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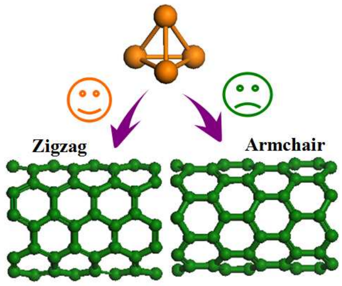

The zigzag-type SWNTs not only stablize the Ir clusters but also enhance their catalytic performance.

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# Adsorption of $Ir_4$ cluster on single-well carbon nanotubes: the zigzag types are more suitable

Jiguang Du,[*,†] Xiyuan Sun,[‡] and Gang Jiang[¶,§]

*College of Physical Science and Technology, Sichuan University, Chengdu 610064, China, College of Sciences, Sichuan Agricultural University, Ya′an 625014, China, Institutes of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China, and The Key Laboratory of High Energy Density Physics and Technology, Ministry of Educatuon, Chengdu 610065, China*

E-mail: dujg@scu.edu.cn

Fax: +86 (0)28 85405155

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[*] To whom correspondence should be addressed

[†] Sichuan University

[‡] Sichuan Agricultural University

[¶] Institutes of Atomic and Molecular Physics

[§] The Key Laboratory of High Energy Density Physics and Technology

### Abstract

The density functional calculations have been performed to investigate the adsorption of the $Ir_4$ cluster on different SWNTs. We find that the tetrahedral isomer adsorbed on the studied tubes with triangular face on SWNT are predominantly favored. The metal-SWNT interaction in zigzag tubes supported $Ir_4$ systems are significantly stronger than that in armchair supported systems. A strong hybridization between p orbital of SWNT and d orbital of Ir atoms is formed when $Ir_4$ cluster adsorbed on the SWNT surface. Charge density difference also shows that the substantial concentration of electrons accumulates as Ir-C bonds. The CO/NO adsorption on SWNT-supported $Ir_4$ cluster is also investigated. All zigzag tubes supported $Ir_4$ clusters possess the lower adsorption energies relative to the free and armchair supported $Ir_4$ clusters. Our investigation indicates that the zigzag-type SWNTs not only stablize the Ir clusters but also enhance their catalytic performance.

# Introduction

Several $5d$ transition metal (TM) clusters, such as Pt, Au, Ir possess effective catalysts and present interesting cluster size effects on catalytic reactivity.[1–5] The studies on Iridium as a catalyst were limited to little reactivity in experiments,[6–11] due to high cost of Ir resource. In experiment, the shape and stability of $Ir_n$ clusters with $n = 18 - 39$ on the closepacked Ir (111) plane were studied using a low-temperature field ion microscope by Wang *et al*[12] to characterize the energetics of surface clusters. They reported that the high coordination hexagonal clusters, like $Ir_{19}$ and $Ir_{37}$, are far more stable than the less compact ones. The extended X-ray absorption fine structure (EXAFS) measurements of fully decarbonylated systems show that the Ir-Ir coordination number is three, suggesting that the tetrahedral $Ir_4$ frame of the precursor is preserved. The catalytic behaviors of tetrairidium clusters on the solid supports (MgO) were investigated by Xiao *et al*[13] with infrared spectroscopy and chemisorption measurements, and they found that more $O_2$ molecules were chemisorbed on solid supported $Ir_4$ than on metallic iridium. The low uptake of hydrogen and of CO on nearly uniform $Ir_4$ clusters in comparison with those for adsorption on metallic irid-

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ium show that chemisorption properties of the extremely small clusters are different from those of highly dispersed metal particles. Structural and catalytic characterization of oxide-supported ($\gamma$-$Al_2O_3$, MgO and $La_2O_3$) iridium nanoclusters was studied by extended X-ray absorption fine structure (EXAFS) spectra.[14] The EXAFS data indicate that the metal clusters, while remaining intact and maintaining their bonding to the supports during catalysis, underwent slight rearrangements to accommodate reactive intermediates.

Adsorption and activation properties of small Pt, Au and Ir clusters toward to NO molecule are investigated by Endou *et al.*[15] with DFT approach. They found that the order of the energetic stability of the adsorption states of NO is Ir $>$Pt $>$Au and dependent on the neither the geometries of pentamers nor the cluster sizes considered in the reference. The CO, $O_2$ and NO molecules and the cubooctahedral model of $Ir_{13}$ cluster were selected as the adsorbates and model cluster, respectively, to investigate the catalytic reactivity of $Ir_{13}$ clusters.[16] The charge transfers between the surface atoms of cubooctahedral $Ir_{13}$ cluster and the adsorbates indicated the strong interaction between them. Bussai *et al*[17] investigated the structures and binding energies of various isomers of $Ir_4$ cluster and its complexes with one H atom based on the relativistic density functional theory. Recently, Stevanović *et al*[18] using DFT based on ultrasoft pseudopotentials to investigate the structural properties of the gaseous and MgO(100) supported $Ir_4$ clusters. They also investigated the effect of several adsorbates, including H, C, O, CO and OH, on the equilibrium atomic structure of the clusters. The C or CO adsorption significantly influences the relative stability of $Ir_4$ isomers. For MgO(100)-supported $Ir_4$, atomic carbon is able to change the isomer preference from the square to the tetrahedral geometry. As we know, carbon nanotube (CNT) has high surface area and high chemical stability. Recently, it has been found to be an ideal support material for metal clusters.[19]

In the present paper, we have employed *ab initio* calculations to investigate the structural and electronic characteristics of $Ir_4$ cluster on two types of single well carbontube (SWNT) with chiral angle either 0° or 30°. The geometric and electric structures of $Ir_4$ cluster on these two types of SWNT were compared and discussed in detail. Also the CO/NO adsorption on SWNT supported

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$Ir_4$ cluster is investigated to understand the catalytic properties of support metal clusters.

## Computational details

All spin-unrestricted calculations are carried out utilizing density functional theory (DFT) in Dmol$^3$ package.[20] The exchange correction energies were evaluated with generalized gradient approximation Perdew-Burke-Ernzerhof (PBE)[21] functional. Iridium atom has as many as 77 electrons, the all-electron relativistic calculations is time consuming. Therefore, the DFT-based semi-core pseudopotential (DSPP)[22] including scalar relativistic effects, which is generated by fitting all-electron relativistic DFT results, is employed in our calculations. With the double numerical basis set augmented with polarization *p*-function (DNP), which has a computational precision being comparable with split-valence basis set 6-31g$^{**}$,[23] the decent description for valence electrons of Ir ($5s^2 5p^6 5d^7 6s^2$) could be obtained. All electron DNP treatments were used for C, N and O atoms. In the generation of the numerical basis sets, a global orbital real-space cutoff of 4.5Å is used. The geometry optimizations are performed with the convergence criterion as follows: $10^{-5}$ a.u. for the total energy, $10^{-6}$ for electron density, $2 \times 10^{-3}$ and $5 \times 10^{-3}$ a.u. for gradient of force and atomic displacement, respectively. We choose the octupole scheme for multipolar expansion of charge density. The thermal smearing (0.002 a.u) was applied to the orbital occupation to speed up self-consistent field (SCF) convergence. The Brillouin-zone sampling was restricted to the $\Gamma$-point in the geometry optimization, and $1 \times 1 \times 28$ k-points mesh was used in property calculations.

Six single-well carbon nanotubes (SWNT), including zigzag tubes, (7, 0), (8, 0), and (10, 0) and armchair types, (7, 7), (8, 8), and (10, 10) are considered in our calculations to discuss the differences on adsorption of $Ir_4$ tetramer. The studied tubes which were placed in a rhombic supercell with dimensions of $a = b = 30$Å, $c = 4c_0$ ($c_0$ is the lattice parameter of SWNT studied) were large enough to avoid the interaction between $Ir_4$ tetramer and its periodic images. In the NO, CO adsorption cases, the supercell dimensions perpendicular to the tube axes are extended to $a = b = 35$ Å for (10, 10) tube.

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The relaxed isomers of $Ir_4$ tetramer adsorbed on the tubes considered have been optimized without any symmetry constrains. Different adsorbed sites were considered in the geometry optimization. The initial adsorptions sites of NO and CO molecules on supported $Ir_4$ were determined based on the Fukui function, and then the molecules adsorbed systems are full relaxed without symmetry constrain. The formation energy of SWNT-support $Ir_4$ system was calculated as the energy difference between SWNT-support $Ir_4$ and isolated SWNT and $Ir_4$ cluster. As for adsorption energy of CO, NO on SWNT-supported $Ir_4$ system, it is defined as the energy difference between molecule-adsorbed SWNT-$Ir_4$ and free molecules and SWNT-$Ir_4$.

# Results and discussion

## Absorbed structures and stability

For free $Ir_4$ clusters, there are three isomers found in the geometry optimization, and the square (S) structure with Ir-Ir bond length of 2.40 Å is most favored in energy. This favorable isomer corresponds to spin magnetic moment of $2.0\mu_b$ per atom. The nonmagnetic tetrahedron (T) isomer with bond length of 2.53 Å, corresponding to relative energy of 0.17eV comes next in energy (the relative energy designed as the energy difference relative to the lowest energy isomer). One butterfly-like structure was found to be less stable than square and tetrahedron isomers. Our calculated geometry parameters and energy orders for these three isomers are in excellent agreement with previous relativistic DFT calculations.[17] By considering the low stability of butterfly-like structure, only square (S) and tetrahedron (T) isomers adsorbed on SWNT are investigated in the present work. Three different adsorbed modes depicted in Fig 1 are considered for every type SWNT in the geometry optimizations of SWNT-support $Ir_4$ system: i) one Ir atom directly bonding to tubes labeled as T-1 for tetrahedron and S-1 for square in Fig 1, ii) two Ir atoms directly bonding to tubes labeled as T-2/S-2, iii) three or four Ir atoms directly bonding to tubes labeled as T-3, S-4 respectively. Therefore, there are as many as 36 structures are relaxed in the optimization. Among these structures, the relaxed structures with corresponding coordinations of the

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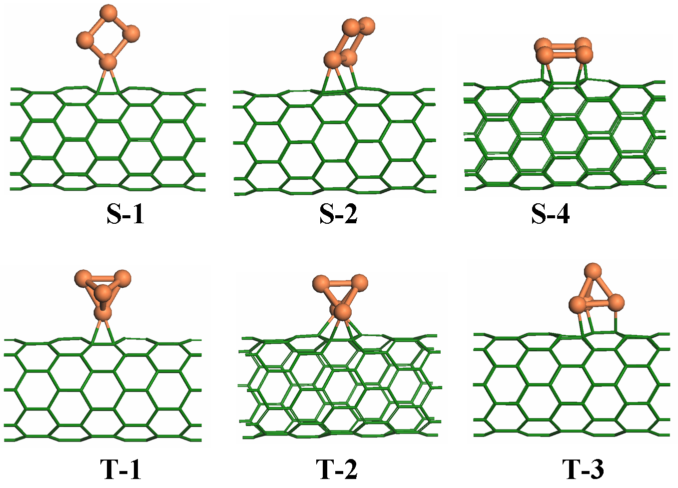

Figure 1: The scheme representation of the different absorption modes for the square (S) and tetrahedron (T) isomers of $Ir_4$ cluster on SWNT.

supported tetrahedron isomer in T-3 are given in the Fig S1 of the supporting information. The relative energies calculated for all 36 SWNT supported $Ir_4$ systems are depicted in Fig 2, from which one can clearly see that the tetrahedron isomer adsorbed on the studied tubes with T-3 mode are predominantly favored in energy. This result is in line with experimental conclusion in which the tetrahedron shape corresponding to coordination of 3 was suggested to exhibit in supported environment.[24] On the other hand, the stability of square structure which is most stable in free condition is significant decreased. Except for T-3 isomer, other isomers of SWNT-supported $Ir_4$ system exists great competition in stability. The existence of many energetically competitive isomers implies that the structural fluxionality of $Ir_4$ cluster might be in a degree occured on SWNT support. The armchair-supported tetrahedron structure with T-2 adsorption mode also possesses considerable stability. To further investigate the adsorption dependence of $Ir_4$ cluster on two types of SWNTs, the formation energies ($E_f$) of supported SWNT-$Ir_4$ systems are evaluated using the expression $E_f = E_{Pt_4} + E_{SWNT} - E_{SWNT-Pt_4}$, where $E_{Pt_4}$ and $E_{SWNT}$ represent the total energy of isolated $Pt_4$ cluster and SWNT, respectively, and $E_{SWNT-Pt_4}$ represents the total energy of supported systems. The calculated formation energies were depicted in Fig 3. The detailed data can be found in Table S1 in supporting information. The formation energies of square isomer deposited

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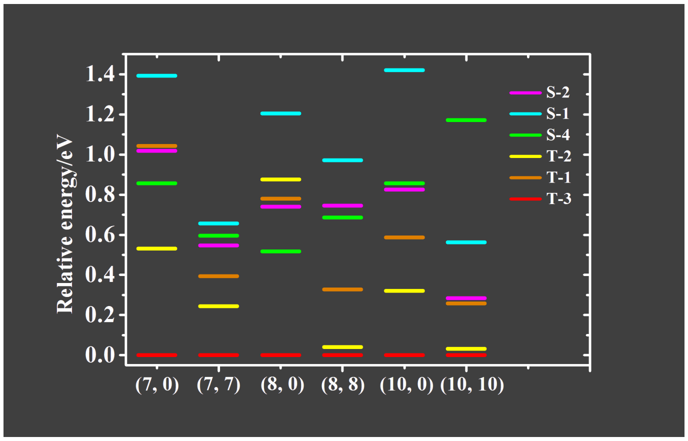

Figure 2: The relative energies of different SWNT supported square (S) and tetrahedron (T) isomers.

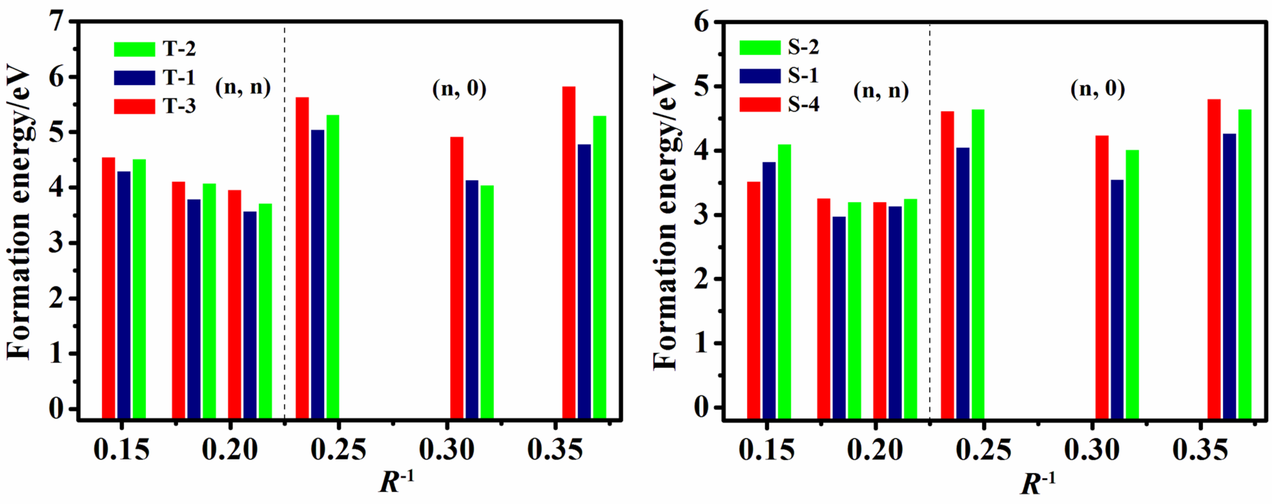

Figure 3: The formation energies of studied SWNT supported square (S) and tetrahedron (T) isomers versus curvatures of SWNT.

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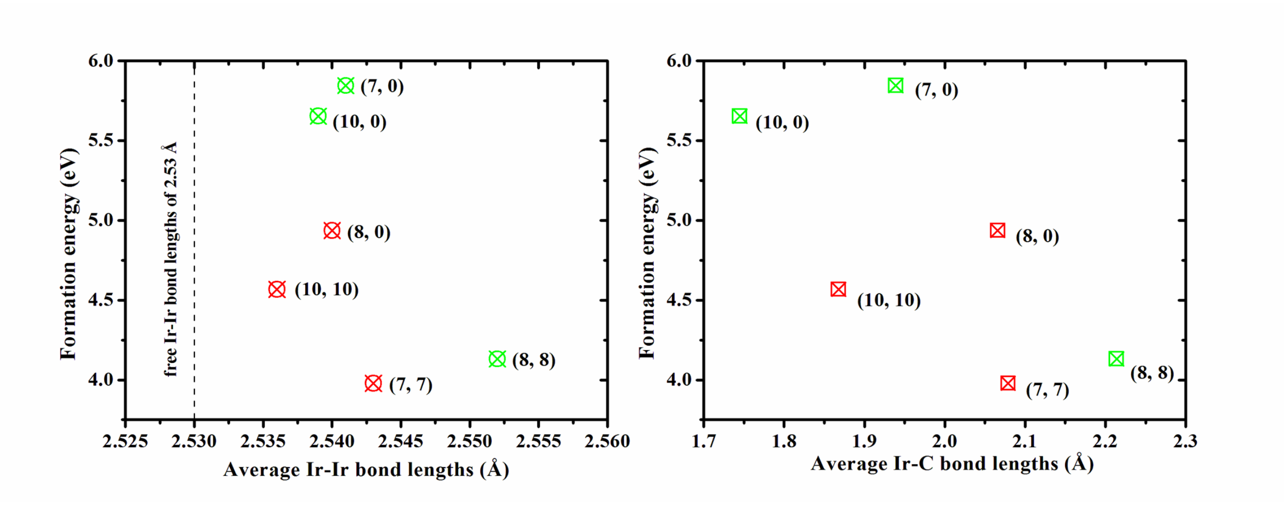

Figure 4: The average Ir-Ir and Ir-C bond lengths in SWNT-support tetrahedron structure (T-3) versus formation energy.

SWNT are in the range of 2.99-4.82eV, much lower than those of supported tetrahedron structure ranging from 3.58-5.85eV, identifying the weaker interaction between SWNT and square structure. This result is consistent with the prediction of relative energy discussed above. As Fig 3 shows, it is important to note that the formation energies show obvious different for two types of SWNTs studied. The zigzag supported $Ir_4$ systems (for the two isomers studied) correspond to significantly larger formation energies relative to armchair supported systems. Take T-3 structures as an example, the formation energy of zigzag (10,0) supported tetrahedron is 5.85eV, about 1.3eV larger than the largest value for armchair supported one (4.57eV for (7,0) supported tetrahedron). This means that the interaction between $Ir_4$ and zigzag SWNT is much stronger than that in armchair tubes. Moreover, the interaction energies between tetrahedron isomer and zigzag tubes in T-3 mode are larger by 1-2eV than that of 3.82eV in MgO (100)-supported tetrahedron system studied previously at DFT level of theory.[18] In this sense, these zigzag SWNTs are more suitable used as substrates for the Ir cluster assembly. To quantify the structural deformation of $Ir_4$ cluster after being deposited on SWNT substrates, we depicted in Fig 4 the formation energy versus average Ir-Ir (left in Fig 4) and Ir-C (right in Fig 4) bond lengths. The average Ir-Ir bond lengths in the most stable isomer of SWNT-supported tetrahedron structure (T-3) are in the range of 2.536 Å (10,

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10) to 2.552 Å (8, 8). Comparing with the Ir-Ir bond distance of isolated tetrahedron isomer also displayed in Fig 4, the structure is slightly deformed after being deposited on SWNT. Also the structural deformation is found for supported square isomers, take S-4 isomer as an example, the Ir-Ir bond lengths ranging from 2.428 Å (10, 10) to 2.449 Å (7, 0) are slightly elongated relative to that of 2.40 Å for isolated square isomer. We attribute this structural deformation to the formation of Ir-C bonds, which decreases the degree of undercoordination of the three Ir atoms bonded to neighboring carbon atoms of SWNT. From Fig 4, one can also find that the average Ir-C bonds in zigzag supported tetrahedron isomers (T-3) are in general slightly shorter than those in corresponding armchair supported isomers, reflecting the stronger cluster-SWNT interaction in zigzag supported isomer.

## Interaction natures between $Ir_4$ cluster and SWNT.

Electronic structure analyses based on projected density of states (PDOS) and charge-density difference were carried out to facilitate a deeply understanding of the interaction characters between SWNT and $Ir_4$ cluster. For the reason of comparison, we will take (8, 0)-supported tetrahedron and square isomers as an example to identify the bonding nature in SWNT-$Ir_4$ system. The total density of states (DOS) was projected on to the p orbitals of C atoms in SWNT and d orbitals of Ir atoms. The summed *p* DOS of C atoms and *d* DOS of Ir atoms are depicted in Fig 5, the *p* and *d* DOS for the same atoms in isolated SWNT substrates and clusters are also shown in this figure to facilitate an understanding of how the *p* and *d* states are modified after cluster being adsorbed. For isolated $Ir_4$ cluster, tetrahedron (T) and square (S) isomers show significantly different band peaks. The DOS peaks are evidently discrete for the tetrahedron structure as compare to those of square isomer, this difference stems from the higher $T_d$ symmetry of tetrahedron structure resulting in the appearance of degenerate energy level relative to $D_{4h}$ symmetry of square structure. We also note that the Fermi energy level of isolated square structure is much lower than that of tetrahedron isomer, this is responsible for the higher stability of square structure. By comparing PDOS of isolated and supported $Ir_4$ cluster in Fig 5, it is immediately appeared that the d states of Ir atoms undergoes

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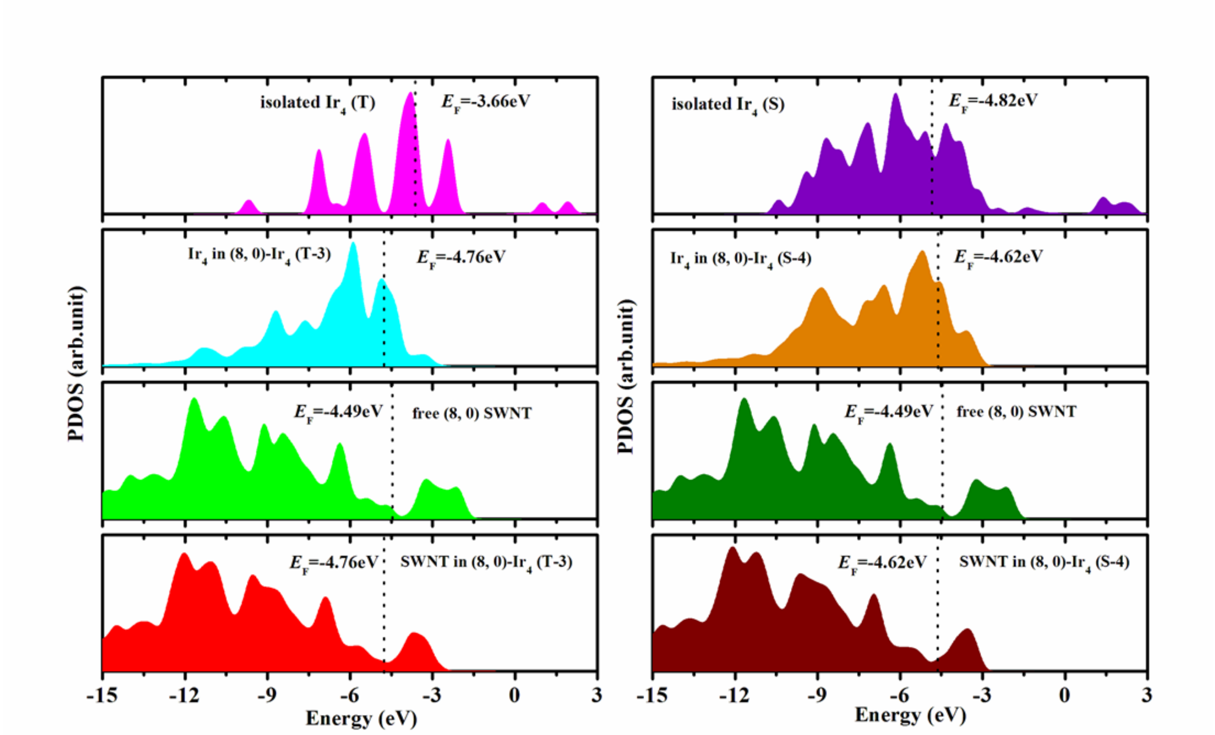

Figure 5: The projected density of states (PDOS) of isolated (8, 0) SWNT and $Ir_4$ and (8, 0)-supported two isomers (tetrahedron and square) of $Ir_4$ cluster

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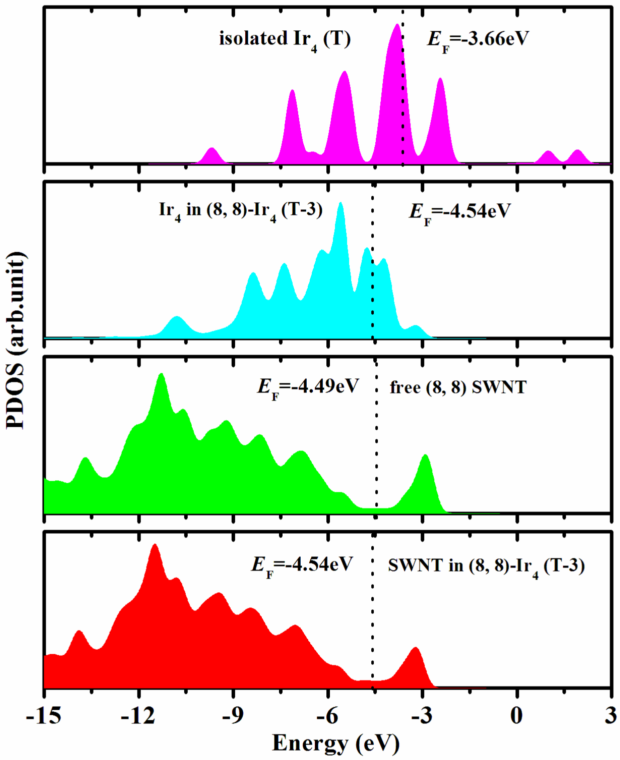

Figure 6: The projected density of states (PDOS) of isolated (8, 8) SWNT and $Ir_4$ tetrahedron isomer and (8, 8)-supported tetrahedron isomer.

significant broadening upon cluster adsorption. The newly hybrid orbitals in a wide range from -7.5eV to Fermi level can be found, this indicate that a strong hybridization between *p* orbital of SWNT and *d* orbital of Ir atoms is formed. This hybridization gives rise to the delocalization and broadening of *d* states of the $Ir_4$ cluster. The *d* states of Ir atoms are not only involved in Ir-Ir metal bonds but also in Ir-C interactions. We also note that the *p* DOS peaks of SWNT in supported tetrahedron structure are clearly shifted by 0.27eV toward to the low energy level by comparing with free SWNT. The energy shift is much great in supported tetrahedron structure relative to that in supported square system (0.13eV) indicating to some degree the higher stability of supported tetrahedron system. The PDOS of armchair-supported (8, 8) tetrahedron isomer shown in Fig 6 are also analyzed for comparison. As expect, the d states of Ir atoms are also broadened due to the for-

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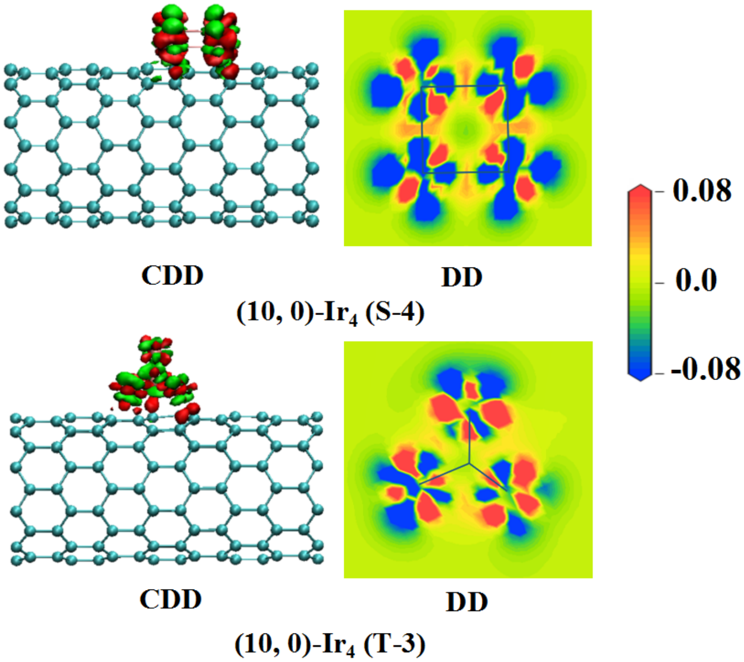

Figure 7: Charge-density difference in Ir$_4$ isomers deposited on (10, 0) SWNT (left) and deformation density mapped on total density on cutoff plane of Ir-Ir bonds.

mation of $p$(C)-$d$(Ir) hybrid orbitals. However, the d broadening is less wide than zigzag-support system (8, 0). Moreover, the energy level shift of p DOS peaks of (8, 8)-SWNT system toward to the low energy region is less significant than that in (8, 0)-support system.

The electron deformation density (DD) which is calculated as the density difference between (10, 0)-Ir$_4$ system and isolated C and Ir atoms to investigate the bonding changes of Ir-Ir chemical bonds after being deposited on SWNT. The charge-density difference (CDD) is also calculated to probe into the interaction nature between SWNT and metal cluster. The CDD is defined as the difference between the charge density of the (10, 0)-Ir$_4$ and sum of the charge density of isolated Ir$_4$ isomers (tetrahedron and square) and (10, 0) SWNT,$\Delta\rho = \rho_{SWNT-Ir_4} - (\rho_{SWNT} + \rho_{Ir_4})$. Two types of density difference are depicted in Fig 7 for (10, 0)-supported tetrahedron and square isomers. From deformation density (right in Fig 7) mapped on total density, it is appeared that the electron accumulation is obviously shown between two Ir atoms. Therefore covalent nature of Ir-Ir bonds is still maintained after deposited on the SWNT. We also note that the electron accumulation among Ir atoms in square isomer is more significant than that in tetrahedron structure, indicating

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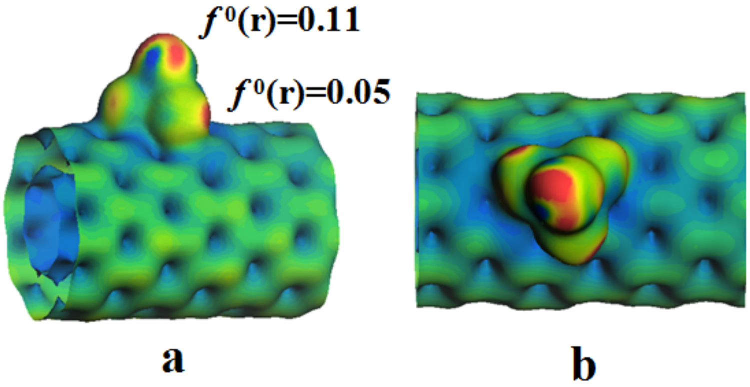

Figure 8: The radial Fukui function mapped on total electron density of (8, 0) SWNT supported $Ir_4$ tetrahedron isomer, the condensed radial Fukui index is also shown.

the stronger Ir-Ir bond strength. From charge density difference (left in Fig 7), one can find that the electron density is significantly modified for both isomers of $Ir_4$ cluster when adsorbed on SWNT. On the other hand, the C atoms which is not bonded with metal cluster show unchanged density distribution. Changes in the electron densities occur mainly at interface region between the $Ir_4$ clusters and the SWNT, where a substantial concentration of electrons accumulates as Ir-C bonds.

## CO and NO adsorption on SWNT support tetrahedron isomer.

CO and NO molecules are important reactive intermediates in many processes, we have investigated the behavior of CO and NO molecules adsorbed on SWNT-support $Ir_4$ cluster. In the present work, only the SWNT supported tetrahedron isomer in T-3 model is considered due to its high stability. We first calculated the Fukui index[25] to predict the local adsorption sites of CO, NO molecules on SWNT-$Ir_4$ system. Many previous reports have shown that the Fukui index is successful in predicting local reactive sites of metal clusters. The radial Fukui index mapped on total electron density is shown in Fig 8, as expect the top Ir atom which is only bonded to metal atoms corresponds to large $f^0(r)$ value of 0.11,is significant larger than other metal atoms ($f^0(r)$=0.05), therefore the top Ir atom shows the higher chemical reactivity than other rest Ir atoms bonded to C atoms of SWNT. The structures of SWNT supported tetrahedron (T-3) with CO, NO molecules

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**Table 1: Geometry parameters, average distances between Ir and Ir atoms, Ir and C atoms of SWNT, Ir and adsorbed molecules in different SWNT supported tetrahedron isomers with and without CO/NO adsorbed, $^a$ SWNT-Ir$_4$ system, $^b$ SWNT-Ir$_4$-CO system, $^c$ SWNT-Ir$_4$-NO system**

| substrates | Ir-Ir$^a$ | Ir-C$_G^a$ | Ir-Ir$^b$ | Ir-C$_G^b$ | Ir-C$_{CO}$ | C-O | Ir-Ir$^c$ | Ir-C$_G^c$ | Ir-N$_{NO}$ | N-O |
|---|---|---|---|---|---|---|---|---|---|---|
| free | 2.530 | | 2.540 | | 1.866 | 1.172 | 2.542 | | 1.785 | 1.183 |
| (7, 0) | 2.541 | 1.939 | 2.558 | 2.013 | 2.195 | 1.166 | 2.571 | 2.058 | 2.155 | 1.179 |
| (8, 0) | 2.540 | 2.066 | 2.545 | 2.050 | 2.179 | 1.155 | 2.568 | 2.125 | 2.058 | 1.173 |
| (10, 0) | 2.539 | 1.745 | 2.552 | 1.752 | 1.712 | 1.168 | 2.566 | 1.841 | 1.737 | 1.183 |
| (7, 7) | 2.543 | 2.079 | 2.556 | 2.113 | 2.176 | 1.175 | 2.564 | 2.106 | 2.115 | 1.175 |
| (8, 8) | 2.552 | 2.214 | 2.557 | 2.222 | 2.095 | 1.176 | 2.572 | 2.151 | 1.775 | 1.179 |
| (10, 10) | 2.536 | 1.868 | 2.603 | 2.155 | 1.821 | 1.179 | 2.601 | 2.175 | 1.810 | 1.180 |

bonded to the top Ir atom are completely relaxed without any constrains. The key structural parameters are listed in Table 1. The relaxed geometry structures and corresponding coordinations of CO, NO molecules attached systems are depicted in Fig S2 and Fig S3 of supporting information, the corresponding coordinations are also listed in supporting information.

In CO and NO environment, the Ir-Ir bond distances of supported cluster are more or less elongated as compare to the free supported counterparts. Also the elongation of the distance between Ir and neighboring C atoms in SWNT is found when CO, NO molecules attached. The C-O bond lengths are significantly stretched by 0.03 Å after being adsorbed on the cluster. There is however no obvious bond stretch found for NO molecule, this may arise from the strong N-O bond which can not be easily broken. It is worth noting that the Ir-N$_{NO}$ bond lengths are generally smaller than those of Ir-C$_{CO}$ bond lengths in the same substrates systems. This indicates that the interaction between NO molecule and supported cluster would be stronger than Ir-C$_{CO}$ interaction. The adsorption energies (E$_{ads}$) which were evaluated as the difference between total energy of SWNT-Ir$_4$-CO (NO) system and SWNT-Ir$_4$ and CO (NO) molecule are summarized in Table S2 of supporting information. We depicted the E$_{ads}$ values versus curvature of studied tubes in Fig 9. By comparing the E$_{ads}$ of CO

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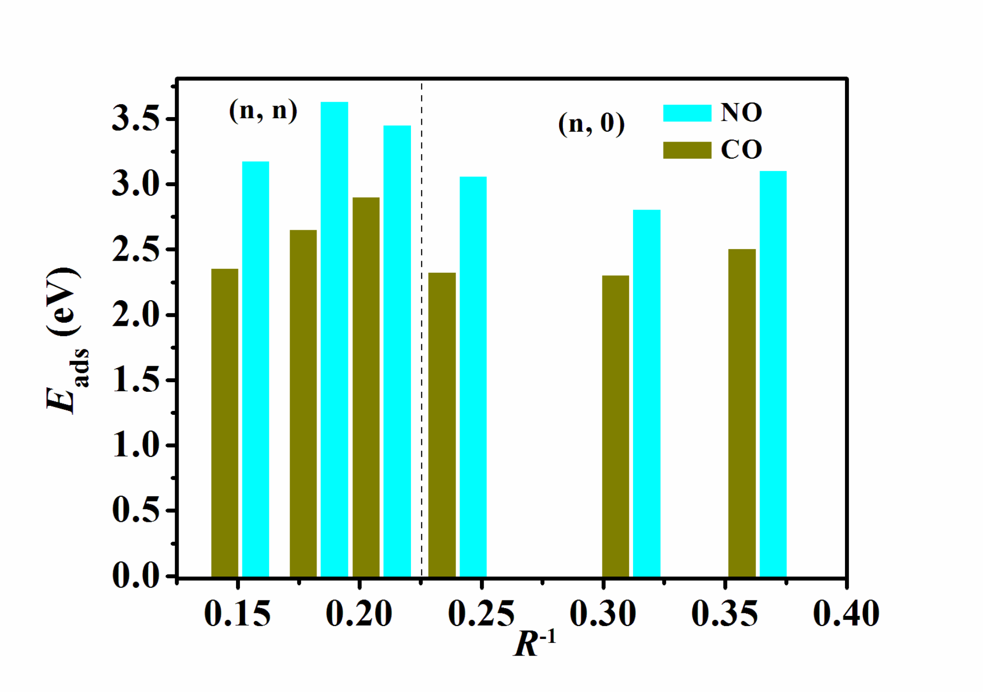

Figure 9: The CO and NO adsorption energies on different curvature SWNT supported $Ir_4$ tetrahedron isomer in T-3 model.

and NO molecules, it is immediately apparent that the adsorption energies of NO in all studied tubes ranging from 2.82-3.47eV are much larger than CO counterparts which are in the rang of 2.31-2.91eV. The high adsorption energy of NO is in line with the shorter Ir-$N_{NO}$ bond length. It is very interesting that the adsorption energy for both CO and NO shows clearly differences for two types of SWNTs studied. All zigzag tubes supported $Ir_4$ clusters possess the lower adsorption energies relative to free and armchair supported $Ir_4$ clusters. Specifically, the adsorption energies of CO on zigzag SWNT-supported $Ir_4$ ranging from 2.31-2.52eV are significantly lower than the value of 2.83eV in free $Ir_4$-CO system. For NO molecule, the zigzag SWNT-supported $Ir_4$ possess adsorption energies of 2.82-3.11eV, also being lower than the value of 3.15eV in free $Ir_4$-NO system. This result indicate that the catalytic performance of zigzag SWNT-supported Ir cluster can be enhanced, especially for CO molecule. More importantly, the $Ir_4$ clusters are more favored to be deposited on zigzag tubes from the formation energy analyses above. Therefore, we obtain one important information that the zigzag SWNTs will be more excellent substrates in the catalytic

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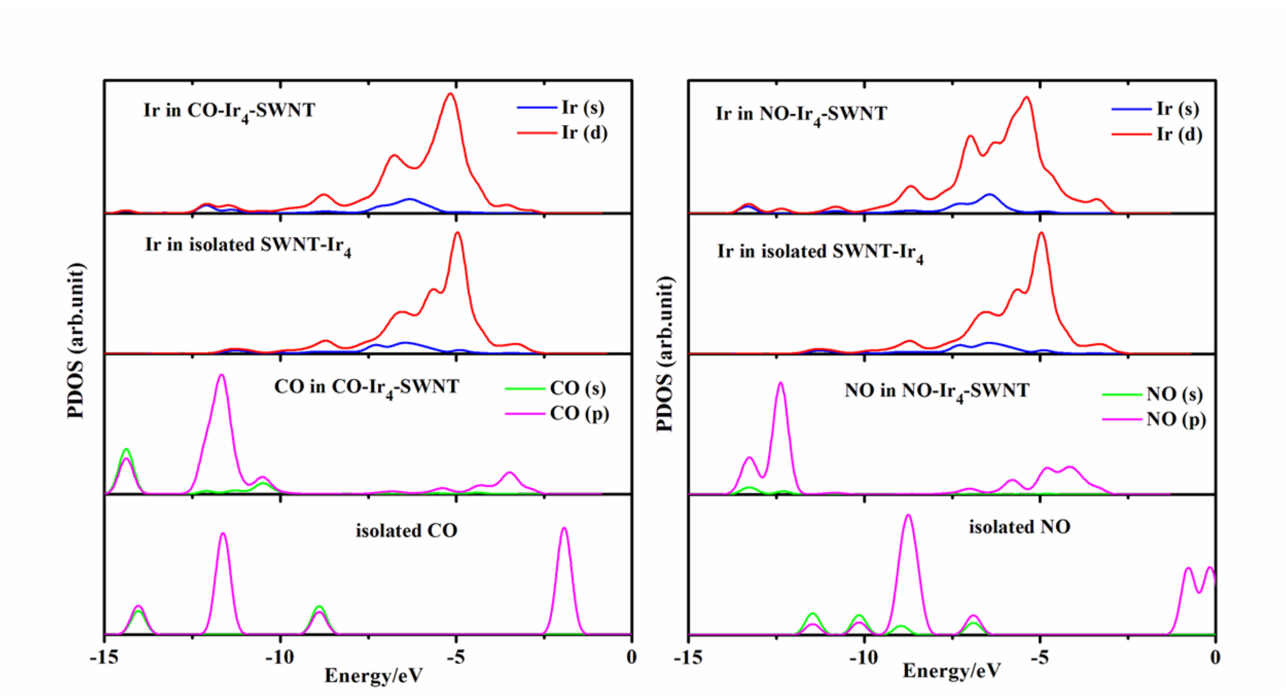

Figure 10: The projected density of states (PDOS) of CO/NO molecule and supported Ir atoms with and without CO/NO adsorption.

application of Ir clusters. We now perform electronic structure analyses based on projected density of states (PDOS) to gain insights into the interaction between supported $Ir_4$ cluster and adsorbed CO/NO molecules. The $s/p$ PDOS of CO/NO molecules and $s/d$ PDOS of bonding Ir atom in (8, 0)-supported $Ir_4$ cluster (T-3) are shown in Fig 10. Under CO/NO environment, the d orbital of metal atoms undergoes broadening to be involved in meta-CO/NO bondings. The electronic states of adsorbed molecules are also significantly modified after being bonded to metal atoms. There are significant overlaps between $d$ orbitals of Ir atoms and $p$ orbitals (mainly $2\pi^*$antibonding state), $s$ orbitals ($5\sigma$ bonding state) of CO molecule. Similar overlaps are also formed for $p$ and $s$ orbitals of NO molecule and d bands of Ir atoms. We also note the orbital coupling between $p/s$ orbitals of NO molecule and d states of Ir atoms is much stronger than that in CO adsorbed system. This can be to some extent used to explain the higher adsorption energy of NO in SWNT supported $Ir_4$ cluster.

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# Conclusion

We have systemically investigated $Ir_4$ cluster on armchair and zigzag types of SWNT using *ab initio* calcualtions. The relative energies show that the tetrahedron isomer adsorbed on the studied tubes with triangular face on SWNT (T-3 mode) are predominantly favored in energy. The zigzag supported $Ir_4$ systems (for the two isomers studied) correspond to significantly larger formation energies relative to armchair supported systems. Therefore, the zigzag type SWNTs are more appropriate used as substrate for the Ir cluster assembly. The d states of Ir atoms undergoes significant broadening upon cluster adsorption. The newly hybrid orbitals in a wide range from -7.5eV to Fermi level can be found, this indicate that a strong hybridization between *p* orbital of SWNT and d orbital of Ir atoms is formed. Covalent nature of Ir-Ir bonds of $Ir_4$ cluster are maintained after deposited on SWNT. Charge-density difference shows that the substantial concentration of electrons accumulates as Ir-C bonds from the machanism of charge transfer from metal atom to bonding C atoms. The CO/NO adsorption on SWNT-supported $Ir_4$ cluster is also investigated. All zigzag SWNT supported $Ir_4$ clusters possess the lower adsorption energies relative to free cluster and armchair supported tubes. This suggests that these zigzag-type SWNTs not only stablize the Ir clusters but also enhance their catalytic performance to a certain extent. The analyses of PDOS indicate that there are significant overlaps between d orbitals of Ir atoms and *p* orbitals of CO or NO molecule.

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