

# First-principles study of transition metal adsorbed on porphyrin-like motifs in pyrrolic nitrogen-doped carbon nanostructures



Luis E. Jiménez-Ramírez, Dulce C. Camacho-Mojica, Emilio Muñoz-Sandoval, Florentino López-Urías\*

Advanced Materials Department, IPICYT, Camino a Presa San José 2055, Col. Lomas 4a Sección, San Luis Potosí, Mexico

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## ABSTRACT

First-principles density functional theory calculations were performed on a porphyrin-like motif into the lattice of carbon nanotubes and graphene. The porphyrin-like motif was generated by applying the Stone-Thrower-Wales (STW) transformation twice on two consecutive carbon bonds in a semiconducting (10 0) single-walled carbon nanotube (SWCNT) and graphene, resulting in a porphyrin-like motif that contained an octagon surrounded by four pentagons, two hexagons, and two heptagons. When one carbon atom of each pentagon is substituted by nitrogen (N-pyrrolic doping), the motif mimics the skeleton of a porphyrin molecule (DSTW-N4-porphyrin-like motif). Transition metals (TMs) (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) are incorporated to the double Stone-Thrower-Wales (DSTW)-N4-porphyrin motif. The band-structure, electronic density of states, binding energy, formation energy, and wave functions were calculated. The binding and formation energy calculations demonstrated that the proposed TM-DSTW-N4 defects are stable and energetically competitive with other types of defects. The calculated systems exhibit spin-dependent semiconducting band gap and half-metallicity. Our investigations offered insights into how TM atoms are adsorbed by  $sp^2$  carbon materials doped with N-pyrrolic. The interplay between the type of nitrogen doping (pyridine, substitutional, and pyrrolic) and structural defects in  $sp^2$  carbon materials are crucial for tailoring the electronic, magnetic, and catalytic properties.

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## 1. Introduction

The combination of topological defects and chemical doping has been found to play a crucial role in tailoring the physical and chemical properties of carbon nanostructures [1–3]. For instance, nitrogen can be found in the lattice of  $sp^2$  carbons as N-pyrrolic, N-quaternary, and N-pyridinic [4]. Some molecular systems contain these types of nitrogen in a natural way, such as polyacrylonitrile-polymers [5],  $C_3N_3S_3$ -polymers [6], DNA bases (guanine, cytosine, adenine, thymine) [7], and porphyrins [8]. The incorporation of metals into porphyrin molecules, N-doped carbon nanotubes, and graphene, is an interesting topic due to the potential applications in oxygen reduction reaction catalysis and spintronics [9,10]. For example, Zeng et al. [11] performed theoretical investigations on the electron transport under a magnetic field considering the spin

response [10]. They found that the magnetoresistance depends on the magnetic configuration, which is crucial to spintronic devices. Due to the importance of electronic transport in biomolecular devices, Chylarecka et al. [12] fabricated cobalt films on copper substrate to study the ferromagnetic interaction between manganese-porphyrin and these films. Because of their stable spin polarization, Tan et al. studied the possibility of using two-dimensional polyporphyrin frameworks for spintronic applications [13]. Wende et al. [14] investigated paramagnetic Fe-porphyrin molecules interacting with cobalt (Co) and nickel (Ni) thin films magnetic metallic material, showing that porphyrin molecules act ferromagnetically with films. Berner et al. [15] demonstrated that oxygen can play an intermediate role between Fe-porphyrin molecules and Co and Ni films to produce an antiferromagnetic coupling between them. The above-mentioned research highlights the importance of the role of the transition metal (TM) phorphyrin system to provoke changes in metallic or semiconducting materials to enhance the spin transport.

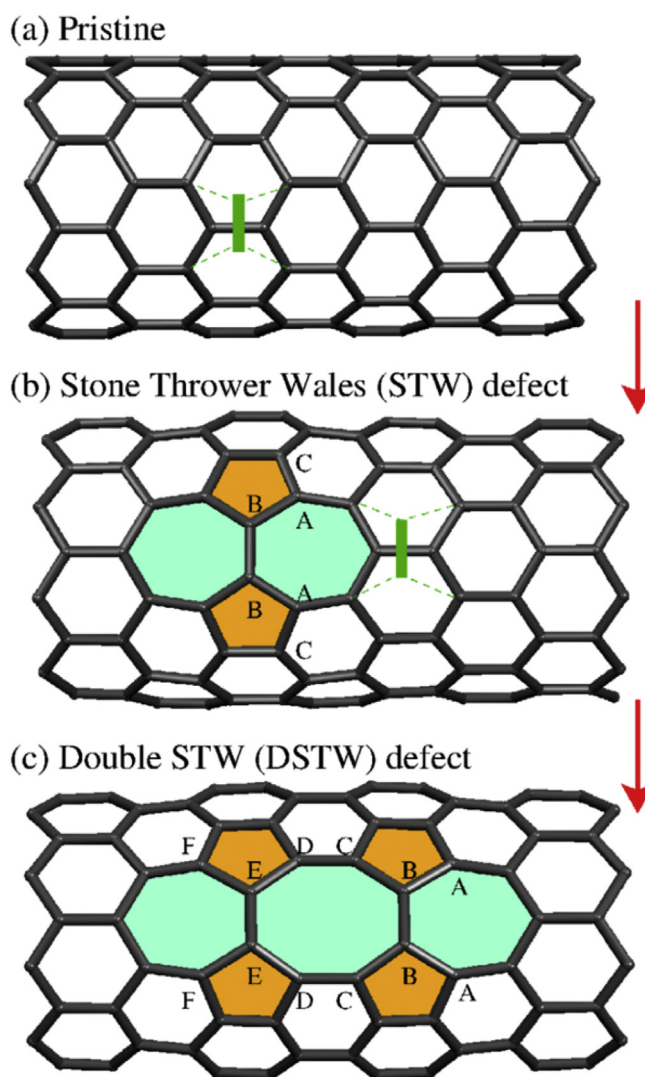
\* Corresponding author.

E-mail address: [flo@ipicyt.edu.mx](mailto:flo@ipicyt.edu.mx) (F. López-Urías).

Porphyrin is an N4 macrocycle molecule in which nitrogen atoms are set in a pyrrole fashion. The functionalization of porphyrinic molecules with 3d-TM is a widely studied topic [16–24]. For instance, Shubina et al. performed a theoretical and experimental study on a monolayer of Co(Zn)-porphyrin deposited on Ag and demonstrated that the reaction is a redox process with the liberation of H<sub>2</sub> [16]. Other calculations showed that the TM encrusted in the porphyrin-like defects of single-walled carbon nanotubes (SWCNTs) that modified the magnetic properties could be used as hydrogen store materials [17]. Studies conducted by Mananghaya et al. [18] using spin-polarized calculations showed that semiconducting SWCNTs become metallic when they are in contact with metal-transition metal porphyrin systems. Recently, Fe atoms were deposited into a phthalocyanine (C<sub>32</sub>H<sub>18</sub>N<sub>8</sub>) monolayer on Ag(111) surface, and the authors demonstrated by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) that the Fe atoms are exclusively coordinated by the pyrrolic central nitrogen atoms which belong to the phthalocyanine molecules [25]. On the other hand, Lee et al. [26] investigated the incorporation of Fe into the lattice of carbon nanotubes via pyridine N-doping. They reported the synthesis of Fe-porphyrin-like defects into the lattice of carbon nanotubes using the chemical vapor deposition method [26]. They correlated the XPS signals corresponding to N-pyridine (with a binding energy of ~398 eV) and the Fe-coordinates (with a binding energy of ~710 eV). These signals were intensified for high nitrogen-doping concentrations, indicating the presence of Fe trapped by four pyridine nitrogen atoms (Fe-porphyrin-like motif) into the nanotube lattices. The Fe-porphyrin-like motif proposed by Lee et al. [26] consisted of the incorporation of two adjacent vacancies, replacing the two coordinated carbons (four atoms) with nitrogen atoms so that the nitrogen atoms are at the hexagonal rings (N-pyridine). We will call V2-N4-porphyrin motif. When the Fe approaches the V2-N4-porphyrin motif, it is adsorbed, creating bonds with the pyridinic nitrogen atoms. In this work, we propose a novel design of 3d-TM porphyrin-like motif with pyrrolic nitrogens into the lattices of carbon nanotubes and graphene. This motif is created when two Stone-Thrower-Wales (STW) transformations are performed [27,28]. An STW transformation consists of the 90° rotation of a C–C bond in a honeycomb-hexagonal lattice (see Fig. 1a). After an STW transformation, two opposing pentagonal rings and two opposing heptagonal rings are obtained (see Fig. 1b). Thus, more complex topological defects can be created when several bond rotations are performed, generating non-hexagonal carbon rings. In this case, two STW transformations were performed on two adjacent bonds along the axis of a zigzag nanotube, generating pentagonal, heptagonal, and octagonal carbon rings (see Fig. 1c). When the pentagonal rings were doped with nitrogen atoms (N-pyrrolic doping), it was found that, in types C and D (see Fig. 1c), the doping defect was very similar to that of the porphyrin molecule, which is labeled as double Stone-Thrower-Wales (DSTW)-N4-porphyrin. We investigated the electronic properties of the DSTW-N4-porphyrin motif through the framework of first principles density functional theory. To the best of our knowledge, investigations of the DSTW-N4-porphyrin motif have not been reported. The stability of TM atoms adsorbed by the DSTW-N4-porphyrin-like motif was studied, and the method of calculations and results is discussed in detail.

## 2. Methodology

Electronic calculations were performed using Density Functional Theory [29]. Generalized gradient approximation (GGA)



**Fig. 1.** Optimized geometries of (10, 0) SWCNTs: (a) pristine without topological defects, (b) topological defects (55–77) generated by STWs, and (c) DSTW (5555-787). The STW transformation consists of a 90° rotation of a carbon-carbon bond (see dashed lines in (a) and (b)). The labels (A, B, C, D, E, and F) represent the nonequivalent sites into the defect. Note that by replacing sites C and D with nitrogen atoms, the skeleton of a porphyrin-like molecule can be identified. (A colour version of this figure can be viewed online.)

[30] with PBE parameterization was selected for the exchange-correlation function [31] implemented in the SIESTA code [32,33]. The wave functions for the valence electrons were represented by a linear combination of pseudoatomic numerical orbitals using a double- $\zeta$  polarized basis (DZP), while core electrons were represented by norm-conserving Troullier-Martins pseudopotentials in the Kleinman-Bylander non-local form [34,35]. The real-space grid used for charge and potential integration is equivalent to a plane-wave cut-off energy of 150 Ry. The pseudo-potentials (pp's) were constructed from 4 to 5 valence electrons from the C and N ions, (C:2s<sup>2</sup>2p<sup>2</sup>, N:2s<sup>2</sup>2p<sup>3</sup>). For the transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) the pseudopotentials were constructed from 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 valence electrons (Sc:3d<sup>1</sup>4s<sup>2</sup>, Ti:3d<sup>2</sup>4s<sup>2</sup>, V:3d<sup>3</sup>4s<sup>2</sup>, Cr:3d<sup>5</sup>4s<sup>1</sup>, Mn:3d<sup>5</sup>4s<sup>2</sup>, Fe:3d<sup>6</sup>4s<sup>2</sup>, Co:3d<sup>7</sup>4s<sup>2</sup>, Ni:3d<sup>8</sup>4s<sup>2</sup>, Cu:3d<sup>10</sup>4s<sup>1</sup> and Zn:3d<sup>10</sup>4s<sup>2</sup>). Four unit cells of the semiconducting (10, 0) nanotubes were used. For instance, the DSTW-N4 motif has 4 nitrogen atoms and 156 carbon atoms. The N-

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