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Final Report

Hetero-doped Carbon Nanomaterials as Bi-functional Catalysts for Fuel Cell Applications

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Summary

Fuel cells offer a great opportunity to obtain clean and sustainable energy; however, the use of expensive catalyst (Pt-based materials) for oxygen reduction reaction (ORR) hinders their developments, but opens a market for metal-free catalysts. As a result, the exploration of metal-free catalysts with low cost, but still high catalytic activity and durability is needed. Therefore, in the present project, we carried out the production of nitrogen and phosphorous co-doped graphene as an efficient metal-free catalysts for ORR. The experimental observations were complemented by a computer-based design, where *ab initio* theoretical simulations were used to optimize the catalytic activity of doped graphene, and thus guiding the experimental development of the electrocatalysts.

1. Introduction

The outstanding and versatile properties of graphene (a two dimensional allotrope of carbon, see **Figure 1a.**) make it an interesting class of carbon material for various applications, especially as catalyst for oxygen reduction. After the fabrication of a single graphene layer by the Novoselov's method,^[1] diverse mass production routes for graphene and graphene oxide have been developed,^[2,3] increasing the opportunity for real life applications. Both theoretical and experimental reports have shown that graphene and its derivatives are highly influenced by impurities, grain boundaries, and topological defects,^[4,5] strongly modifying their electronic properties and enhancing their chemical reactivity. As a consequence, these sites might act as "reactive spots" useful for nanoparticles deposition, adsorption of molecules and even as catalysts for diverse chemical reactions.^[6]

Similarly, the selective functionalization of nanocarbons has been widely used to enhance their interaction with the surrounding environment, giving the opportunity to tune the electronic properties and increasing the area of applications.^[6, 7] In this way, chemical doping

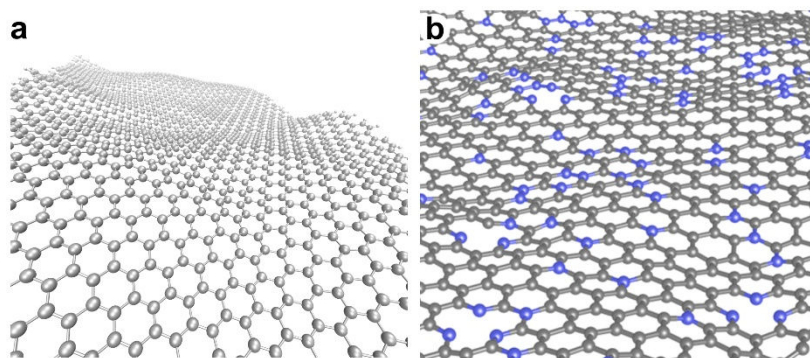


Figure 1. (a) Molecular models of non-doped graphene and **(b)** nitrogen-doped graphene with substitutional and pyridine-like nitrogen doping.

is a feasible method to modify the electronic properties of carbon-based nanomaterials,^[8,9] and depending on the foreign atom (dopant), it is possible to tune the chemical properties of the host materials improving their performance for specific applications. Nowadays, the most widely introduced heteroatom is nitrogen, where substitutional and pyridine-like doping are the most abundant configurations in carbon nanostructures,^[10, 11] **figure 1b** illustrate both doping configurations. Nitrogen doping in graphene allows to explore new applications such as Li-ion batteries, biosensors, and fuel cells.^[11,12] Specifically, nitrogen-doped graphene has shown significant electrochemical activity for ORR,^[13,14] exhibiting long-term stability and tolerance to poisoning as metal-free catalysts.

Also the introduction of phosphorous^[6,15] has proved to be an excellent way to tune the chemical reactivity of the host material. However, the configuration of phosphorous in the graphene lattice is not clearly identified, although its catalytic capabilities for ORR has been already demonstrated.^[16,17] Phosphorous belongs to the same group as nitrogen in the periodic table, sharing some characteristics with it. However, due to its atomic size, the introduction of phosphorous into graphene generates a much more distorted structure than in the case of nitrogen (in **Figure 2**). These structures were obtained using density functional theory (DFT) which allows to illustrate the resulting configuration of substitutional nitrogen and phosphorous the graphene lattice. These results suggest that the out-of-plane doping of phosphorous will exhibit a better access and probable improved interaction with the oxygen molecule which in turn might result in larger catalytic activity. Information of this kind has however not been investigated previously, and further studies are clearly necessary to identify the reaction mechanism, as well as the limiting step and ORR overpotential.

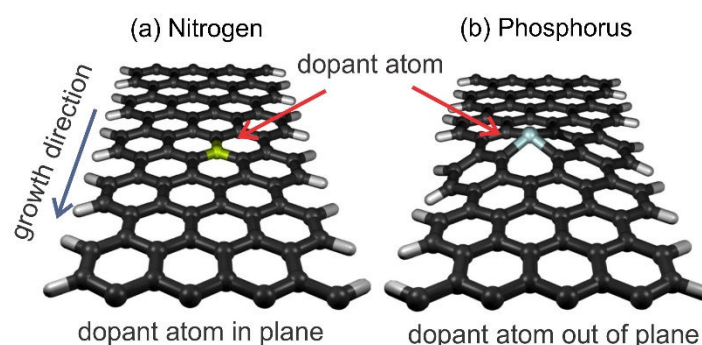


Figure 2. Hetero-doped graphene structure with **(a)** nitrogen and **(b)** phosphorous doping. It is possible to observe the structural change generated by the introduction of the foreign atom, especially phosphorous, that may exhibit better access and improved interaction that might improve the catalytic activity for ORR.^[18]



As already mentioned, the high cost of the noble metal catalyst and the slow oxygen reduction reaction kinetics hinders the commercialization of fuel cells opens the opportunity for alternative non-noble ORR catalysts. The recent reports of metal-free nitrogen-doped graphene exhibiting ORR catalytic activities superior to commercial Pt-C catalysts clearly motivates further studies of the involved mechanisms. However, the exact mechanism of ORR is still unknown, but it has been reported that the associative mechanism is the preferred pathway to perform the oxygen reduction in nitrogen-doped graphene^[19]. Here, the clear disadvantage is that this reaction pathway may promote the $2e^-$ process, generating H_2O_2 as a subproduct. Phosphorous-doped graphene is likely to exhibit larger interaction with the oxygen molecule and thereby promote the dissociative pathway, a desirable $4e^-$ reduction. However, the effect of the dopant concentration, structural configuration and changes in reaction mechanism have not been previously studied, thus making further investigations on this topic necessary.

In this first part of the project, we performed the synthesis of nitrogen- and phosphorous-doped graphene using diverse nitrogen and phosphorus sources. Additionally, a computer-based design was carried out using state-of-the-art theoretical simulations. These simulations assisted the experimental development of the catalysts, allowing a deeper understanding into the reaction mechanism and design of new metal-free nanocatalysts.

2. Results and discussion

2.1 Computational design

The computational study involve the design of diverse nitrogen- (N-Gr), phosphorous- (P-Gr) and phosphorous-nitrogen co-doped (P-N-Gr) graphene systems with different dopant concentrations and spatial configurations. The aim of the computational design is to facilitate the experimental synthesis by indicating what type of “doping configurations” are most catalytically active, and thus directing the experimental synthesis towards those specific configurations. The computational design was performed by analyzing the electronic and catalytic properties of more than 60 hetero-doped graphene configurations by means of Density Functional Theory (DFT). Mainly, two state-of-the-art DFT-codes were used, SIESTA and ATK. Both, SIESTA and ATK, allows the study systems with a large number of atoms (> 200 atoms), facilitating the description of diverse process ate the nanoscale, such as solvent effects. These software are installed on the Abisko cluster which belong to the High Performance Computer Center North (HPC2N) located at Umeå University (www.hpc2n.umu.se), where we have access up to 150,000 CPU hours per month.

We previously identified that graphene exhibit better catalytic performance towards ORR under alkaline conditions, i.e at higher pH values. Therefore, the catalyst design is carried out under these conditions by considering the following reaction mechanism:

1. $O_2 \rightarrow *O_2$
2. $*O_2 + H_2O + e^- \rightarrow *OOH + OH^-$
3. $*OOH + e^- \rightarrow *O + OH^-$
4. $O^* + e^- + H_2O \rightarrow *OH + OH^-$
5. $*OH + e^- \rightarrow OH^-$

These electrochemical reactions describe the non-dissociative oxygen reduction pathway under alkaline conditions, where * indicates adsorbed species. By calculating the change in Gibbs free energy (ΔG), it is possible to determine the limiting step and the reaction overpotential (η_{ORR}). The limiting step and η_{ORR} depends on the concentration and spatial distribution of the dopant atoms (N, P or P-N) on doped graphene. Therefore, by modifying the doping configuration, it is possible to find a system with the small η_{ORR} , and hence a better catalytic performance towards ORR.

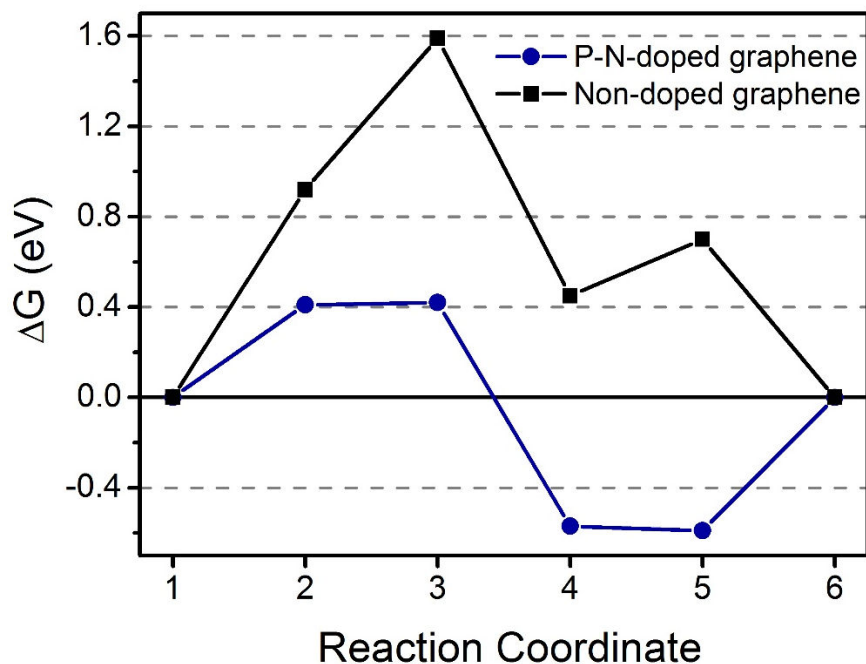


Figure 3. Change in Gibbs free energy (ΔG) during ORR for non-doped graphene (black squares, $\eta_{ORR} = 0.98$ eV) and phosphorous and nitrogen co-doped graphene (P-N-Gr, blue circles). The smaller step size for co-doped graphene indicates lower overpotential for ORR, $\eta_{ORR} = 0.60$ eV.

A total of 61 systems with diverse doping concentrations and configurations have been built and tested, where N, P or both (P and N) atoms are introduced into the graphene lattice using different configurations (i.e. various spatial distributions and concentrations). The optimized system is reported in **Figure 3**. The phosphorous and nitrogen co-doped graphene (P-N-Gr, blue circles) exhibit a significant improvement on the ORR performance by decreasing the overpotential (additional energy needed to drive the reaction) up to 0.60 eV, while the non-doped graphene (black squares) exhibit an overpotential of 0.98 eV. This clearly indicates that the introduction of phosphorous and nitrogen on a single graphene strongly benefit the oxygen interaction, thus being a better ORR catalyst. These results are unique and they signify a great opportunity to experimentally produce those types of nanomaterials, and even other exotic type of configurations.

2.2 Experimental synthesis of hetero-doped graphene

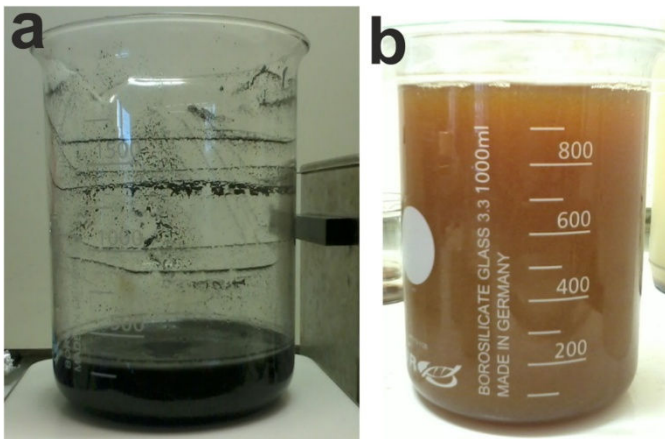


Figure 4. (a) Graphite just before the chemical exfoliation, note the black color. (b) Graphene oxide, the brown-yellowish color indicate the formation of a few-layer graphene.

The synthesis of graphene oxide has been achieved by using chemical exfoliation. This technique involve the use of strong acids and others oxidizing agents to introduce oxygenated functional groups into the graphite. As a results, the graphite layers start to separate, increasing the inter-layer distance, and finally a highly oxidize few-layer graphene is obtained, most commonly known as graphene oxide (GOx). GOx is a brown- yellowish powder, see **Figure 4**, contrary to graphite which is black. This GOx is used as starting material to produce hetero-doped graphene. The type and

concentration of the foreign atom, N or P in this case, can be controlled by selecting different chemical precursors, resulting in materials with complete different properties. Therefore, the doping methodology involves the use of more than 10 different chemical reagents as a nitrogen or phosphorus sources.

The doping procedure was performed by mixing the GOx with diverse phosphorous, and nitrogen compounds, later the samples were collocated inside a modified-microwave oven (see **Figure 5**) and treated for several minutes. The microwave oven was modified to allow an

inert atmosphere, such as Ar or N₂, which maximize the introduction of P and N into the graphene lattice. Under the optimized experimental conditions, we achieved a maximum phosphorus-nitrogen ratio of 1:2, according to X-ray photoelectron spectroscopy (XPS), while the total atomic concentration of phosphorous and nitrogen are 2.1 and 1.1 At%, respectively.

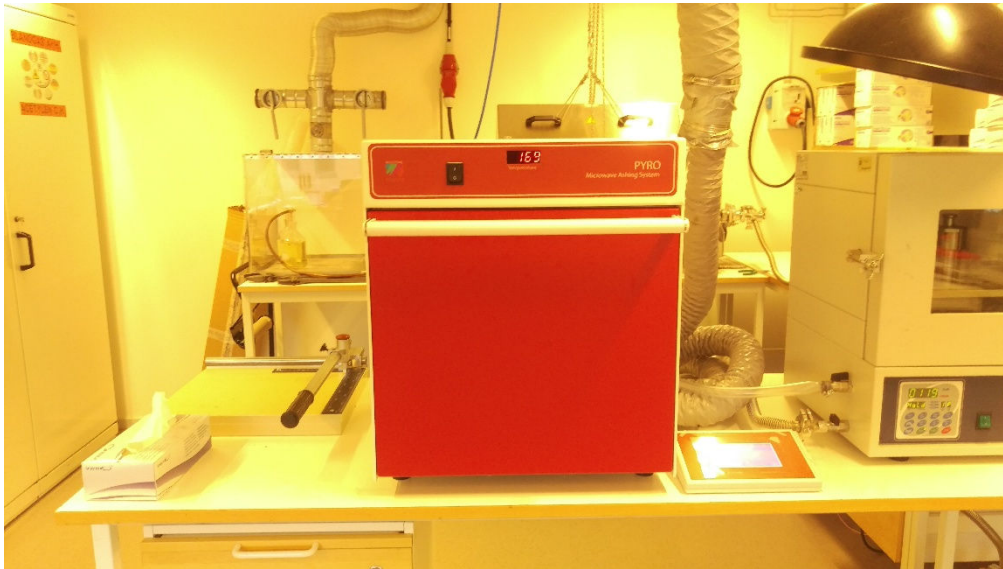


Figure 5. Modified-microwave oven used for synthesis of co-doped doped graphene.

3. Conclusions

The project was originally planned for two years, and right now the first part concerning the experimental synthesis, characterization and computational study of doped graphene is complete. In this first part, we have optimized the synthesis of doped graphene using a modified microwave oven obtaining high amount of nitrogen and phosphorous incorporated into the graphene structure. Additionally, the computational design has demonstrated that these newly co-doped graphene should exhibit enhanced activity towards oxygen reduction reaction.

The obtained knowledge allows to successfully continue with the next step in the original research plan, which involves the bulk production and test of doped graphene in phosphoric acid and hydrogen fuel cells.



4. List of publications supported by the project

Thanks to the financial support from the Åforsk foundation, a total of 7 scientific papers has been published in diverse international journals in collaboration with researchers from Sweden, Mexico and USA.

1. **Gracia-Espino E.**, Rebollo-Plata B., Martínez-Gutiérrez H., Muñoz-Sandoval E., López Urías F., Endo M., Terrones H., Terrones M. "Temperature Dependence of Sensors Based on Silver-decorated Nitrogen-doped Multiwalled Carbon Nanotubes". *J. Sensors*, article in press (2015)
2. Sharifi T., **Gracia-Espino E.**, Jia X., Sandström R., Wågberg T., "Comprehensive Study of an Earth-Abundant Bifunctional 3D Electrode for Efficient Water Electrolysis in Alkaline Medium", *ACS Appl. Mater. Interfaces*, DOI: 10.1021/acsami.5b10118 (2015)
3. Hu G., **Gracia-Espino E.**, Sandström R., Sharifi T., Cheng S., Shen H., Wang C., Guo S., Yang G., Wågberg T., "Atomistic Understanding on the Origin of High Oxygen Reduction Electrocatalytic Activity of Cuboctahedral Pt₃Co-Pt Core-Shell Nanoparticles" *Catal. Sci. Technol.* DOI:10.1039/C5CY01128K (2015)
4. **Gracia-Espino E.**, Barzegar H. R., Sharifi T., Yan A., Zettl A., Wågberg T., "Fabrication of One Dimensional Zigzag [6,6]-Phenyl-C61-Butyric Acid Methyl Ester Nanoribbons from Two Dimensional Nanosheets" *ACS Nano*, 9, 10516–10522 (2015)
5. **Gracia-Espino E.**, López-Urías F., Terrones H., Terrones M. "Self-Assembly Synthesis of Decorated Nitrogen-Doped Carbon Nanotubes with ZnO Nanoparticles: Anchoring Mechanism and the Effects of Sulfur" *J. Phys. Chem. C*, 119, 741–747 (2015)
6. González V.J., **Gracia-Espino E.**, Morelos-Gómez A., López-Urías F., Terrones H., Terrones M. "Biotin molecules on nitrogen-doped carbon nanotubes enhance the uniform anchoring and formation of Ag nanoparticles" *Carbon* 88, 51–59 (2015)
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