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.

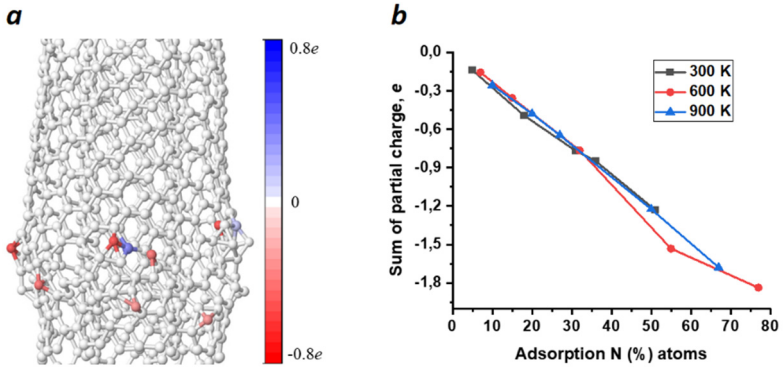

Figure 3. (a) N atoms chemisorbed onto DWNT(5,5)@(10,10) are introduced, and system atoms exhibit partial charges from -0.8e to +0.8e, which range from red to blue is depicted by the color spectrum, which shows the transition from electron-rich regions to electron-poor regions, respectively, (b) The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

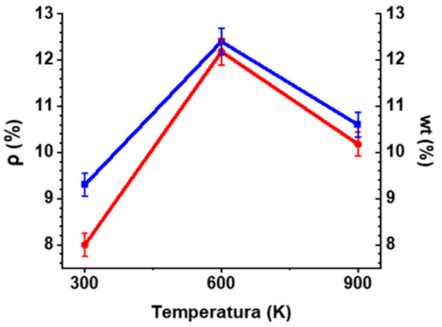

Figure 4. The gravimetric density of chemisorbed N atoms (right, blue) and the adsorption coverage (left, red) as a function of temperature

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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REFERENCES

[1] S. Iijima, "Carbon nanotubes: past, present, and future", Phys. B Condens. Matter, **323**(1-4), 1–5 (2002). https://doi.org/10.1016/S0921-4526(02)00869-4

[2] M. Soto, et al., "Effect of interwall interaction on the electronic structure of double-walled carbon nanotubes", Nanotechnology, **26**(16), 165201 (2015). https://doi.org/10.1088/0957-4484/26/16/165201

[3] Q. Wei, X. Tong, G. Zhang, J. Qiao, Q. Gong, and S. Sun, "Nitrogen-Doped Carbon Nanotube and Graphene Materials for Oxygen Reduction Reactions", Catalysts, **5**(3), 1574–1602 (2015). https://doi.org/10.3390/catal5031574

[4] E.N. Nxumalo, and N.J. Coville, "Nitrogen Doped Carbon Nanotubes from Organometallic Compounds: A Review", Materials, **3**(3), 2141–2171 (2010). https://doi.org/10.3390/ma3032141

[5] F. Shojaie, "N2 adsorption on the inside and outside the single-walled carbon nanotubes by density functional theory study", Pramana, **90**(1), 4 (2018). https://doi.org/10.1007/s12043-017-1498-5

[6] M. Jamshidi, M. Razmara, B. Nikfar, and M. Amiri, "First principles study of a heavily nitrogen-doped (10,0) carbon nanotube", Phys. E Low-Dimens. Syst. Nanostructures, **103**, 201–207 (2018). https://doi.org/10.1016/j.physe.2018.06.003

[7] C. Zhao, Y. Lu, H. Liu, and L. Chen, "First-principles computational investigation of nitrogen-doped carbon nanotubes as anode materials for lithium-ion and potassium-ion batteries", RSC Adv. **9**(30), 17299–17307 (2019). https://doi.org/10.1039/C9RA03235E

[8] S.-P. Ju, *et al.*, "A molecular dynamics study of the mechanical properties of a double-walled carbon nanocoil", Comput. Mater. Sci. **82**, 92-99 (2014). https://doi.org/10.1016/j.commatsci.2013.09.024

[9] V. Zólyomi, *et al.*, "Intershell interaction in double walled carbon nanotubes: Charge transfer and orbital mixing", Phys. Rev. B, **77**(24), 245403 (2008). https://doi.org/10.1103/PhysRevB.77.245403

[10] T. Koretsune, and S. Saito, "Electronic structures and three-dimensional effects of boron-doped carbon nanotubes", Sci. Technol. Adv. Mater. **9**(4), 044203 (2008). https://doi.org/10.1088/1468-6996/9/4/044203

[11] K.-Y. Chun, H.S. Lee, and C.J. Lee, "Nitrogen doping effects on the structure behavior and the field emission performance of double-walled carbon nanotubes", Carbon, **47**(1), 169–177 (2009). https://doi.org/10.1016/j.carbon.2008.09.047

[12] S.H. De Paoli Lacerda, J. Semberova, K. Holada, O. Simakova, S. Hudson, and J. Simak, "Carbon Nanotubes Activate Store-Operated Calcium Entry in Human Blood Platelets", ACS Nano, **5**(7), 5808–5813 (2011). https://doi.org/10.1021/nn2015369

[13] H. Wu, D. Wexler, and H. Liu, "Effects of different palladium content loading on the hydrogen storage capacity of double-walled carbon nanotubes", Int. J. Hydrog. Energy, **37**(7), 5686–5690 (2012). https://doi.org/10.1016/j.ijhydene.2011.12.120

[14] D. Xia *et al.*, "Extracting the inner wall from nested double-walled carbon nanotube by platinum nanowire: molecular dynamics simulations", RSC Adv. **7**(63), 39480–39489 (2017). https://doi.org/10.1039/C7RA07066G

[15] J.D. Correa, E. Florez, and M.E. Mora-Ramos, "Ab initio study of hydrogen chemisorption in nitrogen-doped carbon nanotubes", Phys. Chem. Chem. Phys. **18**(36), 25663–25670 (2016). https://doi.org/10.1039/C6CP04531F

[16] H. Soleymanabadi, and J. Kakemam, "A DFT study of H2 adsorption on functionalized carbon nanotubes", Phys. E Low-Dimens. Syst. Nanostructures, **54**, 115–117 (2013). https://doi.org/10.1016/j.physe.2013.06.015

[17] R. Kronberg, H. Lappalainen, and K. Laasonen, "Hydrogen Adsorption on Defective Nitrogen-Doped Carbon Nanotubes Explained via Machine Learning Augmented DFT Calculations and Game-Theoretic Feature Attributions", J. Phys. Chem. C, **125**(29), 15918–15933 (2021). https://doi.org/10.1021/acs.jpcc.1c03858

[18] Y. Fujimoto, and S. Saito, "Structure and stability of hydrogen atom adsorbed on nitrogen-doped carbon nanotubes", J. Phys. Conf. Ser. **302**, 012006 (2011). https://doi.org/10.1088/1742-6596/302/1/012006

[19] M. Terrones, A. Jorio, M. Endo, A.M. Rao, Y.A. Kim, T. Hayashi, H. Terrones, *et al.*, "New direction in nanotube science", Mater. Today, **7**(10), 30–45 (2004). https://doi.org/10.1016/S1369-7021(04)00447-X

[20] M. Glerup, M. Castignolles, M. Holzinger, G. Hug, A. Loiseau, and P. Bernier, "Synthesis of highly nitrogen-doped multi-walled carbon nanotubes", Chem. Commun. **20**, 2542 (2003). https://doi.org/10.1039/b303793b

[21] B.J. Alder, and T.E. Wainwright, "Phase Transition for a Hard Sphere System", J. Chem. Phys. **27**(5), 1208–1209 (1957). https://doi.org/10.1063/1.1743957

[22] A.P. Thompson, H.M. Aktulga, R. Berger, D.S. Bolintineanu, W.M. Brown, P.S. Crozier, P.J. Veld, *et al.*, "LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales", Comput. Phys. Commun. **271**, 108171 (2022). https://doi.org/10.1016/j.cpc.2021.108171

[23] K. Chenoweth, A. C. T. Van Duin, and W. A. Goddard, "ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation", *J. Phys. Chem. A*, vol. 112, no. 5, pp. 1040–1053, 2008, https://doi.org/10.1021/jp709896w

[24] G. Chen, *et al.*, "Chemically Doped Double-Walled Carbon Nanotubes: Cylindrical Molecular Capacitors", Phys. Rev. Lett. **90**(25), 257403 (2003). https://doi.org/10.1103/PhysRevLett.90.257403
[25] H.J.C. Berendsen, J.P.M. Postma, W.F. Van Gunsteren, A. DiNola, and J.R. Haak, "Molecular dynamics with coupling to an external bath", J. Chem. Phys. **81**(8), 3684–3690 (1984). https://doi.org/10.1063/1.448118
[26] J. Sun, P. Liu, M. Wang, and J. Liu, "Molecular Dynamics Simulations of Melting Iron Nanoparticles with/without Defects Using a Reaxff Reactive Force Field", Sci. Rep. **10**(1), 3408 (2020). https://doi.org/10.1038/s41598-020-60416-5
[27] G. Bussi, D. Donadio, and M. Parrinello, "Canonical sampling through velocity rescaling", J. Chem. Phys. **126**(1), 014101 (2007). https://doi.org/10.1063/1.2408420
[28] D. Ugarte, A. Châtelain, and W.A. De Heer, "Nanocapillarity and Chemistry in Carbon Nanotubes", Science, **274**(5294), 1897-1899 (1996). https://doi.org/10.1126/science.274.5294.1897
[29] P. Ayala, A. Grüneis, T. Gemming, D. Grimm, C. Kramberger, M.H. Rümmeli, F.L. Freire Jr., *et al.*, "Tailoring N-Doped Single and Double Wall Carbon Nanotubes from a Nondiluted Carbon/Nitrogen Feedstock", J. Phys. Chem. C, **111**(7), 2879–2884 (2007). https://doi.org/10.1021/jp0658288
[30] W. Su, X. Li, L. Li, D. Yang, F. Wang, X. Wei, W. Zhou, *et al.*, "Chirality-dependent electrical transport properties of carbon nanotubes obtained by experimental measurement", Nat. Commun. **14**(1), 1672 (2023). https://doi.org/10.1038/s41467-023-37443-7
[31] U. Khalilov, A. Bogaerts, B. Xu, T. Kato, T. Kaneko, and E. C. Neyts, "How the alignment of adsorbed ortho H pairs determines the onset of selective carbon nanotube etching", Nanoscale, **9**(4), 1653–1661 (2017). https://doi.org/10.1039/C6NR08005G
[32] X. Sha, B. Jackson, and D. Lemoine, "Quantum studies of Eley–Rideal reactions between H atoms on a graphite surface", J. Chem. Phys. **116**(16), 7158–7169 (2002). https://doi.org/10.1063/1.1463399
[33] T. Zecho, A. Güttler, X. Sha, D. Lemoine, B. Jackson, and J. Küppers, "Abstraction of D chemisorbed on graphite (0001) with gaseous H atoms", Chem. Phys. Lett. **366**(1-2), 188–195 (2002). https://doi.org/10.1016/S0009-2614(02)01573-7
[34] R. Czerw, M. Terrones, J.-C. Charlier, X. Blase, B. Foley, R. Kamalakaran, N. Grobert, *et al.*, "Identification of Electron Donor States in N-Doped Carbon Nanotubes", Nano Lett. **1**(9), 457–460 (2001). https://doi.org/10.1021/nl015549q

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*