



Effect of Fe/N-doped carbon nanotube (CNT) wall thickness on CO₂ conversion: A DFT study

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ABSTRACT

Many researches on CO₂ adsorption using carbon nanotubes (CNTs) have been actively studied, but experimental and theoretical studies on CO₂ conversion are still in demand. In particular, the effect of CNT wall thickness on CO₂ conversion is not yet established clearly. This study employed two different-walled CNT catalysts doped with iron and nitrogen, single-walled CNT (Fe-N-SWCNT) and double-walled CNT (Fe-N-DWCNT). The structural and electrical properties of these CNTs and their influences on CO₂ conversion were characterized and compared using density functional theory (DFT) calculations. As a result, Fe-N-DWCNT was shown to improve catalyst stability with higher formation energy and adsorption energy for CO₂ adsorption than Fe-N-SWCNT. Also, the CO₂ molecules were found to be highly delocalized and strongly hybridized with Fe-N-DWCNT, leading to more active charge transfer in the catalyst. These findings demonstrate the potential of selective CO₂ conversion, as wall thickness differences can lead to different electrical properties of CNTs by showing that the larger the thicknesses, the lower the energy barrier required for CO₂ conversion. Specifically, Fe-N-DWCNT is easier to convert CO₂ to HCOOH than Fe-N-SWCNT at lower overpotential (0.15 V) obtained with limiting potentials and free energies calculated by understanding the possible reaction pathways in the proton-electron transfer process. Therefore, these results support the hypothesis that the wall thickness of CNT influences CO₂ conversion by showing that the double-walled heterogeneous CNT (Fe-N-DWCNT) is a potential catalyst to selectively produce HCOOH from CO₂ conversion.

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1. Introduction

The study of CO₂ conversion to hydrocarbon-based liquid fuels has the potential to significantly reduce global climate change by achieving a zero-carbon footprint through carbon recycling and supplying the demand for rapid consumption of natural energy resources [1]. With a great interest in CO₂ conversion, many catalysts based on noble metals (Au, Ir, and Ag) [2] or base metals (Pd—Sn alloy [3], Pd—In alloy [4], and Cu—Fe [5,6]) have been applied to reduce the energy barriers in the electrochemical or photoelectrochemical reduction of CO₂ molecules by promoting the electron transfer process. Previous studies have revealed that the metallic surface can provide active sites for adsorption of CO₂ molecules and subsequent CO₂ conversion, which can reduce the energy barriers required for selective CO₂ conversion by the electron-donating ability of the metals [7]. Also, since CO₂ has both the C-centered Lewis acid and the O-side Lewis base, the metals

coordinating with substance possessing electron-accepting ability such as oxide [7] or nitrogen [1] can strongly bind with the CO₂ molecules on its surface in various CO₂ adsorption modes.

Recently, carbon nanostructures (e.g., nanobelt [8], graphene [9,10], nanotube [11]) have been considered as an up-and-coming new class of carbonaceous materials. They can behave as suitable supporters for various metal (In [8], Au [12], Pt [13], Fe [13]) or non-metal (nitrogen and polymers [14–17]) elements to improve the catalytic ability for CO₂ conversion [8] or storing capability for others gases such as H₂ [18]. Of the carbon nanocomposites, carbon nanotubes (CNTs) have been developed to form an upright 1D nanoscale device by doping with metals and non-metals. This device has been used for CNTs applications in many areas, such as water treatment [19–21], proton-exchange membrane fuel cell [22], photocatalysis [23,24], solar cells [25], gas sensors [26], and H₂ storage [27].

Specifically, the N-doped CNTs, functionalized by various nitrogen precursors such as pyridinic, pyrrolic, or graphitic N, have attracted considerable attention in CO₂ reduction reaction (CO₂RR) [2,14,16,28]. The incorporation of the nitrogen to the structural frame of CNTs

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considerably reduces the overpotential for CO₂RR and increases the selectivity towards the production of CO [14,16]. The combination of N-doped CNT with iron, a cost-effective metal, can substantially improve its catalytic function, which converts metallic properties-free CNT into a catalyst with a magnetic moment suitable for the CO₂RR [29]. A previous study on the electrochemical CO₂RR process using metals (Fe and Mn) containing N-doped porous carbon black-based catalyst showed that N-coordinated metal ions in the carbon network produce large amounts of hydrocarbons. In the CO₂RR process, nitrogen is mainly involved in CO production, while metals can protonate or re-absorb CO to produce hydrocarbons such as CH₄ or CH₃OH [30].

Few studies have theoretically explained the effect of single-walled CNTs (SWCNTs) structures on CO₂ conversion by optimizing and identifying the inherent properties of CNTs (high conductivity and elasticity) based on experimental results [31,32]. Also, CNT catalysts are still limited to applications to adsorption or energy storage rather than CO₂ conversion. Previous studies have reported that multi-walled CNT (MWCNT) structures with two or more walls are more stable in energy and structure than single-walled CNTs and are more useful for gas adsorption [33], but little research has been done on CO₂ conversion by multi-walled CNTs (MNCNTs).

In this study, the structural and electronic properties of heterogeneous CNT catalysts were investigated using DFT to provide a clue to answering questions about what thermodynamic relationships are involved in forming liquid fuels in CO₂ conversion. Here, CNTs doped with polyaniline and iron (labeled "Fe-CNT-PA") as precursors of N and Fe were developed in previous studies and were selected for this study as catalyst candidates for CO₂ conversion [29,34]. Moreover, to investigate whether wall thickness can affect CO₂ conversion, this study compared single and double walls representing the simplest multi-walls in the selected catalyst structure. Thus, this study will be the basis for predicting the ability of CNTs to convert CO₂ into liquid chemicals and theoretically driving the critical parameters necessary for proper use in other gas adsorption and conversion applications.

2. Computational methodology

This study employed density functional theory (DFT) tool with FHI-aims and ATK-DFT in the framework of Virtual NanoLab (VNL) to theoretically characterize the electrochemical properties of the "Fe-CNT-PA" electrode sample used in the previous studies on oxygen reduction reaction (ORR) [29,34]. The ideal geometry of the pristine CNT sample was simply made of a (10,0) single-walled nanotube (SWCNT), which were the supercell of zigzag and bamboo-like structure, and the distance between the C atoms in the geometry of the pristine CNT was used at 1.42 Å. In the case of an MWCNT prototype, a double-walled CNT structure was chosen to describe how a thick wall affects the CO₂RR. Thus, a pristine double-walled CNT (DWCNT) structure was constructed to have two walls in a (5,0) inner tube with a (10,0) center tube while maintaining a zigzag shape-like an SWCNT structure. In addition to the pristine CNT structure, two different heterogeneous structures of CNT (Fe-N-SWCNT and Fe-N-DWCNT) consisting of a total N of 4.41% (N_p of 2.49% and N_c of 1.92%) and Fe of 1.48% were considered for CO₂RR [34]. All atoms in the structures were relaxed and optimized with the convergence criterion of 0.005 eV/Å by using the generalized gradient approximation (GGA) / PBE exchange-correlation function, respectively. The Brillouin zone was applied using a 4 × 4 × 1 Monkhorst-Pack *k*-points. To compare the electronic properties of Fe-N-SWCNT and Fe-N-DWCNT, the density of states (DOS) was investigated in 1 × 1 × 7 matrices of *k*-point samplings. Bader charge analysis was performed by calculating the electron density of all atoms consisting of the two different heterogeneous CNT structures. Next, adsorption energy

(E_{ads}) was calculated to evaluate the stability of adsorbed species on CNT structures by

$$E_{\text{ads}} = E_{\text{Fe-N-CNT}/m} - E_{\text{Fe-N-CNT}} - E_m \quad (1)$$

where $E_{\text{Fe-N-CNT}/m}$, $E_{\text{Fe-N-CNT}}$, and E_m are the total energies of the CO₂ molecule adsorbed on the optimized Fe-N-SWCNT or Fe-N-DWCNT catalyst, the clean catalysts with no adsorbates, and an isolated CO₂ molecule, respectively.

The formation energies (E_{for}) of Fe-N-SWCNT and Fe-N-DWCNT structures were calculated from the following equation to determine the energy stability [35,36].

$$E_{\text{for}} = E_{\text{Fe-N-CNT}} + \alpha E_C - (E_{\text{CNT}} + \beta E_N + \gamma E_{\text{Fe}}) \quad (2)$$

where $E_{\text{Fe-N-CNT}}$ is the total energy of optimized Fe-N-SWCNT and Fe-N-DWCNT structures, E_{CNT} is the total energy of pristine SWCNT and DWCNT structures, and α , β , and γ are the number of removed or substituted C atoms, added N atoms, and adsorbed Fe atoms, respectively. Also, E_C is the total energy per C atom consisting of the pristine SWCNT and DWCNT structures, E_N is the energy of an isolated N atom obtained from half of total energy of N₂ gas molecule, and E_{Fe} is the total energy for a Fe atom. In establishing the reaction pathway for electrochemical CO₂RR, the computational hydrogen electrode (CHE) models were used to calculate the changes in Gibbs free energy explaining energy levels in each reaction step.

A change in Gibbs free energy indicating the energy level at each reaction step was calculated to establish the reaction pathway for electrochemical CO₂RR through the hydrogen electrode (CHE) model proposed by Nørskov et al. [37,38]. The free energy at each electrochemical reaction step is defined by [39].

$$\Delta G(U) = \Delta G(U=0) + eU \quad (3)$$

Here, $\Delta G(U)$ is the change of free energy at each reaction step according to the applied electrical potential, U (vs. RHE). Assuming that the effect of the electric field on adsorption is negligible in this study, and when $\text{pH} = 0$, the change of free energy in each reaction step with no external potential ($\Delta G(U=0)$) can be expressed as:

$$\Delta G(U=0) = \Delta E_{\text{DFT}} + \Delta E_{\text{ZPE}} - T\Delta S \quad (4)$$

where ΔE_{DFT} is the change of the reaction energy by DFT calculations. ΔE_{ZPE} is the change of the zero-point energy correction defined as $\text{ZPE} = \sum 1/2h\nu_i$ where h is the Planck's constant and ν_i is the frequency of the i^{th} vibrational mode based on DFT calculations [36]. ΔS is the change of entropy at the ambient temperature (298.15 K). From Eq. (4), the limiting potential, U_L , can be expressed as

$$U_L = -\frac{\Delta G(U=0)}{e} = -\frac{(\Delta E_{\text{DFT}} + \Delta E_{\text{ZPE}} - T\Delta S)}{e} \quad (5)$$

Herein, U_L can be calculated by a function of the chemical potential of adsorbed species. The limiting potential (U_L) represents the lowest potential at which all the reaction steps of electrochemical CO₂ reduction are downhill in free energy, as reported in previous studies [40]. In the proton-electron transfer step, $A^* + H^+ + e^- \rightarrow B^*$, it can be rewritten as

$$U_L = -\frac{\mu[B^*] - \mu[A^*] - \mu[H^+ + e^-]}{e} \quad (6)$$

where $\mu[H^+ + e^-]$ can be represented as $1/2\mu(\text{H}_2(\text{g}))$. "*" designates an adsorbed state. $\mu[B^*]$ and $\mu[A^*]$ are the chemical potentials of B* and A*, respectively. Besides, the overpotential (η) value from the limiting potential can be obtained as follows [41].

$$\eta = U_{\text{equ}} - U_L \quad (7)$$

where U_{eq} is the equilibrium potential. The overpotential (η) represents the additional potential applied to the electrode reaction to initiate the production of formic acid or CO from CO₂.

3. Results and discussion

3.1. CO₂ adsorption sites of Fe-N-SWCNT and Fe-N-DWCNT

Two different types of heterogeneous CNT catalysts, Fe-N-SWCNT and Fe-N-DWCNT, were configured to compare their catalytic activity and selectivity for CO₂ adsorption application. Here, Fe-N-SWCNT and Fe-N-DWCNT structures have one wall and two walls (inner and outer), respectively. To construct the geometry of Fe-N-SWCNT and Fe-N-DWCNT, two different N types (pyridinic-N, N_P; graphitic-N, N_G) and Fe-doped CNTs' structures developed in the previous study were used with theoretical results [29,34]. Herein, the C atom of the pristine CNT was replaced by N_P and N_G atoms, the former binds to two C atoms with one vacancy site, and the latter to three C atoms. Then, Fe atoms were connected between C and N atoms on the outermost walls of each Fe-N-SWCNT and Fe-N-DWCNT. To understand the

CO₂RR that occurs during the protons-electron transfer process, the optimal adsorption sites of two heterogeneous CNT catalysts for protons were investigated. In addition, research on proton adsorption can help determine whether Fe-N-DWCNT and Fe-N-SWCNT can impede hydrogen production and may lead to CO₂ reduction against hydrogen evolution. Fig. 1 shows electron density, Bader charge difference, and adsorption sites of Fe-N-SWCNT and Fe-N-DWCNT for protons. Fig. 1a depicts the number of electrons that make up all the atoms forming the Fe-N-SWCNT catalyst in the bulk cell. We found that N and Fe atoms surrounded by many electrons can provide a reactive site for adsorbate. As shown in Fig. 1d, Fe-N-DWCNT and Fe-N-DWCNT were similarly shown to be rich in electrons around N and Fe. The Bader charge analysis described in Fig. 1b shows the change in charge transfer when N and Fe atoms are present in the carbon network of Fe-N-SWCNT. Fe atom acts as a positive charge by the deficient electrons, and the two N atoms around the Fe atom accept excessive electrons from the C atom as well as the Fe atom. This approach, which deduces the result of determining the charged atom as positive or negative, from the net charge obtained from the Bader charge difference, has been reported in previous work [42,43]. Fig. 1e shows the results of the Bader charge analysis for Fe-N-DWCNT. Like the electron distribution of Fe and N atoms in Fe-N-SWCNT, Fe-N-DWCNT also has electron loss in Fe atom and gain in N atom. Based on the results of electron

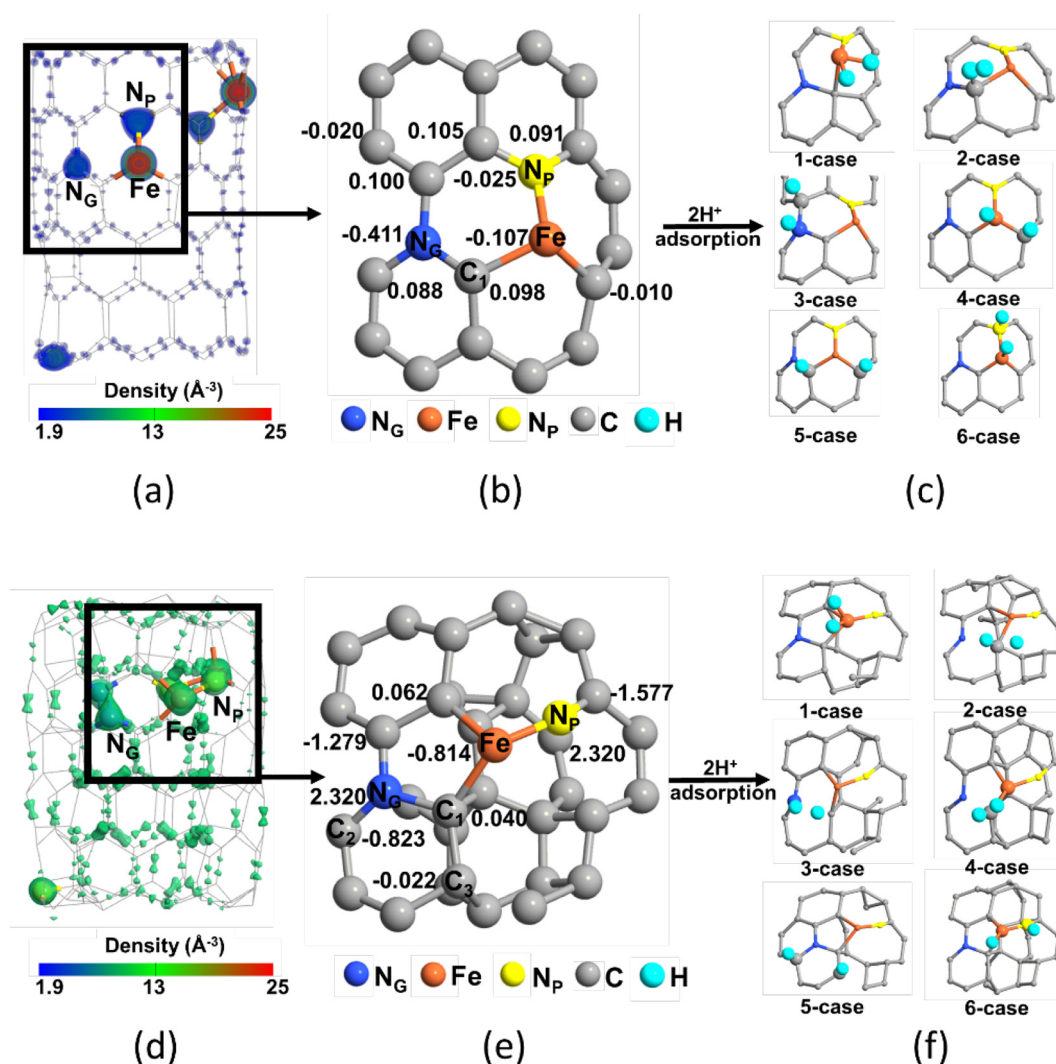


Fig. 1. Schematic illustrations of (a-c) Fe-N-SWCNT and (d-f) Fe-N-DWCNT to show electron density (a and d), Bader charge difference (b and e), and optimized structures (c and f) for two proton atoms adsorbed on the outermost wall of each CNT structure. Different six cases represent various adsorption sites for two protons.

Table 1

The calculated adsorption energies for CO₂ adsorption (E_{ads}), geometrical parameters between the bidentately adsorbed CO₂ molecule and the surface Fe atoms of two catalysts, and molecular O-C-O angle ($\angle O_{\text{ad}}\text{-C}_{\text{ad}}\text{-O}$).

	E_{for} (eV)	E_{ads} (eV)	$d(\text{Fe-C}_{\text{ad}})^1$ (Å)	$d(\text{Fe-O}_{\text{ad}})^2$ (Å)	$d(\text{O}_{\text{ad}}\text{-C}_{\text{ad}})^3$ (Å)	$d(\text{C}_{\text{ad}}\text{-O})^4$ (Å)	$\angle O_{\text{ad}}\text{-C}_{\text{ad}}\text{-O}$ (degree)
Fe-N-SWCNT	-6.81	-7.24	1.97	1.90	1.26	1.20	146
Fe-N-DWCNT	-22.53	-9.08	1.97	2.01	1.23	1.21	147

Note: ¹ $d(\text{Fe-C}_{\text{ad}})$ is the bond length between the Fe atom and the adsorbed C atom of the CO₂ molecule adsorbed on the Fe site. ² $d(\text{Fe-O}_{\text{ad}})$, ³ $d(\text{O}_{\text{ad}}\text{-C}_{\text{ad}})$, and ⁴ $d(\text{C}_{\text{ad}}\text{-O})$ denote bond lengths between Fe atom and adsorbed O atom of CO₂, between adsorbed O and C atoms of CO₂, and between adsorbed C atom and O atom of CO₂, respectively.

density and Bader charge, the adsorption sites for protons to trigger the CO₂RR process were investigated. Based on the results, schematic systems capable of proton adsorption to Fe-N-SWCNT and Fe-N-DWCNT were constructed and are shown in Fig. 1c and f.

Then, the calculated total energy and bond length for the possible proton adsorption configurations are arranged in Table S1. The first case (Case-1) of the Fe-N-SWCNT in Table S1 has the lowest total energy where the Fe site energetically favors the proton adsorption. Herein, the low total energy means that proton can be adsorbed on the catalyst surface while easily desorbed to participate in the electron exchange process. The Case-5 of Fe-N-DWCNT has less total energy, while Cases 2–4 have breakage of N_G-C1 bonds that prevents a single H atom from adsorbing on the catalyst surface.

Next, the formation energies (E_{for}) of Fe-N-SWCNT and Fe-N-DWCNT were calculated to investigate the possibility of CO₂ adsorption. Table 1 shows that the formation energy of the Fe-N-DWCNT structure is higher than that of Fe-N-SWCNT, and the former has higher catalyst stability for CO₂ adsorption than the latter. The adsorption sites of Fe-N-SWCNT and Fe-N-DWCNT using the Case-1 configuration for adsorption of free CO₂ molecules were considered at the same proton adsorption position. When Fe atoms selected as adsorption sites are adjacent to N_p and N_c atoms, the Fe was found to be able to provide as a reaction site for the reduction reaction [29]. When optimizing the geometry of CO₂ adsorbed on a Fe atom, the bidentate adsorption mode was configured in which C and O atoms of CO₂ are simultaneously bonded to Fe atoms (See Fig. 2a and b). Linear current-voltage plots for Fe-N-SWCNT and Fe-N-DWCNT were also obtained to describe conductivity and catalytic stability with distortion of the catalysts after CO₂

adsorption, as shown in Fig. 2c. Fe-N-DWCNT was found to have higher electrical conductivity because of its much lower resistance than Fe-N-SWCNT. Comparing the two catalysts before and after CO₂ adsorption, no significant change in voltage range was found within ± 2 V, indicating that the stability and electrical properties [44] of the catalysts was rarely affected by CO₂ adsorption. There are some peak changes around +2 V and -2 V, but this could be due to the instability of the CO₂ molecule.

The calculated adsorption energies and geometrical parameters for the CO₂ adsorption configuration are presented in Table 1. The parameter values in Table 1 show that linear free CO₂ molecules bend upon adsorption on the catalyst surface and then easily bonded to Fe-N-SWCNT and Fe-N-MWCNT by the negative values of E_{ads} . Since CO₂ adsorption causes a change in the state energy of the catalyst surface, the density of states (DOS) before and after CO₂ adsorption was investigated to determine whether CO₂ molecules bound to the catalyst surface can undergo CO₂RR.

Fig. 3 shows the partial density of states (PDOS) that describes the charge transfer between the adsorbed CO₂ molecule and the surface of Fe-N-SWCNT or the Fe-N-DWCNT. The top of Fig. 3 shows the p -states for the C—O atoms of CO₂ molecules adsorbed in the bidentate mode to Fe atoms on the surfaces of Fe-N-SWCNT and Fe-N-DWCNT. However, the adsorbed CO₂ molecules have higher delocalization states on the Fe-N-DWCNT than Fe-N-SWCNT, indicating that CO₂ molecules are more stably adsorbed to the multi-walled CNT catalyst. The bottom of Fig. 3 compares the change in Fe p -states before and after CO₂ adsorption. In Fe-N-SWCNT, the peak near the Fermi level ($E_f = -4.39$ eV) was reduced by 0.19 eV relative to Fe-N-SWCNT/CO₂ ($E_f = -4.58$ eV),

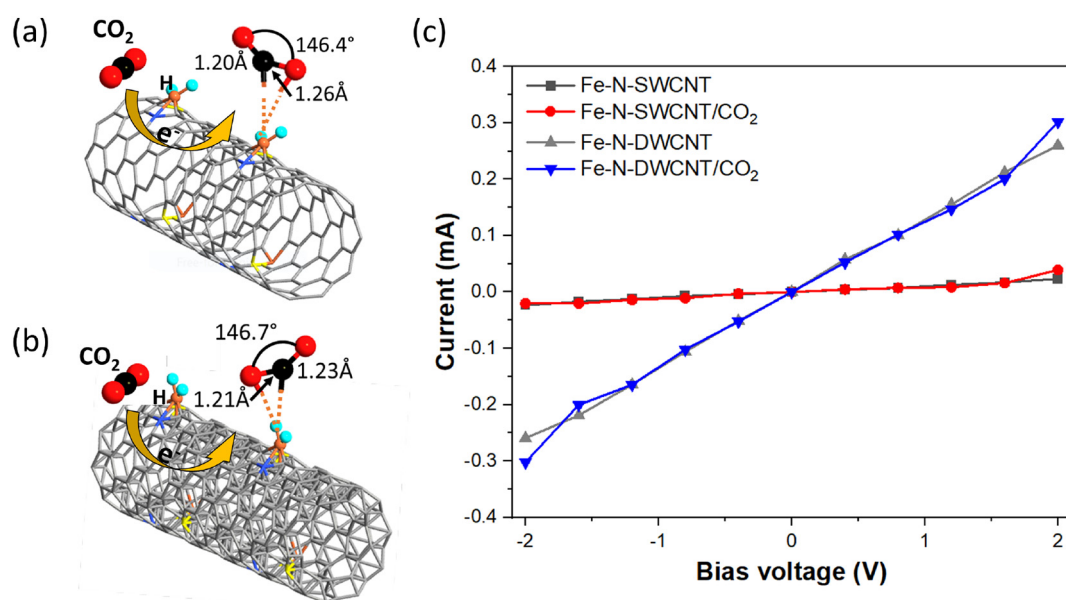


Fig. 2. Adsorption geometries for CO₂ adsorption on the (a) Fe-N-SWCNT and (b) Fe-N-DWCNT surface. (c) Change in current-voltage plot before and after CO₂ adsorption on Fe-N-SWCNT and Fe-N-DWCNT.

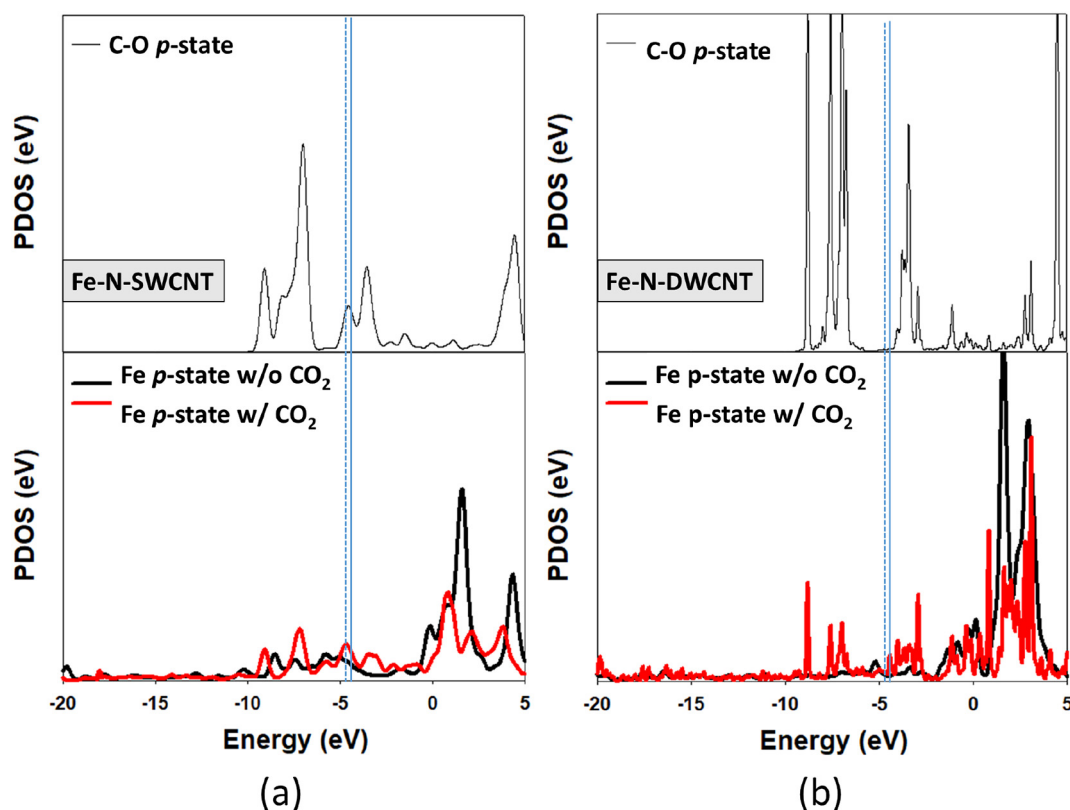


Fig. 3. Calculated partial density of states (PDOS): (above) *p*-states of C–O atom of the CO₂ molecule bound to (a) Fe-N-SWCNT and (b) Fe-N-DWCNT in the bidentate adsorption mode, and (below) Fe *p*-state of (a) Fe-N-SWCNT and (b) Fe-N-DWCNT before (Fe *p*-state w/o CO₂) and after CO₂ adsorption (Fe *p*-state w/ CO₂). The Fermi level before and after CO₂ adsorption is indicated by the vertical solid line and dashed line, respectively.

indicating that CO₂RR occurred. A decrease in Fermi levels was also found between Fe-N-DWCNT ($E_f = -4.46$ eV) and Fe-N-DWCNT/CO₂ ($E_f = -4.59$ eV). Compared to Fig. 3a and b, strong hybridization between the adsorbed CO₂ molecule and Fe-N-DWCNT were observed, indicating more charge transfer between them.

3.2. CO₂RR mechanism via the proton-electron transfer process

A proton-electron transfer process causes the formation of carbon-based compounds in electrochemical CO₂RR. We consider the elementary steps of CO₂RR towards two products (CO and formic acid) formation that are competitively produced through the 2e⁻-mediated reduction pathway. One pathway for CO production (Path-I) is induced via carboxyl intermediate (*COOH), and another pathway for formic

acid production (Path-II) is presented via formate intermediate (*CHOO) as follows.

Path-I



Path-II



where “*” indicates an adsorption state on the catalyst surface. From the above reaction mechanisms, the free energies of the elementary step were calculated by Eq. (4) with the data (E_{ZPE} , TS, $G-E_{\text{DFT}}$) shown in Table 2. For calculations of free energies, the zero-point energy correction (E_{ZPE}) and entropy (TS) for all surface species were calculated, and their contribution to total free energy corrections was provided in Table 2. As a result, the free-energy diagrams calculated for CO and HCOOH production pathways are described in Fig. 4, along with activation energy barriers for CO and formic acid formation at different electrical potentials.

Figs. 4a and b compare the catalytic ability of Fe-N-SWCNT and Fe-N-DWCNT by evaluating the activation energy barriers to CO production through COOH intermediate in O–H bond formation (Path-I). Without any external potential (0 eV vs. RHE), *COOH production follows an uphill process with the activation energy barriers of 0.40 eV and 0.16 eV for SWCNT and DWCNT, respectively. Subsequently, the second reaction step (*COOH + H⁺ + e⁻ → * + CO + H₂O) follows another uphill process by 0.88 eV and 0.52 eV for SWCNT and DWCNT, respectively. To

Table 2

Zero-point energy correction (E_{ZPE}), entropy term (TS), and total free energy correction ($G-E_{\text{DFT}}$). The unit of all data is eV.

Species	E_{ZPE} (eV)	– TS (eV)	$G-E_{\text{DFT}}$ (eV)
H ₂ O (l)	0.53	– 0.65	– 0.02
CO ₂ (g)	0.31	– 0.67	– 0.24
CO (g)	0.14	– 0.61	– 0.38
HCOOH (ag)	0.90	– 1.01	– 0.02
COOH* on Fe-N-SWCNT	0.57	– 0.25	0.42
*OCHO on Fe-N-SWCNT	0.60	– 0.23	0.47
CO* on Fe-N-SWCNT	0.17	– 0.15	0.11
HCOOH* on Fe-N-SWCNT	0.68	– 0.17	0.63
COOH* on Fe-N-DWCNT	0.60	– 0.20	0.49
*OCHO on Fe-N-DWCNT	0.59	– 0.28	0.40
CO* on Fe-N-DWCNT	0.20	– 0.15	0.14
HCOOH* on Fe-N-DWCNT	0.63	– 0.17	0.56

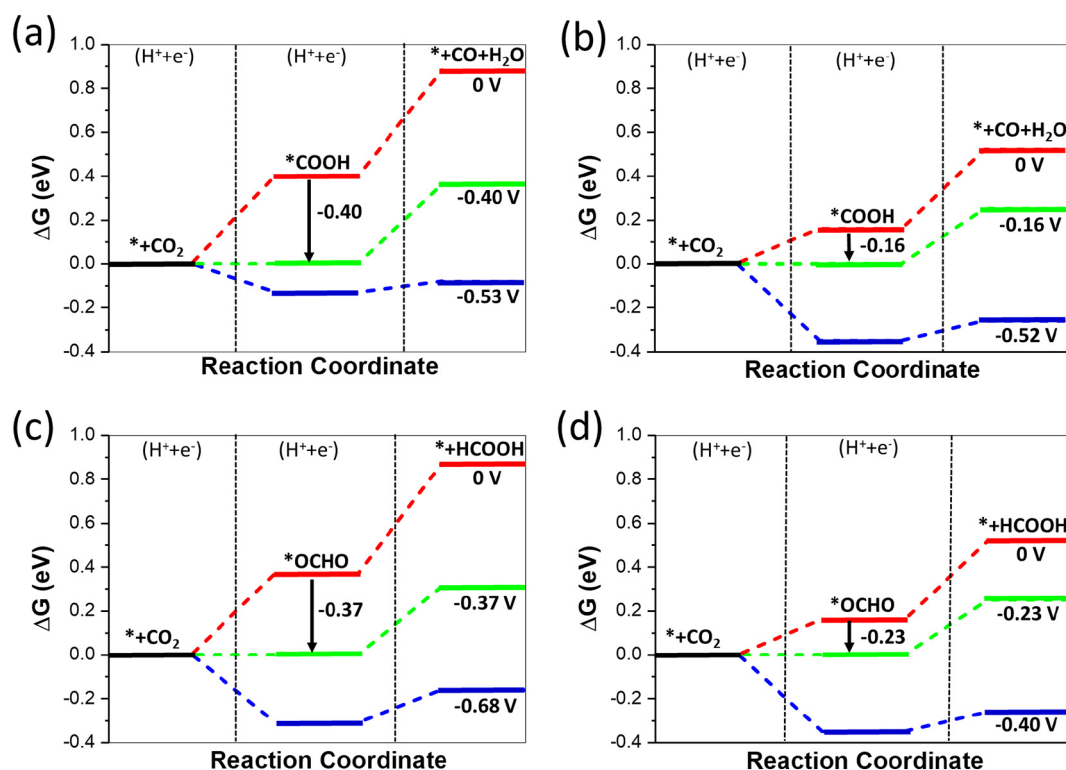


Fig. 4. Free energy diagrams of two CO_2RR pathways for CO production by (a) Fe-N-SWCNT and (b) Fe-N-DWCNT and HCOOH production by (c) Fe-N-SWCNT and (d) Fe-N-DWCNT. The red, green, blue lines represent the non-external potential (0 eV vs. RHE), negative electrode potential, calculated limiting potential, respectively.

remove the energy barriers of the reaction $CO_2(g) + H^+ + e^- \rightarrow ^*COOH$, the negative electrode potentials of -0.40 V and -0.16 V were applied to SWCNT and DWCNT, respectively. However, the Path-I reactions are still undesirable for both catalysts. So, the limiting potentials were calculated using Eq. 6 to predict the possible electrode potentials for CO formation, and the trend lines were extrapolated with these values (Fig. 5). As the limiting potential is given as an external potential, the second reaction step in the Path-I can eventually be favorable. The Path-I is an overall uphill process at $U = 0$ V regardless of the catalyst type but produces an exothermic reaction under the calculated limiting potential conditions, and COOH is identified as a rate-limiting step.

Fig. 4c and d describe the energy barriers of formate production via *OCHO intermediate in C–H bond formation (Path II) using the two catalysts. When compared with Fig. 4a and b, they also follow an uphill

process for *OCHO intermediate production with similar activation energy barriers of 0.37 eV and 0.23 eV for SWCNT and DWCNT, respectively. Similar to CO production, the HCOOH formation step follows an uphill process, but the preference for CO and HCOOH production pathways was shown to lie in Fe-N-DWCNT when negative electrode potentials of -0.37 V and -0.23 V were applied to Fe-N-SWCNT and Fe-N-DWCNT, respectively. The limiting potentials for the possible HCOOH formation obtained by extrapolating the trend line of Path-II were -0.68 V for Fe-N-SWCNT and -0.40 V for Fe-N-DWCNT, respectively (Fig. 5). The pathway of HCOOH formation by both catalysts follows an exothermic reaction with a downhill process in the free energy, indicating that the *OCHO formation is the rate-limiting step. Under each limiting potential, our results show that the formation of HCOOH, as well as CO production, is preferred by the catalytic reaction

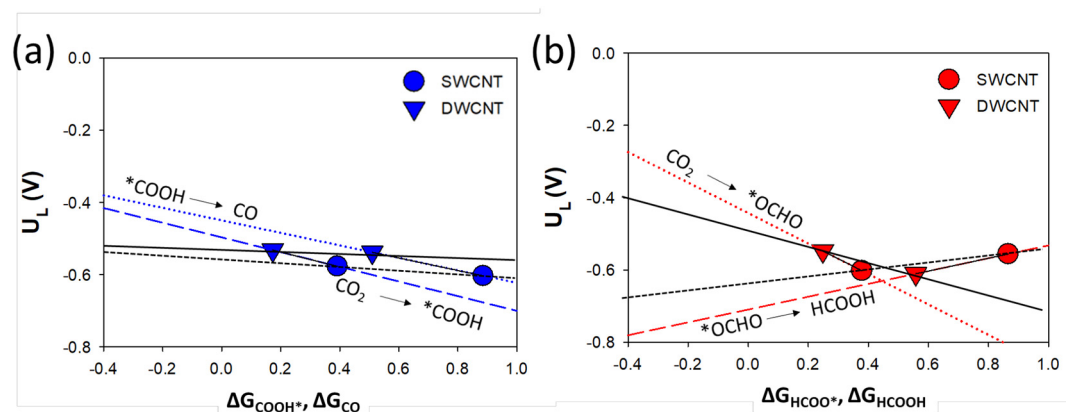


Fig. 5. Free energy diagrams of two CO_2RR pathways towards the formation of (a) CO and (b) HCOOH on Fe-N-SWCNT and Fe-N-DWCNT. The dashed and dotted lines (blue) represent the activation energy barriers of the elementary reaction step. The dashed and straight lines (black) are trend lines that extrapolate the free energy values to predict the limiting potential.

between Fe-N-DWCNT and CO₂. Thus, it was found that the double-walled Fe-N-DWCNT prefers to form CO and HCOOH thermodynamically despite the lower electrode potential than a single-walled Fe-N-SWCNT.

Next, the overpotential can be found indirectly through the limiting potential value obtained above and the theoretically well-known equilibrium potential value. The overpotentials were calculated by using the equilibrium potentials (U_{eq}) of around -0.11 V and -0.25 V at pH 0 required for the formation of CO and HCOOH by CO₂RR [45]. As a result, Fe-N-SWCNT and Fe-N-DWCNT have overpotentials of 0.42 V and 0.41 V for CO and 0.43 V and 0.15 V for HCOOH, respectively. Compared to the overpotentials of Fe-N-SWCNT and other catalysts such as N-doped graphene (0.25 V) [46], Sn porous nanowires with a high grain boundary (0.35 V) and Cu/Ni oxide (0.37 V) [45], Fe-N-DWCNT possesses a higher catalyst performance for CO₂RR to HCOOH with a low overpotential (0.15 V). However, the overpotential values of the two catalysts for CO₂RR to CO are not significantly different, but higher than previous studies with Cu/Ni(OH) nanometers (0.39 V) [45] and lower than pyrrolic N-doped graphene (0.55 V) [46] or monoatomic Ni-N-C catalysts (0.57 V) [45]. After all, CNTs doped with iron and nitrogen show that the catalysts can lead to the CO₂RR process. In particular, Fe-N-DWCNT, as a double-walled heterogeneous CNT, became a much more suitable catalyst to induce CO₂RR performance than Fe-N-SWCNT with low overpotential. Also, Fe-N-DWCNT shows the highly selective production of HCOOH in the CO₂RR process.

4. Conclusions

This study characterized the structural and electrical properties of iron-and-nitrogen-doped single-walled CNTs (Fe-N-SWCNT) and double-walled CNTs (Fe-N-DWCNT) selected as potential catalyst candidates for CO₂ conversion through DFT calculations. As a result, Fe-N-DWCNT was found to have higher catalyst stability towards CO₂RR due to higher formation energy and adsorption energy for CO₂ adsorption than Fe-N-SWCNT, which was strongly supported by the calculated density of states (DOS) values. Also, Fe-N-DWCNT exhibits stronger hybridization with CO₂ molecules as well as higher delocalization of CO₂ molecules than Fe-N-SWCNT, indicating more charge transfer between CO₂ molecules and Fe-N-DWCNT. Although the charge transfer appears to be more active in Fe-N-DWCNT, the energy profile and overpotential values were calculated to predict if CO₂ conversion could occur. In the reaction pathways by two proton-electron transfers, Fe-N-SWCNT and Fe-N-DWCNT require overpotentials of 0.42 V and 0.41 V for CO₂RR to CO, respectively, and 0.43 V and 0.15 V for CO₂RR to HCOOH, respectively. Consequently, our DFT study shows that the CNT wall thickness can affect CO₂ conversion. Particularly Fe-N-DWCNT can be considered a potential catalyst to selectively produce HCOOH in CO₂ conversion.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.susmat.2020.e00224>.

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