial charge of adsorbed nitrogen (N) atoms (%) is demonstrated as a function of temperature.

Adsorption *N* atoms, %	300 K		Adsorption *N* atoms, %	600 K		Adsorption *N* atoms, %	900 K	
	C	N		C	N		C	N
5	0.14*e*	-0.14*e*	7	0.15*e*	-0.15*e*	10	0.25*e*	-0.25*e*
18	0.49*e*	-0.49*e*	15	0.35*e*	-0.35*e*	20	0.48*e*	-0.48*e*
31	0.76*e*	-0.76*e*	32	0.76*e*	-0.76*e*	27	0.65*e*	-0.65*e*
36	0.85*e*	-0.85*e*	55	1.53*e*	-1.53*e*	50	1.22*e*	-1.22*e*
51	1.23*e*	-1.23*e*	77	1.84*e*	-1.84*e*	67	1.67*e*	-1.67*e*

As a result, the sum of maximum partial charges of C and N atoms appropriately 1.23*e* and -1.23*e* (51 %) for 300 K, 1.84*e* and -1.84*e* (77 %) for 600 K, 1.67*e* and -1.67*e* (67 %) for 900 K which corresponds to the values of 5–77 % respectively (Table 1). This indicates that an increase in the concentration of N leads to an increase in negative (n-type) partial charges of the DWNT. This validates the outcomes achieved in earlier investigations [34].

Figure 4 shows the nitrogen adsorption coverage (ρ%=N_N/N_C) and gravimetric density (wt%) of N atoms as a function of temperature. As can be seen from the figure, the ρ % (or, wt%) of N atoms at 300, 600 and 900 K is different, the maximum adsorption of N atoms on the surface at 300 K, 600 K and 900 K level 8 % (or 9.3 wt%), 12.1 % (or 12.4 wt%), 10.18% (or 10.6 wt%), respectively.

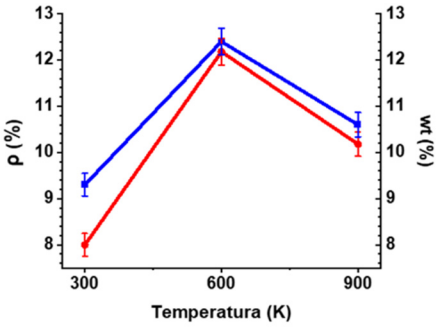

Figure 4. The gravimetric density of chemisorbed N atoms (right, blue) and the adsorption coverage (left, red) as a function of temperature

CONCLUSION

We can conclude that this molecular dynamics simulation has successfully visualized the N adsorption mechanism in DWNT(5,5)@(10,10). In this simulation the trend of N adsorbed in DWNT(5,5)@(10,10) is influenced by temperature factors. The N adsorption by DWNT(5,5)@(10,10) at lower temperatures such as at 300 K has a higher amount of N concentration than at higher temperatures (600 K and 900 K). As the temperature increases at a constant pressure, the amount of N that adsorbed will be decreases. While the trend of the amount of N absorbed will growth with increasing pressure at a constant temperature. The best result of gravimetric density 12.4 wt% (or 12.1% nitrogen concentration) that occurred at 1.94 MPa pressure with temperature (600 K) condition.

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АДСОРБЦІЯ АЗОТУ НА ДВОСТІННИХ ВУГЛЕЦЕВИХ НАНОТРУБКАХ ПРИ РІЗНИХ ТЕМПЕРАТУРАХ: МЕХАНІСТИЧНІ ДОСЛІДЖЕННЯ З МОДЕЛЮВАННЯ МОЛЕКУЛЯРНОЇ ДИНАМІКИ

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Вуглецеві нанотрубки, що адсорбують азот, привернули значну увагу в галузі матеріалознавства завдяки своїм унікальним властивостям і можливому застосуванню. Зокрема, адсорбовані азотом подвійні стінкові вуглецеві нанотрубки (DWNTs) можуть демонструвати широкий спектр регульованих електронних і оптоелектронних властивостей. У статті досліджується вплив різних температур (300, 600 і 900 K) DWNT на адсорбцію азоту за допомогою моделювання молекулярної динаміки з використанням потенціалу ReaxFF. Результати моделювання показують хорошу здатність DWNT зберігати азот, особливо при 600 K, досягаючи максимальної ваговій щільності 12,4% мас. Це дослідження сприяє кращому розумінню механізмів адсорбції азоту на DWNT при різних температурах.

Ключові слова: *двостінна вуглецева нанотрубка; адсорбція азоту; реактивна молекулярна динаміка*