



## Review

## Transition metal and nitrogen doped carbon nanostructures

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## ABSTRACT

We review our theoretical first-principle studies of carbon nanostructures based on graphene sheets, carbon nanotubes, nanocones and fullerenes that are substitutionally doped with transition metal and nitrogen atoms. The results obtained show that metal doping leads to more stable systems in buckled rather than planar structures. The hybrid structures have low-lying excited states, allowing for catalytic activity, in analogy to metalloporphyrins and metallophthalocyanines, as confirmed in recent experiments with Fe-xN-doped carbon nanotubes. Metal-doped carbon nanocones and nanocapsules based on typical fullerenes manifest remarkable electronic and spin polarizations. Additional doping by boron atoms adjacent to the metals increases their HOMO–LUMO gap, stabilizes their electronic structures and causes that their ground states have higher spin multiplicity, where the spin density is spread over the systems. The

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## 1. Introduction

Carbon fullerenes [1–3], nanotubes [4–6], nanocones [7,8] and graphene [9–11] have unique mechanical and electronic properties, since they possess rigid skeletons formed by bonded planar  $sp^2$  molecular orbitals (MO) sandwiched between overlapping unsaturated  $\pi$  MOs [12]. All these types of carbon nanostructures can be doped by boron, nitrogen and other atoms in order to change their electronic properties [13–16] or form chemically active local sites [17–21]. Perhaps, the simplest way how to functionalize these systems is to attach the potential ligands to the nanostructure periphery. For example, one can anchor nucleotides at the CNT rims [22]. When all the C atoms are replaced, BN nanotubes [23,24] and nanocapsules [25] can be formed that are photoactive and piezoelectric [26,27]. Carbonaceous nanostructures can be also chemically modified to gain other activities [28–30]. Functionalized by physisorption [31] and covalent bonding [32], these hybrid systems can be used in molecular sensing [33], controlling [34] or drug delivering [35].

Particularly attractive is the possibility of developing stable metal-doped carbon nanostructures for catalytic applications. Early experiments observed the catalytic activity of Co-phtalocyanines [36] and motivated further studies of transition metal(Fe,Co)-nitrogen-carbon catalysts [37–42]. In particular, Dodelet et al. [43,40,44] have investigated catalysts based on Fe and Co adsorbed on nitrogen-modified carbon supports, which were obtained by high-temperature pyrolysis using a variety of precursors. It was found that the increase of N content in the  $Fe_xC_{1-x-y}N_y$  carbon support materials promotes the incorporation of dispersed metal atoms, which leads to an increase in catalytic activity. Recently, it was also suggested that nitrogenated CNTs arrays might have unusually high electrocatalytic activity for oxygen reduction [45].

Techniques for N-doping of carbon nanostructures were discussed by Ewels and Glerup [46]. Nitrogen atoms bonded to 2–3 C atoms in carbon nanotubes (CNTs) have been observed experimentally by Terrones et al. [47], where the N atoms form 3 stable pyridine-like substitution sites and vacancies in the CNT walls. They have also demonstrated that N-mediated growth of CNTs leads to diameter reduction, tube closures and promotes the formation of bamboo-like structures [48]. Carbon nanocones with “open” pocket-like structures and “spike-like” tips might be especially suitable for functionalization leading to rich potential applications. Their tips have been, for example, functionalized by oxidation and subsequent deposition of Gd atoms [49]. Nitrogen-doped carbon nanocaps (nanobells) self-aggregate by hydrogen bonding and coordinate to gold nanoparticles through the rim N atoms [50,51]. It would be potentially interesting to form universal binding sites on these structures allowing stable chemical, electronic and mechanical connectivity to different types of ligands.

In this work, we review our recent studies devoted to this problem, realized by substitutional metal–nitrogen doping of carbon nanostructures. When we started to search for stable metal–nitrogen complexes that might form in carbon nanostructures, we turned our attention to *metalloporphyrins*. These highly stable systems formed in nature gain their universality from a central metal site coupled to several connected pyrrole rings [52]. Metalloporphyrins, with Fe in different oxidation states, can easily undergo redox reactions in living systems and activate many biochemical reactions [53,54]. They could be used as matrices for hydrogen storage [55] and optical devices [56,57]. Porphyrins can be

part of square planar as well as octahedral complexes that have been thoroughly investigated [58,59]. Recently, porphyrin-based nanostructures, such as nanotapes [60] or nanochannels [61,62] have also been discussed.

After some preliminary calculations, we have been able to show that transition metal atoms coordinated to 3–4 N atoms could be integrated into carbon nanocones by substituting a similar number of C atoms [63–65]. In this way, *metallic binding sites* could be formed in carbonaceous nanostructures and further functionalized. Moreover, external electric fields could easily control the attachment of ligands to and their release from metal-doped carbon nanostructures [66].

We organize this review as follows. In Section 2, we briefly discuss theoretical methods used. In Section 3, we theoretically examine the possibility of integrating metalloporphyrine-like centers into graphene sheets and CNTs [65]. In Section 4, we show how such centers can be formed in carbon nanocones [63]. In Section 5, we discuss formation of single and multi-metallic centers in fullerenes [64]. In Section 6, we explore several potential applications of these substitutionally-doped nanostructures in the fields of catalysis [65] and controlled ion adsorption [66], light-harvesting and nanomechanics [64]. We conclude this Review in Section 7.

## 2. Computational methods

We describe the electronic structures and properties of the metal-doped carbon nanostructures by first-principle techniques at the Density Functional Theory (DFT) level [67]. We calculate their optimized geometries using the B3LYP exchange–correlation functional [68], implemented in the Gaussian03 software package (G03) [69], which successfully accounts for the relative changes in metal–ligand distances [70–73]. For the main-group atoms and first row transition metal atoms, we use the all-electron double- $\zeta$ 6-31G\* [74], triple- $\zeta$ 6-311G\* or 6-311G\*\* basis sets, respectively [75–78]. For the heavy transition metal atoms Ru, Re, Os, Th, and Ce, we apply the Stuttgart–Dresden (SDD) effective core potentials (ECP) for the core electrons and the SDD basis set for the valence electrons [79,80]. In the computationally intense modeling of extended electronic states under external electric field, we employ the SDD ECP for the Ni atom core electrons and the SDD basis set for the valence electrons [79,80], whereas for the main-group atoms, we use the all-electron double- $\zeta$ 3-21G<sup>(\*)</sup> basis set [81]. Closed-shell and open-shell calculations are performed using single and double determinants, respectively. Wiberg bond orders are calculated using Natural Bond Orbital (NBO) [82]. For comparison, we perform optimizations of these structures also with the Amsterdam Density Functional (ADF) [83–87], where we use the Generalized Gradient Approximation (GGA) and the BLYP exchange–correlation functional. For all the atoms, we utilize the TZP basis set that is similar to the triple- $\zeta$ 6-311G\* in Gaussian 03. We also use the *ab initio* multiple scattering model of extended X-ray absorption Fine Structure (EXAFS) implemented in FEFF 7.0 package [88].

## 3. Metal-doped graphene and carbon nanotubes

In this section, we review the material obtained in the recent studies [65]. We discuss the optimized geometries and electronic structures of transition metal and nitrogen doping sites formed in graphene monolayers and CNTs.

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