Is N- and B-doped graphene an efficient catalyst for the oxygen reudction reaction?

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Graphene doped with N or B has been reported to be a remarkably efficient catalyst for the oxygen reduction reaction, an important reaction that is, for example, the bottleneck for wide spread use of fuel cells. At present, this reaction is catalyzed by platinum and there would be tremendous savings if the precious metal could be replaced by doped graphene. Experimental measurements have indicated that doped graphene can have as high catalytic activity as platinum and be even more resiliant to poisoning. Theoretical calculations based on density functional theory employing commonly generalized gradient approximation (GGA) functionals (such as PBE) and combined with the thermochemical model for electrochemical reactions have lent support for these claims. However, there are also reports of experimental studies pointing to the persence of transition metal atoms (Mn or Fe) in the doped graphene samples, deriving from the preparation procedures, and indications that the catalytic activity is mostly due to such impurities. Samples prepared without metal impurities or where the metal impurities have been removed show little catalytic activity. The question arises whether the theoretical calculations can resolve this discrepancy and then what level of theory is needed to obtain clear conclusions. Results of calculations of adatom adsorption and diffusion at various levels of theory will be presented and compared with quantum Monte Carlo (QMC) simulations. They show that commonly used energy functionals such as the PBE and other GGA functional are of low accuracy for the present purpose and do not give reliable results. The higher rungs on the Jabobs ladder of DFT, higher than GGA, or explicitly self-interaction corrected functionals are needed to obtain good agreement with the QMC results. The calculated catalytic activity is also shown to depend strongly on the level of theory, the lower rungs of the ladder predicting higher activity.