



Metal-phthalocyanine functionalized carbon nanotubes as catalyst for the oxygen reduction reaction: A theoretical study

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ABSTRACT

The covalent functionalization of metallic single-walled carbon nanotubes (CNTs) with transition metal phthalocyanines (MPc, with M = Mn, Fe and Co) are addressed by density functional calculations. The CNT-MPc catalytic activity toward the oxygen reduction reaction (ORR) is investigated through the O₂ stretching frequency adsorbed on the phthalocyanine metal center. We find better reduction abilities when the CNT functionalization occurs through sp²-like bonds. Multiple stable-spin states for the M-O₂ adduct are also found for M = Mn and Fe, suggesting higher ORR rates. The CNT-MPc complexes show metallic characteristics, suggesting favorable conditions to work as ORR cathode catalysts in fuel cells.

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1. Introduction

Transition metal-N₄ macrocycles such as iron and cobalt phthalocyanines (FePc, CoPc) have attracted much attention recently as alternative to precious metal cathode catalysts in proton exchange membrane (PEM) fuel cells due to their activity and selectivity toward the oxygen reduction reaction (ORR) [1–3]. Indeed, metal-N₄ centers supported on microporous carbon have shown ORR activity comparable to those observed on Pt-based catalysts [4], whereas the feasibility of using metal phthalocyanines (MPc) in practical fuel cells has been recently verified [5,14]. Although the mechanism responsible for the ORR activity are not clearly understood, recent works point to the atomic structure formed by metal-N₄ and metal-N₂ moieties in a carbon matrix [4,6–8]. However, one of the major challenges of non-pyrolyzed metal-N₄ catalysts is the macrocycle immobilization on suitable conductive support that preserve their catalytic properties in the strong acidic environment of PEM fuel cells.

During the last few years, the chemical functionalization of carbon nanotubes with metal-N₄ macrocycles, hereafter called simply macrocycles, like porphyrins and phthalocyanines have emerged as one of the most promising materials for cathode catalysts in PEM fuel cell [9–14]. These supramolecular complexes meet the outstanding properties of metallic CNTs such as high electrical conductivity, high surface area, and significant mechanical strength, with the well-known ORR electrocatalytic activity of CoPc and FePc. In these macrocycles, the oxygen reduction can proceed through a four-electron (two-electrons) process to produce water (hydrogen peroxide). In order to obtain the maximum free energy

or the highest O₂ oxidant capacity on the cathode of PEM fuel cells, O₂ needs to be reduced via four electrons. It was found that FePc can promote four-electron ORR but CoPc only two-electron ORR [3]. The opposite is observed for porphyrins containing the same metal center. In fact, Co porphyrins anchored to multi-walled CNTs have shown excellent catalytic performance for ORR in acidic medium at room temperature, where a direct four-electron reduction of oxygen to water was experimentally verified [10]. However, fundamental understanding of the O₂ reduction mechanism in Co and Fe phthalocyanines supported on different carbon substrates are needed for designing non-noble cathode catalysts materials for PEM fuel cells.

In previous works, we have investigated the stability and electronic properties of an iron porphyrin adsorbed on a metallic single-walled CNT [15]. It was found that the π-π stacking interaction produces a rather strong macrocycle adsorption on the CNT support but it does not ensure its immobilization. In addition, the charge transfer process between the CNT and the macrocycle is limited by a hopping mechanism. On the other hand, the covalent attachment is found to be a more appropriate mechanism to explain the catalytic properties reported, allowing a direct charge transfer due to the metallic character of the assembly and also ensuring a strong fixation. We also investigated the oxygen adsorption on the metal center of metal-porphyrins-CNT complexes [16]. In the present Letter we have moved forward studying a more complex macrocycles, namely transition metal phthalocyanines (MPc, M = Mn, Co, Fe) attached covalently to a metallic CNT. We investigate the ability of CNT-MPc complexes to work as ORR catalysts based on an atomistic description of the M-O₂ adduct and the role of the spin coupling between the O₂ molecule and the phthalocyanine metal center. Our results reveal a correlation

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between the strength of the CNT–MPc attachment and the weakening of O–O bond in the O₂ adduct, which is the first step toward the dissociation, suggesting that stronger covalent bonds between the MPc and the CNT would increase the ORR catalytic activity. We also find that covalently-functionalized metallic CNTs preserve their electrical conducting properties suggesting improved performance as a catalyst support.

2. Theoretical approach

The calculations were carried out using the density functional theory within the generalized gradient approximation to the exchange and correlation functional (GGA) [17], as implemented in the SIESTA *ab initio* simulation package [18]. A basis set of localized atomic orbitals (double- ζ plus polarization functions), and norm-conserving pseudopotentials were employed. The partial core correction and relativistic effects for transition metal pseudopotentials were included. The transition metal phthalocyanines are covalently linked to a metallic (8,8) CNT of 11 Å in diameter. The CNT–MPc complexes are described within large cubic supercells of side $12a_0$, where $a_0 = 2.49$ Å is the length of the CNT unit cells. The Brillouin zone sampling was performed with the Γ point for the geometry optimization and with a $2 \times 2 \times 2$ k -point mesh for the electronic properties. The CNT–MPc complexes are fully relaxed until the force on each atom is less than 0.05 eV/Å. Binding energies are calculated by the energy difference between adsorbed and separated constituents, considering corrections due to the basis set superposition error.

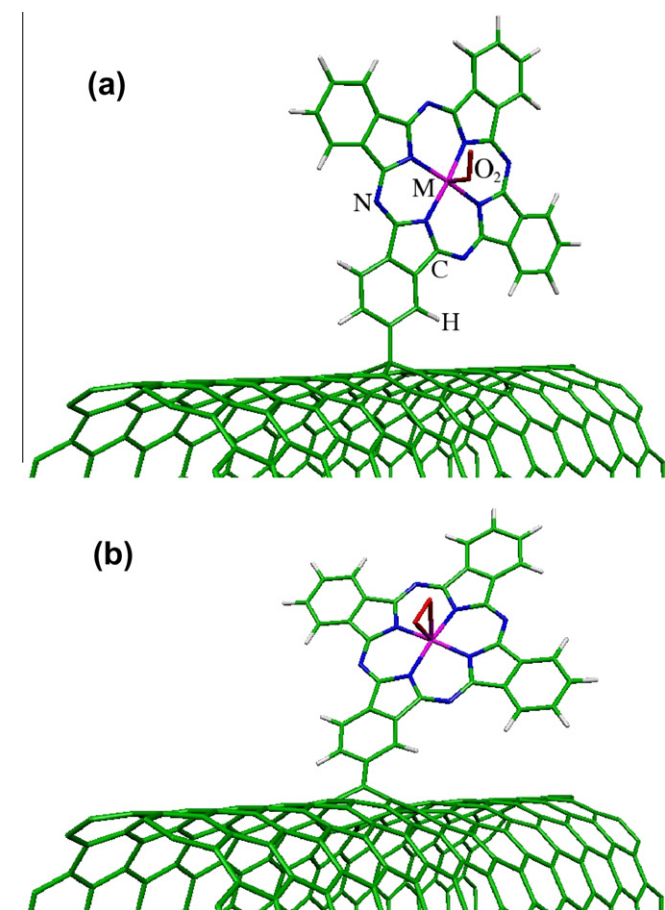


Figure 1. Stable geometries of the O₂ molecule adsorbed on the phthalocyanine metal center of the CNT–MPc complex. (a) CNT–MPc in the sp^3 bonding structure and M–O₂ adduct in the *endon* geometry. (b) CNT–MPc in the sp^2 bonding structure and M–O₂ adduct in the *sideon* geometry.

Figure 1 shows the two most probable geometries for the CNT–sidewall covalent functionalization with metal phthalocyanines as considered in the present Letter. In one case, a macrocycle radical MPC[•] (without an H atoms) binds a C atom of the pristine CNT, forming a sp^3 bonding structure (Figure 1a). In the equilibrium geometry, the MPC is normal to the CNT surface and its plane forms an angle of 30° with the CNT axis. In the other case, a sp^2 bonding structure could be formed when a MPC[•] finds a twofold-coordinated C atom in the CNT surface (Figure 1b). In the equilibrium geometry, the MPC is tilted 60° with respect to the CNT surface. Twofold coordinated C atoms in CNTs are typically found at vacancy defects with odd numbers of missing atoms or at the end of open CNTs [19]. Figure 1 also shows the two equilibrium geometries found for the O₂ molecule adsorbed on the phthalocyanine metal center, known as *endon* (Figure 1a) and *sideon* (Figure 1b).

3. Results and discussion

Table 1 shows results for the average M–N and N–C bond lengths, the energy difference between the highest-occupied and lowest-unoccupied molecular orbitals (HOMO and LUMO), and the spin magnetic moment or the number of unpaired electrons in the macrocycles. We observe small changes in the phthalocyanine geometries for different metal centers, where the M–N bond distances are slightly overestimated (less than 1%) with respect to the available experimental data, in particular for FePc and CoPc [20,21]. Our results also agree well with previous calculations [22,23]. The equilibrium spin multiplicity tends to favor high-spin configurations, showing that the number of unpaired electrons increase from one to three for increasing occupation of the metal 3d orbital.

Table 2 shows results for the geometry and electronic properties of the CNT–MPc complex attached by sp^2 and sp^3 covalent bonds. For these structures we find binding energies of about 4 and 1 eV, respectively, which are independent of the metal centers. The small changes in the geometries and magnetic moments of CNT–MPc as compared with the isolated MPc strongly suggest that the ORR catalytic properties of metal phthalocyanines would be preserved when attached to the CNTs. Figure 2 shows the density of states of the CNT–MPc complexes in the sp^2 and sp^3 linking geometries. We observe that in both cases they show available states at the Fermi level, indicating that electrons can be transfer

Table 1
Bond distance (d), HOMO–LUMO energy (E_{HL}), and magnetic moment (m) of metal phthalocyanines.

Molecule	$d_{\text{M-N}}$ (Å)	$d_{\text{C-N}}$ (Å)	E_{HL} (eV)	m (μB)
MnPc	1.955	1.403	1.45	3.0
FePc	1.937	1.400	1.46	2.0
CoPc	1.924	1.397	1.47	1.0

Table 2
Bond distance (d), binding energy (E_b) and spin magnetic moment (m) of MPc linked to the CNT surface through sp^2 and sp^3 covalent bonds.

Complex	$d_{\text{M-N}}$ (Å)	$d_{\text{C-N}}$ (Å)	E_b (eV)	m (μB)
CNT–MnPc (sp^2)	1.948	1.402	3.82	3.1
CNT–FePc (sp^2)	1.932	1.399	3.89	1.9
CNT–CoPc (sp^2)	1.916	1.396	3.86	0.9
CNT–MnPc (sp^3)	1.952	1.402	0.97	3.1
CNT–FePc (sp^3)	1.930	1.399	0.96	1.9
CNT–CoPc (sp^3)	1.922	1.396	0.96	0.9

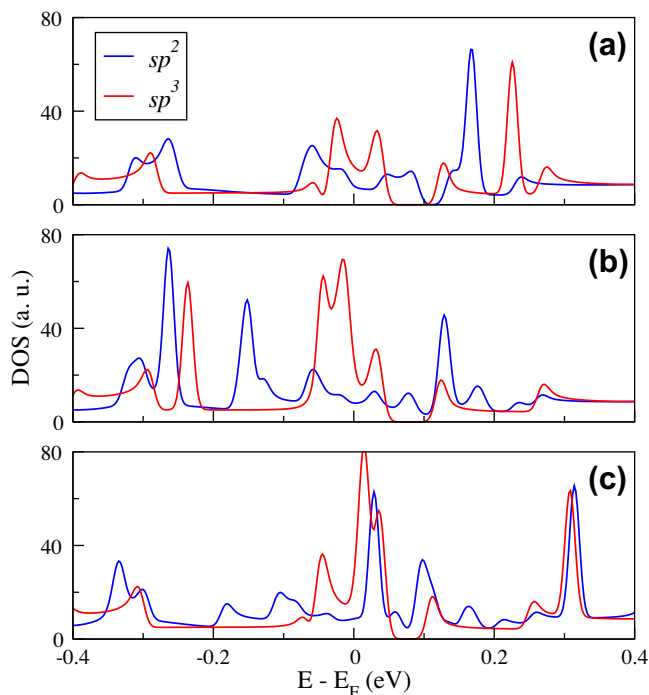


Figure 2. Density of states (DOS) for metal phthalocyanine-carbon nanotube complexes: (a) CNT-CoPc, (b) CNT-FePc, and (c) CNT-MnPc. Blue (red) curve indicates the DOS for the complexes in the $sp^2(sp^3)$ linking geometry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

from the CNT to the phthalocyanine metal center upon interacting with the O_2 molecule. Next we present our results for the O_2 interaction with isolated metal phthalocyanines. As mentioned earlier, the O_2 molecule can take two equilibrium positions when adsorbed on the metal center: endon (Figure 1a) and sideon (Figure 1b). Because of the triplet spin configuration of O_2 ($m = 2 \mu_B$) and the unpaired electrons at the phthalocyanine metal centers, the occurrence of stable $M-O_2$ adducts are driven by the spin coupling between them. Therefore, we search for stable $M-O_2$ adducts considering all possible spin configurations by fixing the total magnetic moment. The ORR activity of metal phthalocyanines is estimated considering the O_2 binding energy and the strength of the O–O bond in the $M-O_2$ adduct. The bond strength of the adsorbed O_2 is obtained by calculating its stretching frequency. Table 3 shows our results for the adsorption of the O_2 molecule on the phthalocyanines metal center. For $MnPc:O_2$ we find three stable geometries, two sideon with O_2 binding energies of 0.6 and 0.3 eV, and one endon with a binding energy of 0.2 eV. The most stable $Mn-O_2$ adduct (sideon) shows a total magnetic moment of

Table 3
Binding energy (E_b), bond length (d), stretching frequency (ν), and magnetic moment (m) for O_2 adsorbed on the MPc metal center in the equilibrium geometry. Theoretical results for gas phase O_2 are also included for comparison.

Adduct	E_b (eV)	d_{O-O} (Å)	d_{M-O} (Å)	ν_{O-O} (cm^{-1})	m (μ_B)
O_2	–	1.241	–	1574	2.0
$MnPc:O_2$ (sideon)	0.61	1.370	1.901	1111	3.0
$MnPc:O_2$ (sideon)	0.29	1.299	2.339	1350	5.0
$MnPc:O_2$ (endon)	0.21	1.273	1.939	1380	1.0
$FePc:O_2$ (endon)	0.29	1.270	1.884	1378	0.0
$FePc:O_2$ (sideon)	0.10	1.286	2.360	1368	4.0
$CoPc:O_2$ (endon)	0.23	1.265	1.934	1388	1.0

3 μ_B which indicates an intermediate spin configuration, whereas the second (sideon) and third (endon) stable geometries show ferromagnetic and antiferromagnetic coupling, respectively, with magnetic moments of 1 and 5 μ_B . For $FePc:O_2$ we find two stable geometries, the most stable (endon) with binding energies of 0.3 eV, shows a Fe– O_2 antiferromagnetic coupling ($m = 0$), and the second stable (sideon) with a binding energy of 0.1 eV shows a ferromagnetic coupling ($m = 4 \mu_B$). Finally, for $CoPc:O_2$ we find only the endon geometry with a binding energy of 0.2 eV and total magnetic moment $m = 1 \mu_B$, indicating an antiferromagnetic coupling. Our results for the O_2 stable geometries on FePc and CoPc agree well with recent calculations, but the binding energies there reported almost double our values [22–25]. This can be explained in part for the different approaches used for the exchange and correlations functional.

According to our results, the O_2 stretching frequencies of most $M-O_2$ adducts lie in a narrow range (1350–1390 cm^{-1}), indicating that metal phthalocyanines should have a similar ORR activity. Here, the O_2 binding energies lie between 0.1 and 0.3 eV. The exception is the $Mn-O_2$ adduct in the most stable sideon geometry (binding energy of 0.6 eV), which shows the lowest O_2 stretching frequency (1111 cm^{-1}) and consequently the weaker O–O bond. The above results suggest that the ORR catalytic activity of a metal phthalocyanine would depend on the number of stable spin states of the O_2 adduct, which would increase the ORR rate. Similar results have been found for the O_2 adsorption on metal porphyrins [26].

Table 4 summarizes the calculated properties of the $M-O_2$ adduct in the CNT-MPc complex attached by a sp^3 -like covalent bond. Our results show the same O_2 stable geometries than those found in the isolated MPc, with close binding energies and also following the same spin coupling. However, the O_2 stretching frequencies tend to be lower compared with the isolated MPc. The only exception is the Co– O_2 adduct which shows the opposite tendency. The situation is quite different for the $M-O_2$ adduct in the CNT-MPc complex attached by the stronger sp^2 -like covalent bonds, as shown in Table 5. Here the O_2 binding energies and stretching frequencies are much lower, at least by 30 cm^{-1} . Another important difference is that the $Mn-O_2$ adduct takes two stable geometries, sideon ($m = 5 \mu_B$) and endon ($m = 1 \mu_B$), while in the sp^3 complex it takes an extra sideon geometry ($m = 3 \mu_B$). These differences can be associated with the strength of the CNT-MPc complex. In the weaker sp^3 attachment (binding energy of ~ 1 eV), the $M-O_2$ adduct shows properties close to the isolated MPc, whereas in the stronger sp^2 attachment (binding energy of ~ 4 eV), the tendency points to lower O_2 stretching frequencies, suggesting weaker O–O bonds or better ORR catalytic activity.

Recent experiments on non-pyrolyzed FePc and CoPc catalysts supported on various types of CNTs have shown ORR performance close to the Pt/C reference, particularly for FePc [13]. Although the authors have attributed the macrocycle immobilization to a π – π stacking interactions on the CNT surface, we think that some covalent fixation might be present to explain the high current density

Table 4
Binding energy (E_b), bond length (d) and stretching frequency (ν) of O_2 adsorbed on the metal center of CNT-MPc complexes in the sp^3 geometry.

Adduct	E_b (eV)	d_{O-O} (Å)	d_{M-O} (Å)	ν_{O-O} (cm^{-1})	m (μ_B)
CNT-MnPc: O_2 (sideon)	0.49	1.371	1.900	1084	3.0
CNT-MnPc: O_2 (sideon)	0.43	1.373	1.897	1126	5.0
CNT-MnPc: O_2 (endon)	0.09	1.277	1.968	1350	1.0
CNT-FePc: O_2 (endon)	0.29	1.282	1.766	1304	0.0
CNT-FePc: O_2 (sideon)	0.18	1.297	2.311	1336	4.0
CNT-CoPc: O_2 (endon)	0.29	1.268	1.955	1406	0.9

Table 5

Binding energy (E_b), bond length (d) and stretching frequency (ν) of O_2 adsorbed on the phthalocyanine metal center of CNT-MPc complexes in the sp^2 geometry.

Adduct	E_b (eV)	d_{O-O} (Å)	d_{M-O} (Å)	ν_{O-O} (cm^{-1})	m (μB)
CNT-MnPc: O_2 (sideon)	0.12	1.292	2.402	1298	5.0
CNT-MnPc: O_2 (endon)	0.11	1.277	1.979	1305	1.0
CNT-FePc: O_2 (endon)	0.22	1.281	1.783	1290	0.3
CNT-FePc: O_2 (sideon)	0.10	1.300	2.282	1313	4.0
CNT-CoPc: O_2 (endon)	0.28	1.269	1.949	1370	0.9

reported, for instance at CNT ends or at vacancy defects. It is interesting to note that CNT defects, mainly vacancies, are produced after oxidative chemical treatments, which is exactly the case where an increase in the electrocatalytic performance is reported in Ref. [13]. In a previous work, we found strong π - π interactions between the CNT and a iron porphyrins with a binding energy of about 1 eV and distance from the CNT surface of 3 Å [15]. We also found that at room temperature the porphyrin moves through the CNT surface, suggesting that π - π stacking would be unlikely to explain the electrocatalytic performance reported on phthalocyanine-functionalized CNTs, mainly due to the absence of physical contact, making difficult the charge transfer from the CNT to the catalyst.

4. Summary and conclusion

In summary, we have discussed theoretically the possible use of supramolecular complexes formed by transition-metal phthalocyanines covalently attached to the sidewall of metallic single-walled carbon nanotubes as ORR cathode catalysts in PEM fuel cells. The ORR activity is investigated considering the strength of the O-O bond in the M- O_2 adduct by calculating the O_2 stretching frequency. Our calculations indicate that metal phthalocyanines attached to CNTs would have better oxygen reduction abilities when the CNT functionalization occurs through strong sp^2 -like covalent bonds. In contrast, the weaker sp^3 functionalization shows ORR activity close to those found for the isolated macrocycles. We also find multiple stable spin states for M- O_2 adduct in both the isolated MPc and the CNT-MPc complexes, particularly for Mn and Fe phthalocyanines. These multiple states appear to be key to increase the ORR rate. Regarding the phthalocyanine metal center, we find that the complex catalytic activity increases following the order: Mn > Fe > Co. In addition, the density of states for the CNT-MPc complexes in both sp^2 and sp^3 linking geometries show

metallic characteristics, indicating better charge transfer capabilities from the CNT to the MPc. Therefore, the metallic characteristic of the CNT-MPc complexes added to their high stability, particularly in the sp^2 -like attachment, suggest that the covalent functionalization of CNTs with metal phthalocyanines could be important for the design of ORR cathode catalysts particularly in the strong acidic environment of PEM fuel cells. Our results support experimental evidences of ORR activity in carbon-supported transition metal- N_4 centers [4,7,13].

Acknowledgments

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