Theoretical Study on the Structures of Single-Atom M (M=Fe, Co and Ni) Adsorption Outside and Inside the Defect Carbon Nanotubes

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Abstract

Single-atom confinement inside carbon nanotubes has attracted much attention in many fields. This class of materials may not only serve as a catalyst but also as a support material for certain reactions. In this paper, we have studied the single-walled carbon nanotubes (SWCNT), single vacancy defect (SV) and Stone-Wales defect (SW) carbon nanotubes with Fe, Co and Ni atom by both inside and outside adsorption structures in density function theory (DFT). Our results reveal that the binding abilities of atomic Fe, Co, Ni onto the internal and external surfaces of the SWCNT, SV and SW are in following orders by metals: Ni>Co>Fe. The adsorption energies of SV toward Fe, Co and Ni are more stable than those of SWCNT and SW, which can be attributed to the three active carbon sites created by a C atom removing, while the SWCNT and SW demonstrate similar adsorption energy due to the similar structure. Generally, the stability of external adsorption structures is stronger than those of internal adsorption structures, but as for the SW, the stability of internal and external adsorption structures is close, which means that the defects have improved the confinement of carbon nanotubes to M (M=Fe, Co Ni).

1. Introduction

In recent years, the high catalytic activity of single-atom catalysts has attracted great attentions due to the ultrahigh atom dispersion and unique configuration [1–4]. For metal catalysts, the catalytic performance is related to characters of the supporting materials and interaction between the metal and supporting materials. Thus, it will be great significance to explore the structures of the single-atom dispersed material.

Carbon nanotubes (CNTs) have unique property such as low density, high elasticity, high specific surface area, corrosion resistance, thermal and electrical conductivity. Therefore, CNTs are widely used in heterogeneous catalysts, gas sensitive materials, biological devices, and many other fields, especially in the field of nanomaterial catalysis as an important supporting material. CNTs as an important carrier for dispersion of transition metal have received great attention and research[5–8]. In the formation of CNTs, defects are inevitable. Among the defect types, single vacancy defects (SV) have the highest formation energy, while Stone-Wales (SW) defects have the lowest formation energy. Moreover, once the defects formed, it is generally difficult to removed, eg., the recovery of the CNTs from the SW defect needs to overcome a very high barrier to ca 6eV [9].

We all know that Fe, Co and Ni nanocrystals have been used for organic pollutant removal due to their low cost and high catalytic activity [10–23]. Liu and coworkers report that the defect-rich Pt-M (M = Fe, Co, Ni) ultrathin nanowires can be used as electrode to enhance methanol electrooxidation.Fu et al. study that PtM (M = Fe, Co, Ni) bimetallic nanoclusterscan be used as active and methanol-tolerant to enhance catalytic performances for the reactions of oxygen reduction. However, the poor air stability of Fe, Co and Ni nanocrystals will reduce their catalytic activity. To improve the stability, the group of Bao has studied the Ru, Fe, Cu, MnO₂, TiO₂ and Rh metal nanoparticles filling of small -diameter CNTs [24–26].Li and Yan et al. [27] report that metal-free catalysts ofNi-doped carbon nanosheetscan be improve oxygen
 electroreduction. Recently, Li et al. [28] have reported that atomically dispersed Fe-N sites on hierarchically mesoporous carbon nanotube can be used for CO₂ reduction effectively. In generally, the metal confinement inside CNTs still have some other advantages, such as good stability with continuous leaching of active metal. More recently, the inner iron particles could be slowly oxidized to stabilize the metallic state of Fe, and it might be reasonable to expect that the Fe encapsulated into CNT can show greater stability [29–34]. Metal confining, particularly involving 3d transition metal (such as Fe, Co Ni), can provide more electron orbits through their 3d orbital hybridization with nonmetals.

In this paper, we use density functional theory to study atomic Fe, Co and Ni adsorption outside and inside single-walled CNTs (SWCNT) and defect (SV and SW) CNTs. We have found that different defects have different adsorption and electronic property for metals, which may further influence the subsequent catalytic processes. We will systematically investigate the effect of defect on the M (M = Fe, Co, Ni) adsorption on CNTs. The calculation results reveal that the electronic structure of Fe, Co and Ni on the internal wall differs to that on the external wall of CNTs, and the defects have improved the confinement of carbon nanotubes to M (M = Fe, Co Ni).

2. Computational Details

The calculations were performed in the density functional theory (DFT) with the DMol³ package [35, 36] using the GGA-PBE method [37, 38], which can successfully consider the weak interactions between chemical functional groups. Considering the relativistic effects, the functional semicore pseudopotential (DSPP) was employed for the Fe, Co and Ni atom and other nonmetal atoms were used by all-electron basis sets. All-electrons calculations were employed with polarization function (DNP basis sets) and a dispersion force correction of density functional theory (DFT-D) with Grimme method accounting for the dispersion interactions was adopted [39, 40].

A pristine (6, 6) single-walled CNT (SWCNT) was generated in a periodically repeating tetragonal supercell with lattice constants of 30×30×9.838 Å (Fig. 1: SWCNT). A single carbon atom in the middle of SWCNT model was removed to give a single-vacancy defect in the SWCNT (Fig. 1: SV). A C-C bond in the middle of the SWCNT model was rotated by 90° to give two types of ideal Stone-Wales (SW) defect so that two pentagons and two heptagons emerge instead of four hexagons in the SWCNT (Fig. 1: SW1 and SW2). The brillouin zone integration was calculated with 1×1×5k sampling points for the structures. By calculation, a Fermi smearing of 0.005 hartree was employed to improve the computational performance. In addition, the optimization convergence in energy and force was set to 1.0×10⁻⁵ hartree and 2.0×10⁻³ hartree/Å, and the SCF convergence was set to 1.0×10⁻⁶.

The adsorption energy of Fe, Co and Ni adsorption on SWCNT, SV and SW were defined as follows:

\[ E_{ads} = E_{total} - E_{Fe/Co/Ni} - E_{SWCNT/SV/SW}, \]

where the \( E_{total} \) presents the energies of the combined systems Fe/Co/Ni@SWCNT/SV/SW, respectively; \( E_{Fe/Co/Ni} \) and \( E_{SWCNT/SV/SW} \) present the energies of Fe, Co and Ni atom and the most stable SWNT and defect carbon nanotubes (SV and SW), respectively.
3. Results And Discussions

Our study shows that defects do not significantly change the geometric properties of CNTs. However, the Fermi level shift upward (SV: 0.083eV; SW1: 0.227eV; SW2: 0.011eV) compared with that of SWCNTs due to the introduction of the defects. From Mulliken charge analysis, the average charge of defect carbon is +0.035e and +0.019e in SW1 and SW2 respectively, while the three carbon atoms obtained at the defects in SV are negatively charged (-0.044e, -0.65e and −0.66e). Obviously, the existence of defect changes the distribution of charge.

We investigate the adhesion of M (M = Fe, Co, Ni) atom out- and in- SWNT, and collect the most stable structures of Fe, Co and Ni atom adsorption external and internal SWNT in Fig. 2. As for the adsorption sites of metal on SWNT, we try to put metal atom on the top of C1, C1-C2 bond, C2-C3 bond and T sites (carbon six-membered ring, Fig. 1). For the external adsorption structures, Co atom is more likely to adsorb on the bridge site of C1-C2 bond with the adsorption energy of -2.36 eV (in Fig. 2 and Table 1). The nearest distance between Co and carbon atom of SWNT is 0.206 nm. As for the Fe/Ni@SWCNT-out, the favorable binding site of Fe and Ni atom are atop of C1 with the Fe-C and Ni-C distance of 0.220 nm and 0.187 nm, and the adsorption energies are −2.25 eV and −4.31 eV respectively. Obviously, compared with the Co and Ni atom, the Fe atom is weakly binding with the SWCNT.
We also calculate the binding abilities of Fe, Co and Ni atom on the internal wall of SWNT and find in order by the metal as follows: Ni > Co > Fe, which means Ni atom is easily adsorbed on the both internal and external wall of SWNT compared with Fe and Co atom. The Fe, Co and Ni atom are more likely to adsorb on the internal surface of carbon six-membered ring with the M-C (M = Fe, Co, Ni) distance from 0.196 to 0.218 nm. The binding energy of Ni atom adsorption inside and outside wall of SWCNT are nearly twice that of Fe and Co. However, the structural stability of external adsorption is obviously stronger than that of internal adsorption by about 1 eV (Table 1).

From the Mulliken charge (Table 1) and frontier molecular orbital (Fig. 3) analysis, we find that the electrons transfer from metal to SWCNT and lead to a certain positive charge for metal, which makes the

| Structure       | $q_M/e$ | $q_{C_{sur}}/e$ | $r_{(M-C_{sur})}/nm$ | $E_{ads}/eV$ |
|-----------------|---------|----------------|----------------------|-------------|
| Fe@SWCNT-out    | 0.393   | -0.276         | 0.220                | -2.25       |
| Co@SWCNT-out    | 0.208   | -0.111,-0.080  | 0.206,0.223          | -2.36       |
| Ni@SWCNT-out    | 0.205   | -0.136,-0.136  | 0.187                | -4.31       |
| Fe@SWCNT-in     | 0.644   | -0.108,-0.039,-0.087 | 0.207,0.217,0.210,0.196 | -1.04       |
| Co@SWCNT-in     | 0.226   | -0.044,-0.037  | 0.216,0.217          | -1.97       |
| Ni@SWCNT-in     | 0.263   | 0.025,-0.023   | 0.218,0.203,0.204,0.218 | -3.84       |
| Fe@SV-out       | 0.331   | -0.221,-0.175,-0.175 | 0.183,0.178,0.178   | -8.72       |
| Co@SV-out       | -0.441  | 0.254,-0.094,0.055 | 0.175,0.178,0.188   | -9.18       |
| Ni@SV-out       | -0.048  | -0.134,-0.046,-0.04 | 0.180,0.180,0.180 | -10.03      |
| Fe@SV-in        | 0.206   | -0.104,-0.107,-0.107 | 0.174,0.175,0.175   | -6.63       |
| Co@SV-in        | -0.397  | 0.048,0.109,0.110 | 0.175,0.176,0.176   | -7.31       |
| Ni@SV-in        | -0.154  | 0.19,0.19,0.19  | 0.178,0.178,0.178   | -8.42       |
| Fe@SW1-out      | 0.536   | -0.336,-0.338  | 0.215,0.214          | -2.67       |
| Co@SW1-out      | 0.190   | -0.101,0.072,-0.100 | 0.208,0.207          | -3.04       |
| Ni@SW1-out      | 0.223   | -0.139,-0.135,0.048,0.052 | 0.197,0.197 | -4.86       |
| Fe@SW1-in       | 0.347   | -0.420         | 0.215                | -2.46       |
| Co@SW1-in       | 0.147   | -0.010,-0.022  | 0.205                | -2.75       |
| Ni@SW1-in       | 0.157   | -0.038,-0.037  | 0.193,0.193          | -4.36       |
metal atoms easily to accept electrons with certain electrophilicity. Projected density of states (PDOS) of M@SWCNT (M = Fe, Co, Ni) are shown in Fig. 2. We find that there is little or no overlap between PDOS of metal and carbon in Fe/Co@SWCNT, and as for Ni@SWCNT-out and -in have a better overlap between Ni atom and carbon. The results show that the interaction between Ni and SWCNT is strong, which is consistent with the calculation results of adsorption energy.

In order to utilize the CNTs nanomaterials, it is necessary to enhance the adhesion of metal on CNTs. Therefore, we further studied the modulated interaction between Fe, Co and Ni atom and CNTs by defects.

The SWCNT mainly is $sp^2$, and the HOMO orbital of SWCNT consists of $p_{\pi}$ orbital of carbon atoms, while the LUMO orbital is composed of $p_{\pi}^*$ orbital. When a carbon atom is replaced by Fe, Co and Ni atom, $sp^3$ hybridization is preferred in Fe, Co and Ni atom doped SWCNT. Therefore, orbital of metal atom would be strong hybridizations with the $2p$ orbital of neighboring carbon atoms, inducing electron accumulation around metal atom (see Fig. 3).

In this paper, the adsorption behaviors of Fe, Co and Ni atom on the external and internal surfaces of SV are explored. As shown in Fig. 3, we can clearly see that the localized extent of frontier orbital around the metal in the order of Fe, Co and Ni, which could be explained by the increasing covalent ability of metal compared with M@SWCNT (M = Fe, Co, Ni). In the M@SV-out (M = Fe, Co, Ni) system, the M-C are nearly the same by about 0.18 nm, while the M-C bonds of M@SV-in (M = Fe, Co, Ni) (the M-C bonds: 0.174–0.178 nm) are shorter than that in M@SV-out. The metal atoms are observed to project out of the carbon surface because of their smaller electronegative value and larger covalent radius. Therefore, there is a strong interaction between metal and C1, C2 and C3 of SV. In Table 1, Ni@SV-out is the most stable structure with the adsorption energy of -10.03 eV, followed by Co@SV-out and Fe@SV-out (-9.18 eV and -8.72 eV). As for the M@SV-in (M = Fe, Co, Ni), the stability of these structures are obviously improved compared with the M@SWCNT-in (M = Fe, Co, Ni) with the $E_{ads}$ from -6.63 eV to -8.42 eV.

From the Mulliken charge we can see that the electrons transfer from the SV to Co and Ni, while the electron transfer direction of Fe@SV is opposite (Table 1). It maybe the $3d$ orbit of Fe atom has more unpaired electrons ($3d^64s^2$), so the electrons are easier to transfer away, which makes the Fe forming empty $d$ orbit to accept electrons easier. The PDOS of $d$-M on the M@SV (M = Fe, Co, Ni) is relatively flat and has a certain negative shift, which is quite different from that of free metal atoms. It means that the PDOS of metal atoms are more dispersed more bonding and antibonding states than that on M@SWCNT (M = Fe, Co, Ni), which indicate the interaction between metal and SV is strong.

As for the ideal Stone-Wales defects of CNT (SW1 and SW2), we find the Fe, Co and Ni atom are more likely to adsorb on the SW1. We try to put M (M = Fe, Co, Ni) on the top of C1 and C3 atom, C1-C2 bond, C2-C3 bond, T1 (seven-membered ring) and T2 (five-membered ring) sites, and the metal atoms are more likely to adsorb on the T1 site for the external adsorption structures, while the for the internal adsorption structures, the C1-C2 bond site is the best.
In M@SW1-out (M = Fe, Co Ni), when the metal atoms adsorb on the T1 site, the seven-membered ring has a large space, which makes the interaction between carbon and metal better. In Table 1, the M-C distance of M@SW1-out (M = Fe, Co Ni) is gradually lengthened with the order of Ni, Co and Fe, among which Ni-C distance is the shortest and the corresponding stability is the strongest ($E_{ads} = -4.86\text{eV}$). When the metal confined SW1 to form M@SW1-in (M = Fe, Co Ni), the stability of structures is improved compared with that of M@SWCNT-in (M = Fe, Co Ni). As for the M@SW1-in (M = Fe, Co Ni), the metal atoms are more likely to adsorb inside the defective C1-C2 bond of SW1 with the M-C distance from 0.193 nm to 0.215 nm (Table 1). The Ni@SW1-in is most stable structure compared with the other two with the adsorption energy of -4.36 eV, which is nearly the same as that of Ni@SW1-out.

From the frontier molecular orbital (Fig. 4), we can see that the interaction between metal and carbon atoms of SW1 is similar to that of SWCNT, both of which have weak interactions, and the $d$-M (M = Fe, Co, Ni) orbital nearly no bond with $p$-C orbital. Herein, the adsorption energies of M@SW1 (M = Fe, Co, Ni) are nearly the same as that of M@SWCNT (M = Fe, Co, Ni). Ni@SW1 is the most stable, followed by Co@SW1 and then Fe@SW1. The electrons are transferred from metal to SW1, leading to electrophilicity of M (M = Fe, Co, Ni). As for Fe@SW1-out and -in, there are more electrons transferred from Fe atom to SW1 than that of Ni@SW1 and Co@SW1, which may be the $d$-Fe orbital having more unpaired electrons. The results show that Fe in Fe@SW1 has strong electrophilicity. The PDOS of M@SW1 (M = Fe, Co, Ni) is similar to that of M@SWCNT (M = Fe, Co, Ni), but the overlap of $d$-M and $p$-SW1 is slightly strengthened in M@SW1 (M = Fe, Co, Ni), which is means that the interaction between metal and SW1 is enhanced.

### 3. Conclusion

In this study, we can clearly see that the introduction of defects can enhance confinement stability of metals, and the Ni atom confinement inside CNTs is the most stable. As for the SV, SW1 and SW2 defect, the SV can fix metal better. At the same time, the existence of defects can change the distribution of charge. The existence of SV can make Co@SV and Ni@SV have a certain nucleophilicity, while Fe@SV has a certain electrophilicity. As for SW, although the stability of Fe@SW1 is worse than Co@SW1 and Ni@SW1, there is more charge transfer between Fe and SW1, which makes Fe atom have strong electrophilicity.

### Declarations

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#### Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.
Code availability

The calculations were performed in the density functional theory (DFT) with the DMol3 package.

Authors’ contributions

All authors contributed to the study conception and design. Material preparation and data collection were performed by Qing-Yun Wang, Gang Nan, Guang-Di Liu, Yong-Chun Tong and Xin-Jian Xu. Data analysis was performed by Qing-Yun Wang. The first draft of the manuscript was written by Qing-Yun Wang and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Consent to participate Not applicable.

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