Palladium clusters anchored on graphene vacancies: A density functional study

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Abstract

Palladium adatoms bind relatively weakly to the surface of pristine graphene, with a binding energy much lower (about three times smaller) than the cohesive energy of bulk palladium. A similar behavior has been found for many transition, alkaline-earth, and noble metal adatoms on graphene, exception made of the alkaline metals. In a previous work [1] we have shown that Pd atoms deposited on graphene have a strong tendency to nucleate and form three dimensional clusters. This is a consequence of the stronger Pd-Pd interactions as compared to the Pd-C interaction. The clusters are bound to the graphene surface with adsorption energies ranging from 0.68 to 1.26 eV for Pd_n clusters in the range $n = 1 – 6$.

The small binding energy of Pd clusters to graphene, might be an important drawback for technical applications of Pd doped graphene (or other Pd doped graphene based carbon materials) in catalysis, sensing or for hydrogen storage [2]. However, it has been shown that metal atoms bind stronger to defects in graphene such as vacancies, di-vacancies, graphene edges, etc.

We have performed Density Functional calculations to investigate the adsorption of Pd atoms on graphene single vacancies and the tendency of Pd adatoms to nucleate and form clusters around those defects. A Pd atom binds strongly to a graphene vacancy with a binding energy of 5.1 eV. This energy has to be compared with the binding energy of 1.1 eV of a Pd atom on pristine graphene, showing a strong preference of Pd for the defects in graphene. Pd atoms are much larger than C atoms and, therefore, Pd does not fit in the vacant site left out by a C atom on the graphene layer. Pd attaches to the three C atoms around the vacancy at about 1.6 Å above the graphene layer.

We have found that Pd atoms deposited on graphene have a strong tendency to form three dimensional clusters around graphene vacancies. The Pd clusters build up around the first Pd atom attached to the vacancy. As an example, the Figure shows a Pd_4 tetrahedral cluster attached to a graphene vacancy. Free Pd_n clusters ($n = 2 – 6$) exhibit a magnetic moment of 2 μ_B. The adsorption of these clusters on the surface of pristine graphene preserves their magnetic moments, except for Pd_2 and Pd_5 whose magnetic moments are changed to zero. We have found that Pd_n clusters attached to a graphene vacancy have moments equal to zero, probably due to the stronger interaction of the cluster with the vacancy.

The structural, binding, and electronic properties of Pd_n clusters ($n = 1 – 6$) attached to a graphene vacancy will be discussed in detail. The most salient result of this study is that defects in graphene, in particular single vacancies, behave as attraction centers for Pd atoms and clusters. The atoms and clusters get anchored to the vacancies with significant binding energies, much higher than the corresponding binding energies to pristine graphene. This will be relevant for possible applications of Pd doped carbon materials.

References

[1] I. Cabria, M.J. López and J.A. Alonso, Phys. Rev. B, **81** (2010) 035403.
[2] I. Cabria, M.J. López, S. Fraile and J.A. Alonso, J Phys. Chem. C, **116** (2012) 21179.

Figures

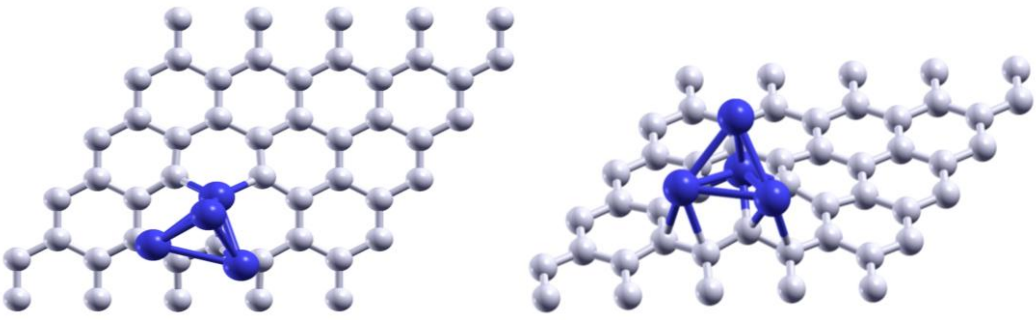

Fig. Top and side view of a tetrahedral Pd_4 cluster attached to a vacancy of graphene.