Summary of scientific results

Objective 1: *- The GraphDuSuCat proposes to calculate the adsorption energies of aryl-halides and aryl boronic acid derivatives, dissociation and activation energies of C-X bond of aryl-halides and the formation and activation energies C-C bond of bifenyls derivatives on different sizes and shapes (ranging from few atoms to tens of atoms –i.e 7,13,55,147) of AuCL/AuNP on simple and modified G. The aim is to establish a trend/linear correlations for how the size, atomic coordination of CL/NP, the support control the adsorption and activation of the investigated molecules. Another aim is to shape the complete mechanism of aryl halide and homocoupling at theoretical level such as to perform activity comparisons inbetween all studied systems.*

Objective 2: *GraphDoSuCat proposes to focus on N modified G and Fe-N modified G, namelly the type and the amount of N, Fe-N4 coordination sites in G will be investigated to establish their effect on the activity for ORR. This aspect was less watched into. Progressivelly new models that describe the active sites as revealed by the experimental evidences will be build such as FeN4C12 and iron(II) phthalocyanine (C32H16FeN8) deposited on the graphene layer (simple and with vacancies), small Fe/Fe3C nanoclusters embbeded in a graphene matrix and small Fe nanoclusters encapsulated in a layer of N-doped carbon, etc. All the results will be integrated in the volcano plot using the model the applicant developed in her previous work mentioned in B2.*

Objective 3: *GraphDoSuCat aim to support the catalytic results obtained experimentally by means of theoretical calculations as much as possible for both Suzuki-Miyaura cross coupling reaction and oxygen reduction reaction in PMFC.*

Objective 4: *Management and dissemination of the results GraphDoSuCat will be developed by Dr. I.C. Man's (presently Traistaru) research group. The project offers a good opportunity for consolidation of the applicant group with new members/ knowledge/experience giving an original heterogeneous aspect in term on multi-disciplinarily. Indeed, proposed research activity will be developed at the border between several domains, such as Organic Chemistry, Catalysis, Computational Chemistry, Surface science, Physical Chemistry.*

Part I -A short Summary of objective 1+3+4:

At this part of the project the team members shared the work as follows:

Theory – Team leader and Dr. Stefan G. Soriga

Experimental work -Team leader, Dr. Natalia Candu, Slabu Andrei, Andrada Simion, Teodorescu Florina and Laura Miu (student)

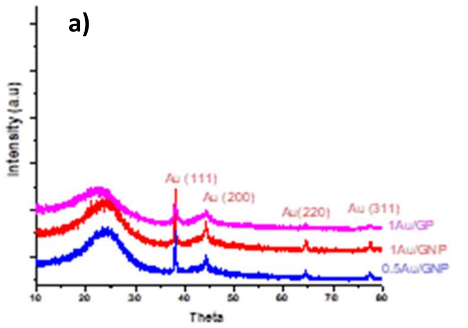
From experimental point of view various methods to prepare gold nanoparticles on graphene substrate were used (pyrolysis of chitosan containing HAuCl4, reduction of $HAuCl_4$ by polyol method (see XRD spectra-Figure 1a), with urea, citrate (see XRD spectra-Figure 1b), borohydrate, p-amino salycilic acid (see XRD spectra Figure 1c), ultrasonication at high power and frequency by using various setups of parameters –

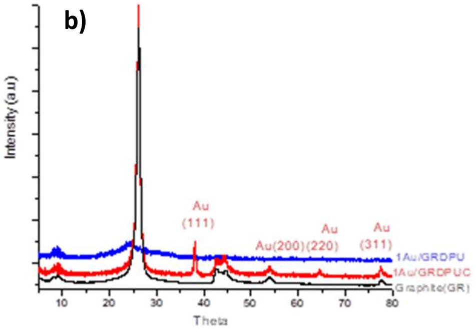
catalyst loading, temperature, pH etc). The pyrolysis method gave the most active catalyst for S-M reaction, while the other ones resulted in very poor catalysts for the reaction. By pyrolysis method nanoparticle in the form of nanoplateles are formed. From theoretical point of view were investigated models that resembles with the facets that are formed on the nanoplatelets. It was identified that the edges between crystallographic orientation of facets ((111)/(100)) are the most active towards the dissociation of X-C bonds (X-Cl,Br,I) with Cl-C bond being the most difficult to be broken. The B-C is the easiest to be broken on all investigated models (surfaces) with the aid of hydroxyl intermediated that might be present on the surface since the reaction proceeds in alkaline conditions. The step that was found to be the limiting for the reaction is the C-C coupling and which proceed quite difficult even on the most active one with relatively high activation energy. This energy it was found that could decrease slightly with increasing the coverage of the surface with reaction intermediates (in our case C_6H_5* fragment). Gold clusters were investigated as well deposited on graphene sheet with and without defects. These theoretical studies could be found in the published article (I.Man, S.G. Soriga, Molec. Cataly.,2020,485,110845). The results were disseminated as well at three conferences: The 12 International Symposium of the Romanian Catalysis Society, 05-07 June, 2019, Bucharest, Romania (oral I.C.Man), EUCO-CTC 2019, 12th European Conference on Computational and theoretical chemistry, 1-5 September 2019. Perugia, Italia (oral I.C.Man), International Conference Catalysis and Organic Synthesis ICCOS 2019, 15-12 September 2019,Moscow, Russia (oral N.Candu).

Interestingly is the fact that – on the clusters (that are not deposited on graphene) the activation energy do not differ significantly from the investigated surfaces – despite the fact that the geometry of the reaction site is totally different and accordingly is expected that the electronic configuration is expected to be different and to influence differently the energetics of the reactions (see Figure 2). When deposited on defectiveless graphene for small Au3 nanocluster, the activation energies are approximatively the same with the systems that are not deposited. This is because during dissociation a rotation of the cluster is still possible on the graphene and ease the dissociation or the association. When it increases the dispersion, forces increase as well and the activation energy increases on the gold cluster deposited on the graphene. If the Au3 cluster is trapped in the graphene defect the activation energies depend on the type of the defect. There are defects that ease the reaction and cases that significantly increase the activation energy of the intermediate steps.

Experimentally there were tested some other materials and substrates – mainly Pd based catalysts that was mixed with Au, Cu, Ni in various concentration and deposited mainly on TiO_2 substrate and active carbon. The main idea was to decrease the amount of Pd and to increase the amount of cheaper materials and to keep the same reactivity and stability. Other tested substrates were ZrO_2 and carbonitride. Depending on the preparation methods the activity varied from almost 100% yield to very low yield. Among the best catalysts with yields over 75% were found: core shell Pd-Au (core shell) nanoparticles deposited on a basic TiO_2 surface, PdCu, PdNi on TiO_2, ZrO_2 and active carbon substrates. Therefore it was succeded to decrease the amount of Pd and to keep the same reactivity.

Theoretically it was investigated as well the capacity of SbO_x nanoclusters and of N doped graphene with applications in other C-C coupling reactions. The results were included and compared with the experimental evidences in two articles (N. Candu et al, J. Catal., 2019,376,238-247; A. Simion et al., J.Catal., 2020, 390, 195-349).





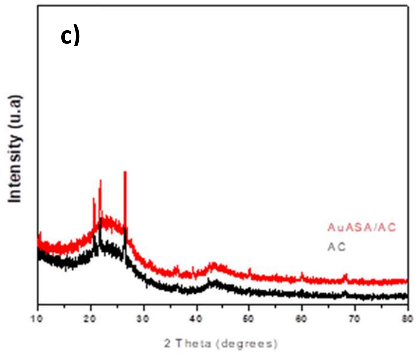


Figure 1 XRD spectra of Au nanoparticles deposited on graphene a) using polyol method with different gold loading. The average crystallites size using the Scherrer equation is 24.4nm for 1Au/GNP, 14.6nm for 0.5Au/GNP and 10.1nm for 1Au/GP b) deposition-precipitation with urea=DPU) and 1Au/ GR-DPUC (DPU and citrate=DPUC). Average dimension of particles 12 nm c) activated carbon (AC), and Au-ASA/AC- no Au peaks detected are likely due to its low loading below the detection limit of the XRD.

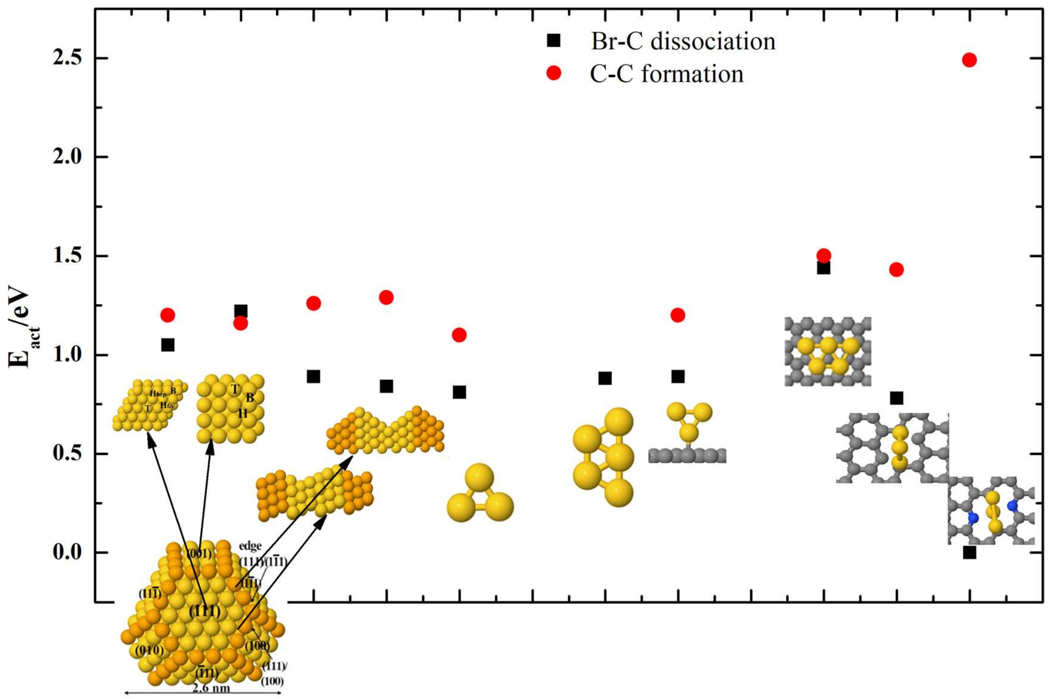


Figure 2 Activation energy on gold surfaces that built the Au nanoplatelet, gold clusters in vacuum and deposited on defectiveless graphene and with vacancies

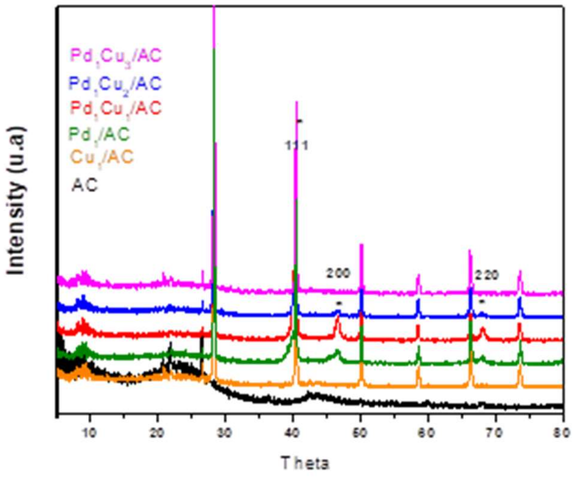


Figure 3 - XRD patterns of prepared monometallic and bimetallic catalysts on activated carbon (XRD pattern of Pd_1/AC (Figure 17), where the peaks at 2θ = 40.0° , 46.6° and 68.0° can be assigned to the (111), (200), (220), crystalline planes of Pd witch start to decrease with increasing the ratio of Cu, also it is observed that the peaks of Pd_1Cu_{1-3}/AC samples are broad and shifted to higher diffraction angles, could suggests the formation of Pd–Cu alloys)

More data could be found in the published articles and in the scientific report uploaded on the project platform.

Part II – Short Summary of objectives 2+3+4

During the project time – structures with different concentration of N and Fe-N sites were investigated with locations on the basal plane and on the edge of graphene and their theoretical activity towards ORR was predicted by plotting the activity volcano plot. Fe_3 cluster embedded in the graphene and Fe/Co/Mn-N_4 deposited on Mo_2C susbtrate were investigated regarding their activity towards ORR. Some studies were conducted to establish the effect of defects on the activities of Fe/Co-N_x sites. When possible correlations with the existing experimental evidences were performed such as to improve the understanding from atomic point of view of the active sites and of the environment around the active sites.

For this part of the project were involved: the team leader, Dr. Stefan G. Soriga and Dr. Isac Dragos.

Part of the presented results are already published in Applied Surface Science **2020**, 510– I.C.Man, I.Tranca, S.G.Soriga - First principle studies of oxygen reduction reaction on N doped graphene: Impact of N concentration, position and co-adsorbate effect and another one is accepted in Journal of Physical Chemistry C. – D.L.Isac, S.G.Soriga, I.C.Man - How do the co-adsorbates affect the ORR activity of undoped and N doped graphene nanoribbon edges? A DFT study" and the results were presented at two conferences – 1 oral and 1 poster presentation.

Part of the studied structures are presented in Figure 1.

Because in a great extent the overpotential of investigated electrocatalysts is given by the strength with which the reactants, intermediates and products interact with the catalyst surface/sites the adsorption energy of the ORR intermediates (HOO*/O*/HO*) were investigated on various potential active sites from the presented sites using the Density Functional Theory method (DFT) and than the theoretical overpotentials were predicted.

In the acidic environment, the ORR can be written as:

$O_2 + 4H^+ + 4e^- + * \rightarrow HOO^* + 3H^+ + 3e^-$ ΔG_1 (1)

$HOO^* + 3H^+ + 3e^- \rightarrow O^* + 2H^+ + 2e^- + H_2O(l)$ ΔG_2 (2)

$O^* + 2H^+ + 2e^- \rightarrow HO^* + H^+ + e^-$ ΔG_3 (3)

$HO^* + H^+ + e^- \rightarrow * + H_2O(l)$ ΔG_4 (4)

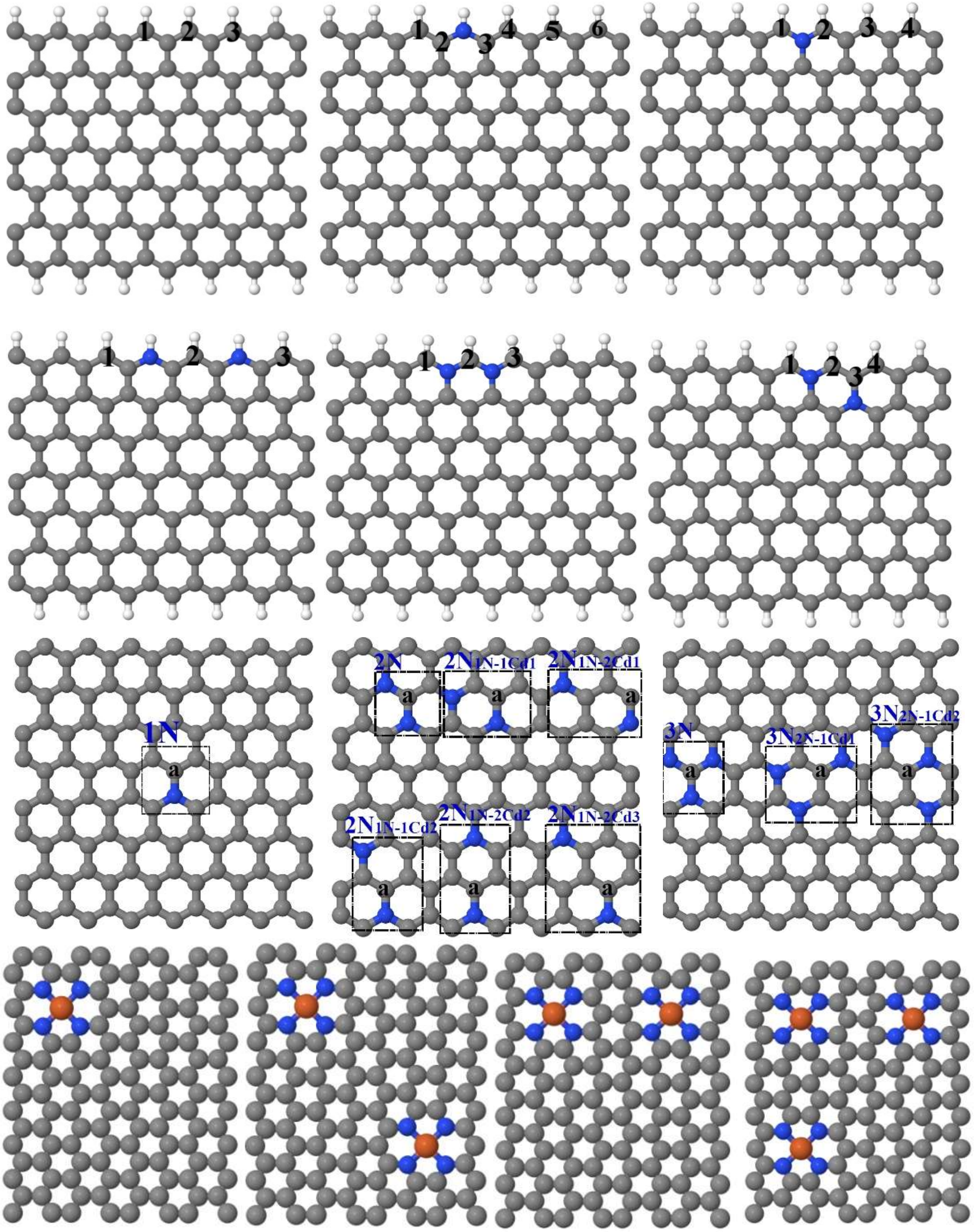
where * stands for an active site on the graphene surface or at the zigzag edge, (l) and (g) refer to liquid and gas phases, respectively, and O*, OH*, and OOH* are adsorbed intermediates, ΔG_{1-4} the free energies of each intermediate step. The adsorption energies of the intermediates using DFT energies that are terms of the free energies, are calculated by subtracting the energies of the isolated adsorbate and the catalyst surface from the total energy of the adsorbed system as follows:

$\Delta E_{HOO*} = E_{HOO*} - E_{*} - (2E_{H2O} - 1.5E_{H2})$ (5)

$\Delta E_{O*} = E_{O*} - E_{*} - (E_{H2O} - 1.5\ E_{H2})$……………………………........ . . (6)

$\Delta E_{HO*} = E_{HO*} - E_{*} - (E_{H2O} - 0.5\ E_{H2})$…………………………………. (7)

Where E_{HOO*}, E_{O*}, E_{HO*} are the DFT energies of the surfaces with adsorbed HOO*/O*/HO* species, E_{*} is the DFT energy of reference surfaces (clean or with preadsorbed species), E_{H2O}/E_{H2} are the DFT energies of the water and hydrogen molecules calculated in vacuum (20 Å of vacuum).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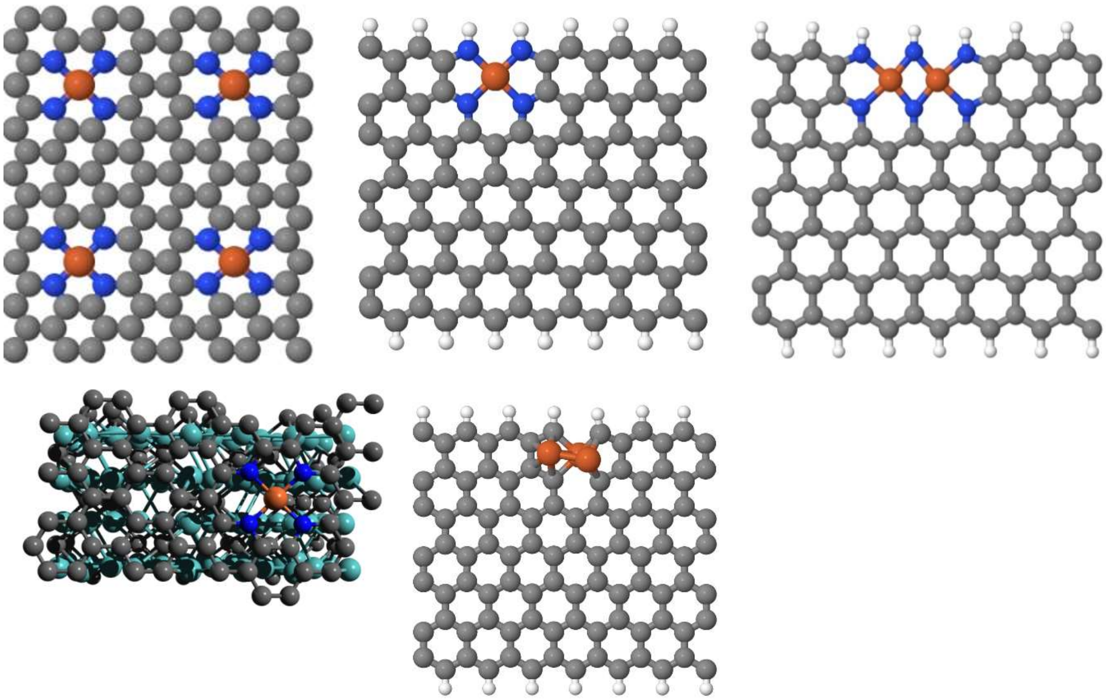

Figure 1 Top view of investigated structures of N and Fe_x-N_x doped graphene – inside planar surfaces and on the edges. Color scheme: C-gray, N- blue, H-white, Fe-orange, Mo-cyan

The variation of the adsorption energies from one structure to the other and one site to the other is summarized in Figure 2. As expected, all changes performed on the structure of undoped graphene leads to large variation of adsorption energies and therefore to large variations of the electrocatalyst activities (theoretical calculated overpotentials) which are pictured in Figure 3 under form of volcano plot.

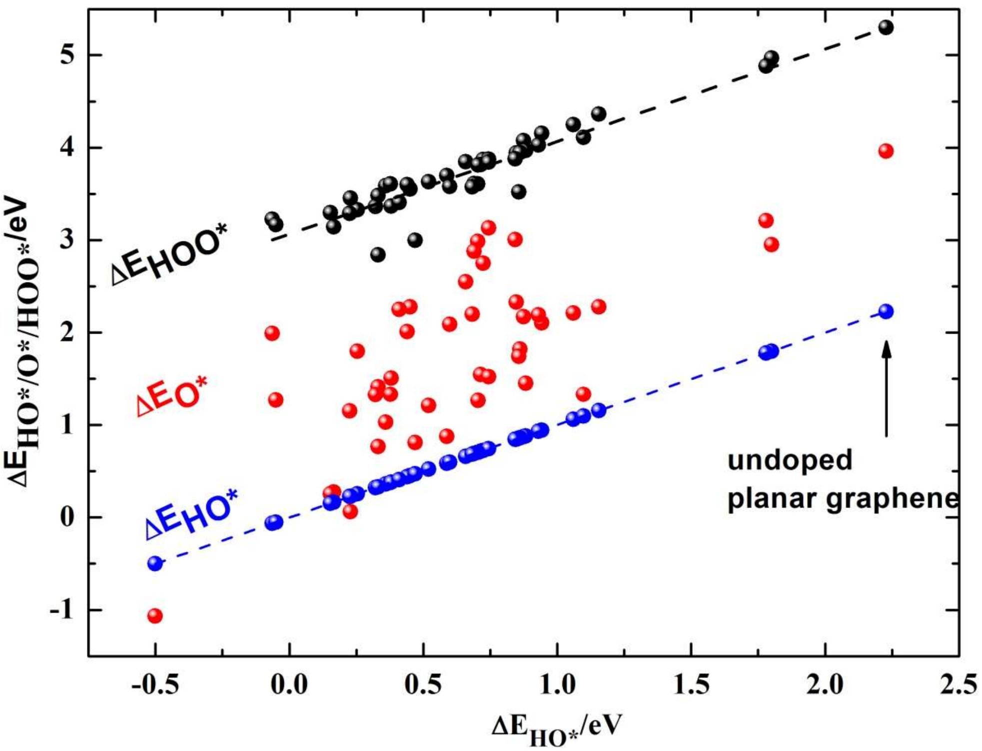

Figure 2 Variation of adsorption energies for ORR intermediates on undoped and N/Fe-N doped graphene (planar and edges sites)

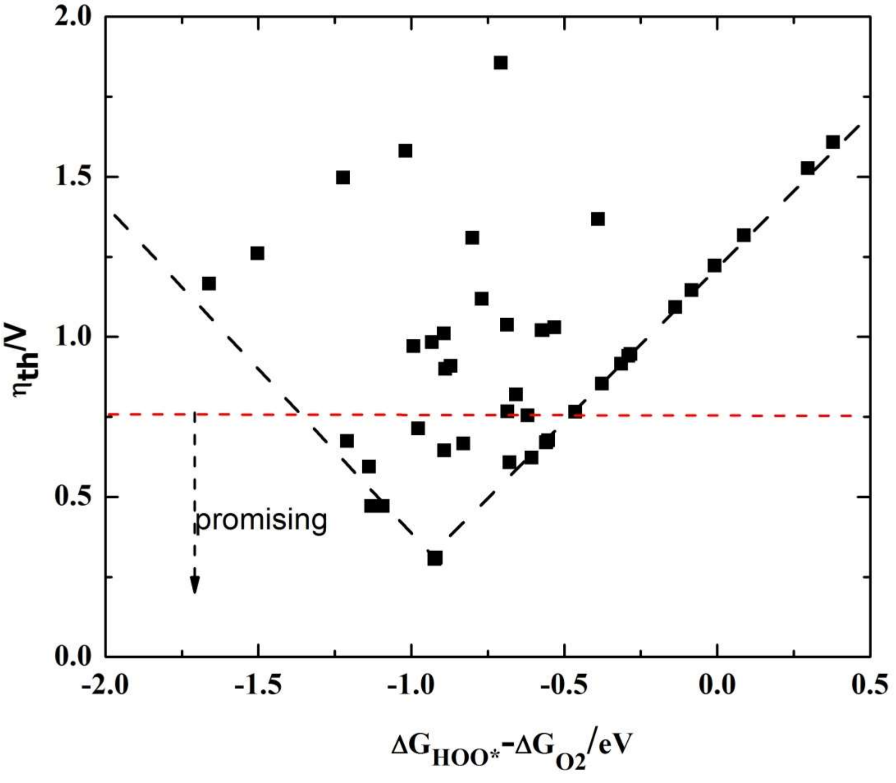

Figure 3 Activity plot of the studied structures

The best active sites of the investigated structures are the ones that are closer to the top of the volcano. Even though, the best catalyst encounter still an overpotential that ideally should be closed to zero.

A detailed analysis for a part of the investigated structures can be found in the published articles and the other part under the form of scientific report uploaded on the project platform.