Catalytic properties of imperfect graphene: first principles modeling

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Recent experimental results evidence unusual catalytic activity of various forms of imperfect graphenes. In our works we have considered three different types of experimentally observed reactions over graphene substrate: (i) oxygen reduction reaction over nitrogen-doped graphene [1]; (ii) oxidation and hydration of alcohols and other compounds over graphene oxide (GO) [2] and (iii) hydration of magnesium over carbon coated Fe and Ni nanoparticles [3].

For the oxygen reduction reaction we performed a modeling of step-by-step oxygen reduction reactions over pure and N-doped graphene for the case of 2 and 4% of nitrogen content [4]. Results of our calculations (see Fig. 1) evidence that 4% N-doped graphene is better than conventional Pt-catalysts from the energetics point of view. Corrugation of N-doped graphene sheets provides diminishment of the oxygen load.

Based on experimental results about significant reduction of GO during oxidation or hydration of various chemical species we propose the model of catalytic properties of this compound. Based on the results of calculations we found that this reactivity stemmed from the transfer of hydrogen atoms from the organic substrate to the GO surface. In particular, epoxide groups decorating GO's basal plane were ring-opened, resulting in the formation of vicinal diols, followed by dehydration. Consistent with the experimentally observed dependence of this chemistry on molecular oxygen, our computations revealed that the partially reduced catalyst was able to be recharged by oxygen, allowing for catalyst turnover. Functional group-free carbon materials, such as graphite, were calculated to have substantially higher reaction barriers, indicating that the high chemical potential and rich functionality of GO are necessary for the observed reactivity. [5]

Combined soft X-ray and theoretical exploring of carbon coated transitional metals nanoparticles demonstrate that the carbon shells of these materials are the multilayer graphene with significant amount of Stone-Wales (SW) defects [6]. Based on our previous computational results about enhancement of the chemical activity of graphene with SW defects [7] we performed systematic survey of the perfect and imperfect (with SW defects) graphene monolayer and trilayers over transitional metal substrates and without its. From the calculated chemisorption energies (see Fig. 2) we can conclude that graphene multilayer with SW defects and all types of graphene monolayers over transitional metal substrate is feasible for catalysis. Based on these results we can predict that graphene on Cu(111) and epitaxial graphene on SiC with established there defects [8] could be also used as catalysts for hydrogen dissociation required for the hydration of magnesium.

Based on aforementioned experimental results and our calculations we can conclude that in contrast to rather chemically inert perfect graphene and high chemical activity of fullerenes and similar compounds imperfect graphene with "moderate" chemical activity, light weight and large surface area is very prospective materials for carbon based catalysis.

References

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Figures

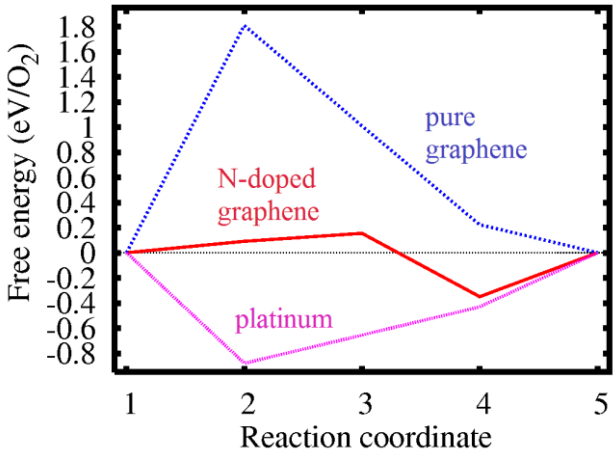

Figure 1 Free energies diagrams for oxygen reduction reactions over platinum, pure and N–doped graphenes.

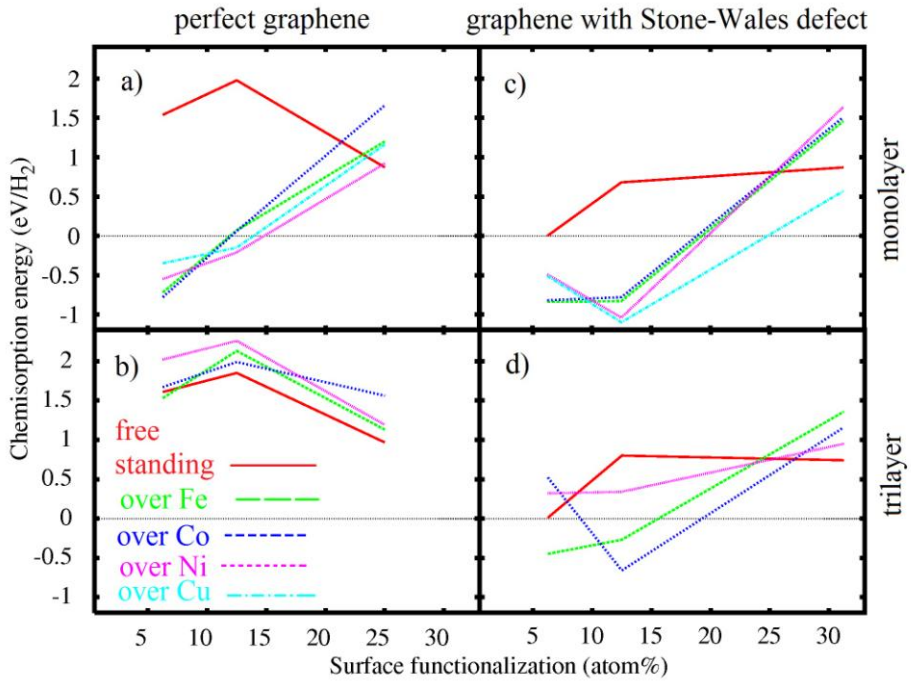

Figure 2 Calculated chemisorption energies for step-by-step hydration of perfect and imperfect graphenes (free standing and over various transition metal substrates).