Interaction of CO and CH₄ Adsorption with Noble Metal (Rh, Pd, and Pt)-Decorated N₃-CNTs: A First-Principles Study

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ABSTRACT: Using a first-principles theory, the structural and electronic behaviors of noble metal atom (Rh, Pd, and Pt)-decorated N₃-CNTs were investigated. Meanwhile, the adsorption behavior of CO and CH₄ molecules onto Rh-, Pd-, and Pt-decorated N₃-CNTs was studied as well to exploit their potential applications. Results indicate that noble metal atoms are likely to be adsorbed on the N₃ center of pyridine-like N₃-CNTs under electrophilic attack. Moreover, the noble metal-embedded N₃ group would provide CNTs with enhanced performance for gas adsorption compared with noble metal-embedded surfaces because of the improvement of chemical activity and electron mobility in our proposed configurations. The findings in this report would be beneficial for exploiting a possible adsorbent for CO scavenging with excellent adsorbing ability and a possible sensor for CH₄ detection with good sensitivity and recovery behavior.

1. INTRODUCTION

In recent years, noble metal atom(s) (including Rh, Pd, Pt, Au, and Ag)-embedded single-walled carbon nanotubes (CNTs), acting as the catalytic center for gas interactions, have aroused considerable interest among the research community. It has been reported that chemisorption could be achieved in systems where noble metal-embedded CNTs were proposed for gas adsorption with a significant change in physicochemical properties and enhanced adsorption behavior compared with intrinsic CNTs which performs weak physisorption instead. Furthermore, the N-modified CNT was exploited not only as an effective catalyst for gas adsorption but also as nanosupport anchoring metal atoms to obtain combined catalytic activity for gas interactions. Increasingly, the existence of the pyridine-like N₃ group in the sidewall of single-walled CNTs has been demonstrated by electron energy loss spectroscopy and X-ray photoelectron spectroscopy measurements. Moreover, it has been reported that the N₃-CNT possesses desirable sensitivity and reactivity to various gas molecules because of the introduction of novel states near the Fermi level for CNTs by doping N atoms. In this regard, the pyridine-like N-modified CNT is regarded as a promising support immobilizing certain noble metal atoms to gain superimposed catalytic property toward gas interactions.

The study of interactions between pyridine-like N₃-doped CNTs (N₃-CNTs) and noble metal atoms is meaningful to understand the transformations in structural and electronic behaviors of that support induced by metal dopants and to exploit potential applications for the metal-embedded structures. In this work, the physicochemical behaviors of Rh-, Pd-, and Pt-decorated N₃-CNTs (MN₃-CNTs, M represents Rh, Pd, or Pt) along with adsorption behavior of MN₃-CNTs upon CO and CH₄ molecules were comprehensively investigated using the first-principles theory. Although there have been experimental reports investigating the sensing behavior of novel nanomaterials toward such two gases, to the best of our knowledge, this is the first theoretical study concerning gas adsorption on MN₃-CNTs at the molecular level. Results indicated that the noble metal-embedded N₃ group would provide CNTs with enhanced performance for...
gas adsorption compared with noble metal-embedded surfaces because of the improvement of chemical activity and electron mobility in our proposed configurations. The findings in this report would be beneficial for exploiting a possible adsorbent for CO scavenging with excellent adsorbing ability and a possible sensor for CH₄ detection with good sensitivity and recovery behavior.

2. RESULTS AND DISCUSSION

2.1. Decoration of Rh, Pd, or Pt Atoms on N₃-CNTs. For comparison, we analyzed the electronic property for pure N₃-CNTs. Results show that three N dopants in the N₃-CNT system perform as electron acceptors withdrawing, from the tube, 0.265, 0.266, and 0.248 e, respectively, thus forming highly localized acceptor-like states at the Fermi level because of the existence of lone pairs of electrons. That is to say, the N₃ group in the N₃-CNT would induce nonbonding electrons in the sp² orbitals of the CNT.

Figure 1 depicts the most stable geometric configurations and deformation charge distribution (DCD) of Rh-, Pd-, and Pt-decorated N₃-CNTs. It would be worth mentioning that the geometric structure of MN₃-CNTs here is in good agreement with the previous report which demonstrates that the most stable decoration configuration for a noble metal on N₃-CNTs is the middle vacancy site. Besides, three metal atoms are protruded outside of the N₃-CNT sidewall to various degrees because of different binding forces of M–N bonds. Detailed analyses for these structures are as follows.

For the RhN₃-CNT configuration in Figure 1a, the Rh dopant is captured by the N₃ group with three Rh–N bond lengths of 2.040, 2.038, and 1.922 Å. The Rh atom acts as an electron donator releasing 0.232 e to the N₃-CNT, while the electron distribution of the N₃ center is further enhanced as a result of its strong electron-withdrawing property. Similarly, three Pd–N bonds are measured to be 2.224, 2.225, and 2.044 Å in the PdN₃-CNT system shown in Figure 1b, while three Pt–N bonds are measured to be 2.167, 2.147, and 1.982 Å in the PtN₃-CNT system shown in Figure 1c. It could be found that the average bond length of Pd–N is the largest, followed by Pt–N, and the shortest one comes to Rh–N. In other words, the binding force of M–N could be ordered as follows: Rh–N > Pt–N > Pd–N. Meanwhile, Pd and Pt dopants donate 0.279 and 0.212 e, respectively, to the supports, which makes the N₃ group more electron-centralized. These confirm the strong electron-accepting property of N₃-CNTs and the active electron-donating behavior of noble metal atoms. Practically, this also could be concluded from the DCD of three MN₃-CNT systems, where metal dopants with a deep red area around behave as electron donators, while the blue area is mainly located on the N₃-CNT, indicating that it accepts electrons from the impure dopants.

The density of states (DOS) analysis for Rh-, Pd-, and Pt-decorated N₃-CNTs was implemented as well to give further insight into the electronic behavior of these structures. As shown in Figure 2, the partial DOS curves of metal dopants (Rh, Pd, and Pt) and the N₃ group match well with total DOS curves of the related whole system, especially those areas near the Fermi level, where the metal dopant in every system even contributes more to the total DOS than the N₃ group. That is to say, the electronic behavior of MN₃-CNTs would be largely tuned by the metal dopants. From the partial DOS, we could find that the Rh 4d, Pd 4d, and Pt 5d orbitals are strongly hybridized with the N 2p orbital, leading to the large area of overlap in their DOS curves. This means that the chemical interaction occurs between Rh, Pd, or Pt atoms and N₃-CNTs, causing evident electron transfer and making the noble metal-decorated systems more active.

2.2. Adsorption of CO onto the Rh-, Pd-, or Pt-Decorated N₃-CNT Surface. The most stable configuration for CO adsorption onto the MN₃-CNT surface and the related total charge density (TCD) are depicted in Figure 3. To begin with, one can see an obvious overlap of electron cloud between MN₃-CNTs and CO molecules, which indicates a strong interaction in the three systems.

Figure 1. Geometric structure and DCD for Rh-, Pd-, and Pt-decorated N₃-CNTs. (a) RhN₃-CNT system; (b) PdN₃-CNT system; and (c) PtN₃-CNT system.
For the RhN$_3$-CNT/CO system shown in Figure 3a, we can find that the Rh–N bonds are stretched to 1.996, 2.145, and 2.090 Å, and the C atom of the adsorbed CO molecule is attached by the Rh dopant with a bond length of 1.897 Å. It is worth noting that the sum of single bond covalent radii of Rh and C (2.00 Å) is even shorter than the obtained bond length Rh–C in this configuration, which provides a potent evidence demonstrating the strong binding force of Rh toward the CO molecule and the chemisorption nature for the CO molecule onto the RhN$_3$-CNT. 13

Upon PdN$_3$-CNT/CO and PtN$_3$-CNT/CO systems in Figure 3b,c, it could be observed that, like the geometry of the RhN$_3$-CNT/CO system, the C atom of the CO molecule prefers to be adsorbed and trapped by metal dopants with formed bond lengths of 1.893 Å for the PdN$_3$-CNT/CO system and 1.840 Å for the PtN$_3$-CNT/CO system. It is interesting to illustrate that the bond lengths of Pd–C and Pt–C in two adsorbed systems are both shorter than the sum of covalent radii of Pd and C (1.95 Å) along with Pt and C (1.98 Å), which confirms the strong binding force of noble metal dopants (Pd and Pt) toward the CO molecule and leads to the formation of chemical bonds in these systems. Moreover, a similar phenomenon in these two configurations is that one M–N bond is broken and the other two deform to various degrees after CO adsorption, enlarging to 2.129 and 2.217 Å for the PdN$_3$-CNT/CO system and to 2.207 and 2.102 Å for the PtN$_3$-CNT/CO system. This is in agreement with the analysis in a previous reference that metal dopants possess a strong binding force toward the CO molecule. 16

The $E_{ad}$ values are calculated to be $-1.90$ and $-2.94$ eV, while $Q_T$ values are calculated to be $0.197$ and $0.178$ e for PdN$_3$-CNT/CO and PtN$_3$-CNT/CO systems, respectively. It would be worth noting that, according to previous reports, $E_{ad}$ and $Q_T$ are $-1.81$ eV and $0.168$ e for the Pd-CNT/CO system, while they are $-1.73$ eV and $-0.12$ e for the Pt-CNT/CO system, respectively. 17 This demonstrates that the embedded MN$_3$ group in the CNT would provide the system with enhanced performance toward CO adsorption compared with its metal-doped counterpart. Moreover, the C–H bond of the CH$_4$ molecule is elongated to 1.160 Å in the PdN$_3$-CNT system and to 1.167 Å in the PtN$_3$-CNT system. This agrees with the adsorption performance order for MN$_3$-CNT toward the CO molecule of Pt$_3$-CNT > RhN$_3$-CNT > PdN$_3$-CNT.

The $E_{ad}$ values for the Rh–N bonds are 1.996, 2.145, and 2.090 Å, and the C atom of the adsorbed CO molecule is attached by the Rh dopant with a bond length of 1.897 Å. It is worth noting that the sum of single bond covalent radii of Rh and C (2.00 Å) is even shorter than the obtained bond length Rh–C in this configuration, which provides a potent evidence demonstrating the strong binding force of Rh toward the CO molecule and the chemisorption nature for the CO molecule onto the RhN$_3$-CNT. 13 $E_{ad}$ in this system is $-2.00$ eV and $Q_T$ is $0.232$ e transferring from the gas molecule to the adsorbent surface. Both values are larger than the reported ones of $-1.94$ eV for $E_{ad}$ and $0.20$ e for $Q_T$ in the Rh-CNT/CO system, 14 which indicates that the N$_3$ dopant could effectively enhance the reaction activity of CNTs and thus improve its adsorption ability toward the CO molecule. In addition, the C–O bond of the CO molecule is somewhat elongated to 1.161 Å after adsorption compared with the value of 1.142 Å for the isolated molecule, which means that the CO molecule is activated during the interaction with the RhN$_3$-CNT surface. 15

Upon PdN$_3$-CNT/CO and PtN$_3$-CNT/CO systems in Figure 3b,c, it could be observed that, like the geometry of the RhN$_3$-CNT/CO system, the C atom of the CO molecule prefers to be adsorbed and trapped by metal dopants with formed bond lengths of 1.893 Å for the PdN$_3$-CNT/CO system and 1.840 Å for the PtN$_3$-CNT/CO system. It is interesting to illustrate that the bond lengths of Pd–C and Pt–C in two adsorbed systems are both shorter than the sum of covalent radii of Pd and C (1.95 Å) along with Pt and C (1.98 Å), which confirms the strong binding force of noble metal dopants (Pd and Pt) toward the CO molecule and leads to the formation of chemical bonds in these systems. Moreover, a similar phenomenon in these two configurations is that one M–N bond is broken and the other two deform to various degrees after CO adsorption, enlarging to 2.129 and 2.217 Å for the PdN$_3$-CNT/CO system and to 2.207 and 2.102 Å for the PtN$_3$-CNT/CO system. This is in agreement with the analysis in a previous reference that metal dopants possess a strong binding force toward the CO molecule. 16

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The DOS distributions for three systems are plotted as shown in Figure 4 to further elaborate the electronic behavior of CO adsorption onto noble metal atom (Rh, Pd, and Pt)-decorated N$_3$-CNTs. We can see that the total DOS and partial DOS of three systems are to some extent similar to each other.
Specifically, the total DOS curves of adsorbed systems witness right shift toward a higher region above the Fermi level compared with isolated MN$_3$-CNT systems. This could put down to the electron-withdrawing behavior of MN$_3$-CNTs that results in the improved effective Coulomb potential consequently. At the same time, the total DOS curves of adsorbed systems have seen significant deformations in comparison with the isolated counterparts because of the dramatic DOS contribution of the activated CO molecule, especially at the areas around the Fermi level, $-6$, $-7$, and $-9.5$ eV. Practically, these areas are mainly where the DOS of the C 2p orbital exists. We can see that there exist apparent overlaps between the Rh 4d, Pd 4d, or Pt 5d orbitals and C 2p orbital around these areas, indicating strong hybridization between the Rh dopant and CO molecule, confirming the obvious chemical interaction between the metal (Rh, Pd, and Pt)-decorated N$_3$-CNT and CO molecule. This finding is in accordance with our previous analysis.

2.3. Adsorption of CH$_4$ onto the Rh-, Pd-, or Pt-Decorated N$_3$-CNT Surface. The most stable configurations and related TCD for MN$_3$-CNT/CH$_4$ systems are portrayed in Figure 5. Unlike the CO system, few overlap of electron cloud between the gas molecule and adsorbent could be found in RhN$_3$-CNT/CH$_4$ and PdN$_3$-CNT/CH$_4$ systems, while just a small area of overlap could be found in the PtN$_3$-CNT/CH$_4$ system. These indicate the relatively weaker adsorption performance of MN$_3$-CNTs upon the CH$_4$ molecule compared with that of CO systems.

Practically, from the adsorption configurations and parameters of MN$_3$-CNT/CH$_4$ systems, we could clearly find out that the MN$_3$-CNT has weak interactions with the CH$_4$ molecule as well. In the RhN$_3$-CNT system, the nearest atom-to-atom distance ($D$) between the adsorbent and gas molecule is measured to be 2.551 Å. Associated with the calculated $E_{ad}$ of $-0.23$ eV and $Q_T$ of 0.091 e, we assume that this is physisorption in the RhN$_3$-CNT/CH$_4$ system. Although the adsorption parameters of $E_{ad}$ ($-0.46$ eV), $Q_T$ (0.187 e), and $D$ (2.048 Å) are somewhat increased in the PdN$_3$-CNT/CH$_4$ system, obvious orbital interactions are not identified, given the lack of electron cloud overlap between the CH$_4$ molecule and adsorbent. After comparison, the PtN$_3$-CNT becomes the only candidate with relatively good adsorption performance upon CH$_4$ for promising applications. One can find that the CH$_4$ molecule is captured by the PtN$_3$-CNT with a Pt-to-H distance of 1.812 Å, which is the shortest distance for CH$_4$ molecule adsorption onto Rh-, Pd-, or Pt-decorated N$_3$-CNTs. On the other hand, the C−H bond of adsorbed CH$_4$ in this system is elongated to 1.163 Å, indicating the strongest activating behavior among Rh-, Pd-, or Pt-decorated N$_3$-CNTs toward the CH$_4$ molecule as well. The PtN$_3$ structure undergoes dramatic deformations with one Pt−N bond broken and the other two elongated largely. All these accord to the large $E_{ad}$ of $-0.67$ eV and $Q_T$ of 0.278 e consequently. It is interesting to note that in all the CO- and CH$_4$-adsorbing systems, electrons transfer from the gas molecule to the MN$_3$-CNT surface. This might be attributed to the strong electronegativity of transition metals that provides the decorated surface with strong electron-withdrawing property. In addition, both the PdN$_3$-CNT and RhN$_3$-CNT show

Figure 4. DOS distribution of the MN$_3$-CNT/CO system. The dashed line represents the Fermi level. (a) RhN$_3$-CNT/CO system; (b) PdN$_3$-CNT/CO system; and (c) PtN$_3$-CNT/CO.

Figure 5. Adsorption configuration and TED of MN$_3$-CNT/CH$_4$ systems. (a) RhN$_3$-CNT/CH$_4$ system; (b) PdN$_3$-CNT/CH$_4$ system; and (c) PtN$_3$-CNT/CH$_4$ system.
stronger performance upon CH₄ adsorption with larger Eₐd and Qₐ compared with Pd-CNT (0.148 eV and 0.072 eV) and Rh-CNT (0.253 eV and 0.075 eV) systems, which confirms the conclusion that the N₃ group could effectively enhance the adsorption performance of metal-doped CNTs toward gas molecules through the improvement of electron mobility and chemical activity.

For detailed comparison of the electronic behavior among MN₃-CNT/CH₄ systems, we plotted the DOS distributions for three configurations as exhibited in Figure 6. It could be clearly seen that in the RhN₃-CNT and PdN₃-CNT systems, the DOS curves for configurations before and after adsorption are basically overlapped, especially one area where novel peaks are found because of the contribution from the adsorbed CH₄ molecule. The slight change in two DOS distributions could be attributed to the weak interactions that lead to small electron transfer and little electron redistribution for the whole systems. On the contrary, pronounced deformations could be identified in the PtN₃-CNT system after CH₄ adsorption. In addition, the DOS peak for the CH₄ molecule around −7 eV is dispersed into several small peaks that contribute to the total DOS of the adsorbed system largely. At the same time, the hybridization between Pt 5d and H 1s could be determined as the strongest among three systems given the largest overlap between the DOS of such two orbitals compared with those in other two systems. These findings are in accordance with previous analysis which manifests that the PtN₃-CNT has better adsorption performance upon the CH₄ molecule compared with the RhN₃-CNT or PdN₃-CNT.

2.4. Application of Noble Metal Atom (Rh, Pd, and Pt)-Decorated N₃-CNTs. We first investigated the recovery time for the desorption of gas molecules from the MN₃-CNT surface based on transition-state theory and van’t Hoff—Arrhenius expression,

\[ \tau = A^{-1} e^{-E_a/K_B T} \]  

where A is the attempt frequency determined as 10¹² s⁻¹ according to previous report,\textsuperscript{23} Eₐ is the potential barrier of desorption that could be deemed as equal with Eₐd, T is the temperature, and K_B is the Boltzmann constant (8.318 × 10⁻³ kJ/(mol·K)). It would be inferred that the larger Eₐ would lead to the harder process for gas desorption and the improvement of temperature can accelerate that process effectively,\textsuperscript{24} although this, the desorption for the CO molecule from the MN₃-CNT surface, even at high temperatures, would be difficult because of the quite large Eₐ. On the other hand, it would be easy for the CH₄ molecule to desorb from the same surface instead, given the small Eₐ.

Detailed analysis of the recovery time for two gases desorbing from the MN₃-CNT surface in various temperatures is exhibited in Figure 7. In short, the RhN₃-CNT and PdN₃-CNT have slight potential that can be exploited to use them as CO sensors with superior sensitivity, but they have bad recovery property with a working temperature of about 700 K for their reversibility. In other words, CO sensing by Rh- or Pd-decorated N₃-CNTs would be a one-off operation, which is too much of a waste of material and its efficiency is low. Given the even harder condition for CO desorption from the PtN₃-CNT surface, it is inappropriate as a CO sensor. In this regard, we assume that Rh-, Pd-, and Pt-decorated N₃-CNTs could behave as an excellent CO adsorbent, especially PtN₃-CNT which has a strong performance toward CO adsorption, for removal of such toxic gas from a specific environment.

On the other hand, we assume that only the PtN₃-CNT is a promising candidate for CH₄ detection compared with the PdN₃-CNT or RhN₃-CNT, given its desirable adsorption and desorption behaviors for practical application at ambient temperature. This allows the application of the PtN₃-CNT for CH₄ sensing with simple working conditions. The sensing mechanism would depend on conductivity increase of the PtN₃-CNT-based device in the presence of CH₄ according to the enlarged Eₐ from 0.012 eV for pure PtN₃-CNT to 0.311 eV for the adsorbed system.\textsuperscript{25} It is hopeful that the detection accuracy would reach the ppm level given the obvious change in Eₐ and whole interactions between the sidewall of the PtN₃-CNT and CH₄ molecules.

3. CONCLUSIONS

In this work, the first-principles theory is adopted to theoretically investigate the geometric and electronic structure of noble metal atom (Rh, Pd, and Pt)-decorated N₃-CNTs, as well as their adsorption behavior upon CO and CH₄.

Figure 6. DOS distribution of the MN₃-CNT/CH₄ system. The dashed line represents the Fermi level. (a) RhN₃-CNT/CH₄; (b) PdN₃-CNT/CH₄; and (c) PtN₃-CNT/CH₄.
molecules. The main conclusions could be summarized as follows:

1. After decoration of noble metal atoms (Rh, Pd, and Pt), the MN group becomes more electron-centralized, confirming the strong electron-accepting property of the N3-CNT and active electron-denoting behavior of noble metal atoms.

2. The embedded N3 group in CNTs would provide the system with enhanced performance toward gas adsorption, leading to larger values of Ead and QT compared with isolated metal-doped CNTs because of stronger orbital interactions and chemisorption between the adsorbent and target gas.

3. Rh-, Pd-, and Pt-decorated N3-CNTs could behave as an excellent CO adsorbent, especially the PtN3-CNT which has strong performance toward CO adsorption, for removal of such toxic gas from a specific environment; while the PtN3-CNT is the promising candidate for CH4 detection, given its desirable adsorption and desorption behaviors for practical application at ambient temperature.

Our calculation would be meaningful for providing fundamental knowledge of the geometric and electronic structure of the noble metal atom (Rh, Pd, and Pt)-decorated N3-CNT, as well as potential applications of the MN3-CNT for CO scavenging or CH4 sensing.

4. COMPUTATIONAL DETAILS

The whole calculations in this work were performed on the DMol3 package.26 The intrinsic (8, 0) single-walled CNT that possesses good sensitivity toward circumstance was created with a supercell periodic boundary condition as 20 Å × 20 Å × 8.5 Å in order to prevent interaction between adjacent cells.3 The generalized gradient approximation with the Perdew–Burke–Ernzerhof was employed to address the electron exchange correlation functions.27 The Brillouin-zone was studied by using the Monkhorst–Pack scheme, sampled into 1 × 1 × 9 k-point,2 while the core treatment used Semicore Pseudopots.28 The density functional computation adopted the double numerical basis set including p-polarization function.29 The energy tolerance accuracy, maximum force, and displacement were set as 10−5 Ha, 2 × 10−5 Ha/Å, and 5 × 10−5 Å, respectively, with a smearing of 5 × 10−3 Ha. A large enough global orbital cutoff radius of 4.5 Å was implemented to ensure the accurate calculation of total energy. All calculations were spin-polarized.

To characterize the adsorption behavior, the adsorption energy (Ead) of each process was defined by the following equation:

\[ E_{ad} = E_{MN3-CNT/gas} - E_{MN3-CNT} - E_{gas} \] (2)

where the \( E_{MN3-CNT/gas} \), \( E_{MN3-CNT} \), and \( E_{gas} \) represent energies of the adsorbed system, metal (Rh, Pd, and Pt)-decorated N3-CNT, and isolated gas molecule, respectively. Apart from that the Mulliken population analysis was adopted to analyze the charge transfer (QT) between the gas species and decorated surfaces, characterized by the electron value carried by each gas molecule. In addition, Tkatchenko and Scheffler's method was employed to deal with the long-range van der Waals force for gas adsorption.32 For basis set superposition errors, little impact could be caused in the Dmol3 package33 and thus we would not analyze it in the following part.

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Author Contributions
X.Z. conceived and designed the research, H.C. performed the research and wrote this manuscript, and J.Z. helped analyze the data.

Notes
The authors declare no competing financial interest.

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