# Graphitic Materials for Electrocatalysis

## Computational investigations of catalytic processes in doped graphitic materials

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### In Short

- Doped graphitic materials have potential as electrocatalysts for oxygen reduction reaction (ORR) and $CO_2$ reduction reaction ($CO_2$RR).

- DFT studies on the incorporation of pyrrolic and pyridinic $MN_4$ motifs and differences in electrochemical reduction behavior.

Due to the great abundance of carbon and high tunability of their electronic properties, graphitic materials find an increasing role in electrochemical applications as eco-friendly substitutes to the conventional, yet unsustainable, electrocatalysts derived from precious metals such as Pt, Pd and Cu. Some potential applications of such materials include the electrocatalysis of the oxygen reduction reaction (ORR), a crucial anodic reaction that occurs for energy production in hydrogen vehicles, and $CO_2$ reduction reaction ($CO_2$RR) which serves to convert the greenhouse gas responsible for global warming into useful synthetic materials such as CO and methanol.

In attempt to optimize the reactivity of graphitic materials, synthesis strategies are designed to incorporate dopants into these materials, typically N in combination with transition metals like Fe, Co and Ni (abbrev. M-N-Cs where M is the metal dopant).[2] Less explored are also non-metals like P and B that could also be incorporated into graphene in combination with N, resulting in metal-free graphitic materials that may have potential applications that is free from harmful metal wastes. While the identity of the dopants are easily traced back to synthesis precursors, the geometric structure of their incorporation often poses an experimental challenge due to the highly disordered nature of these pyrolyzed materials, leading to further difficulties in understanding the mechanistic principles behind the electrocatalysts. In that regard, quantum chemical calculations can assist in identifying feasible binding sites in terms of stability of formation during the synthesis as well as electrochemical activity.

Generally, electrocatalytically-active M-N-Cs are believed to bind in a square planar metal-$N_4$ motif that is reminiscent of metal-bound porphyrin complexes that are commonly found in nature. In this project, we investigate the incorporation of various metal-$N_4$ sites in a planar carbon lattice using density functional theory calculations, including the pyridinic and pyrrolic structures shown in Figure 1.
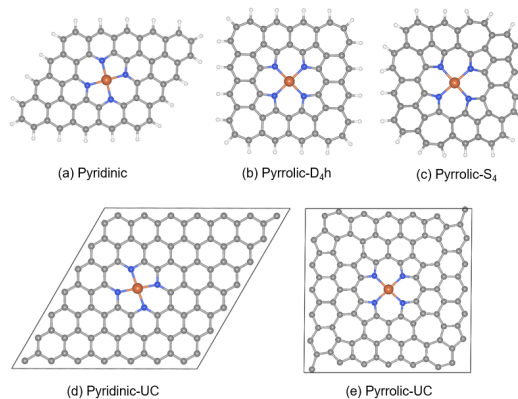


*Figure 1:* Structures of $MN_4$ incorporated in (a) a pyridinic cluster (b,c) two pyrrolic clusters, (d) a pyridinic unit cell and (e) a pyrrolic unit cell.

Although the pyridinic $MN_4$ motif shown in Figure 1**a**,**d** is possibly the most stable incorporation of $MN_4$ into a graphitic lattice, a recent transmetallation strategy, in which an auxiliary metal Zn is introduced in place of desired transition metal, is shown to produce predominantly pyrrolic motif in high dopant concentration, as observed in the good fitting of experimental EXAFS results to our pyrrolic models (Figure 2**b**,**d**).[1][3]

In order to understand the reason behind the different $MN_4$ motifs when different ions are introduced during pyrolysis, we study the binding of the relevant ions in the pyrrolic binding site and compare them to the pyridinic sites. Based on binding geometry and energies, it can be shown that ions such as Zn indeed have a higher affinity towards pyrrolic site formation, thereby providing an explanation towards the favorable formation of purely pyrrolic sites when Zn was used as a templating ion during the synthesis.[1] In addition, reaction path optimization modelling the Zn-Fe ion exchange reveals a small activation barrier (Figure 2**c**) despite the strong binding of the metals in the $N_4$, indicating that transmetallation is feasible once free Fe-ions are in the vicinity of the $ZnN_4$ site. A further advantage of the transmetallation strategy is the possibility to isolate the effects of identity of the metal dopant from other synthesis-dependent variables when studying their electrochemical behavior, allowing for better comparison to computational results.

In collaboration with experimental partners, we will further investigate how the different types of $MN_4$
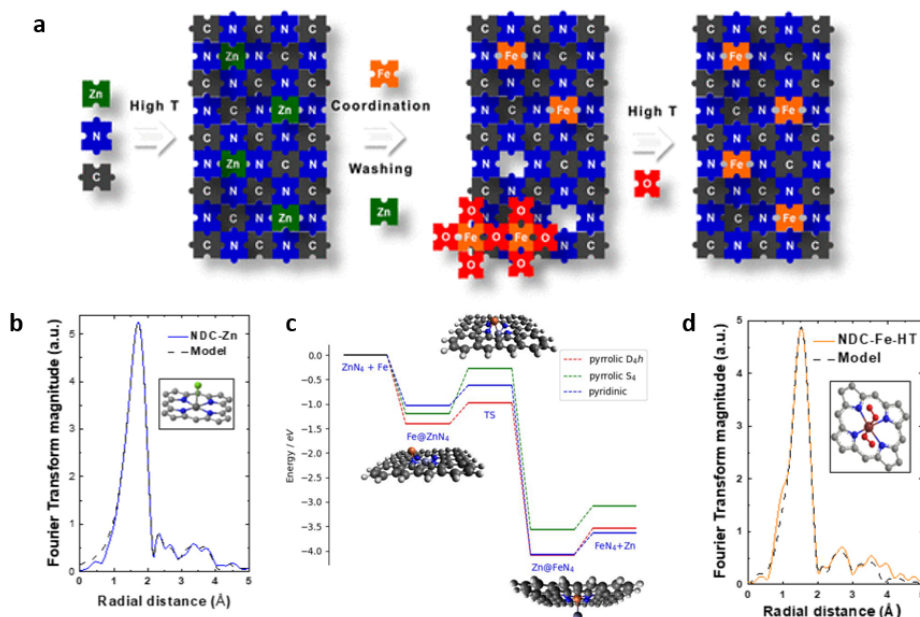
**Figure 2:** *(a) Schematics for the transmetallation synthesis strategy, (b) Fourier-transformed Zn EXAFS spectra and fitted model of material before transmetallation, (c) reaction energy diagram for modelling the transmetallation reaction (d) Fourier-transformed Fe EXAFS spectra and fitted model of material after transmetallation. Adapted from ref [1]*

binding motifs can influence their behavior towards oxygen reduction reaction (ORR), $CO_2$ reduction reaction ($CO_2$RR) and other applications. In order to simulate the electrochemical reactions, we apply the computational hydrogen electrode (CHE) method for the electrochemical reduction processes under constant potential [4] as well as various solvation models for the aqueous environment.

The study of ORR and $CO_2$RR mechanism on doped graphitic materials is an important step towards understanding the microscopic picture behind their catalytic activity will pave the way towards the development of sustainable, high performance carbon-based electrocatalysts. Dispersion-corrected DFT calculations will be performed on a periodic graphene lattice as well as on a finite-sized aromatic cluster with H-termination at the boundary. Periodic calculations are performed with the Vienna Ab Initio Simulation Package (VASP) [5] and cluster calculations are performed with the TURBOMOLE program [6].

## WWW

https://www.bcp.fu-berlin.de/en/chemie/
chemie/forschung/PhysTheoChem/agpaulus/
index.html

## More Information

[1]  D. Menga, J.L. Low, Y.-S. Li, I. Arčon, et al., *J. Am. Chem. Soc.*, 2021, **143**, 18010. doi: 10.1021/jacs.1c04884

[2]  D. Higgins, P. Zamani, A. Yu, Z. Chen, *Energy Environ. Sci.*, 2016, **9**, 357. doi: 10.1039/C5EE02474A

[3]  D. Menga, F. Ruiz-Zepeda, L. Moriau, M. Šala, et al., *Adv. Energy Mater.*, 2019, **9**, 1902412. doi:10.1002/aenm.201902412

[4]  J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, et al., *J. Phys. Chem. B*, 2004, **108**, 17886-17892. doi:/10.1021/jp047349j

[5]  G. Kresse, J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251. doi:10.1103/PhysRevB.49.14251

[6]  R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.*, 1989, **162 (3)**, 165. doi:10.1016/0009-2614(89)85118-8

## Project Partners

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