First-principles modelling of graphene-atomic cluster interactions

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Abstract

The 2D nature of graphene renders its electronic structure extremely sensitive to proximity-induced interactions with e.g. adatoms, atomic clusters, or other 2D materials, to induce desirable properties. In this work, we employed size-selected few-atom transition metal clusters (Au, Cu) to provide a unique atom-by-atom control over the induced physico-chemical properties in graphene. Both Au and Cu clusters have similar geometries in gas phase calculations, but their interaction with graphene is different. While the former adsorb with binding energies of about -1 eV, indicating (weak) chemisorption, the latter are physisorbed with binding energies of a few hundred meV. Cluster size-dependent effects are evidenced by band structure calculations. Clusters with an odd number of atoms dope graphene, due to charge transfer interaction. Clusters with even-numbered atoms open an energy gap of ~20 meV (Cu_n) and ~40 meV (Au_n) at the Fermi level [1].
The adsorbed clusters induce spin-orbit (SO) coupling effects in graphene, which can be evidenced by the spin splitting of the band structure. Overall, cluster adsorption enhances the SO strength of graphene by three orders of magnitude, but the relative spin-splitting values depend on the atomic composition of the cluster. The average spin splitting for Cu_n clusters is in the range of 1-5 meV, whereas Au_n cluster adsorption causes a relatively larger band splitting of 2-9.5 meV [2]. Apart from SO-induced band splitting, these coinage metal clusters are also capable of imprinting cluster-size specific spin textures to graphene's Dirac cone. We observe a hedgehog-type spin texture for clusters with an even number of atoms. For odd-sized clusters, a canted Zeeman-type spin texture is observed, with the spins oriented along a particular direction, due to the local magnetic moment of the cluster.
Graphene/clusters-based devices can also be used to probe the catalytic and chemical reaction kinetics of the clusters. We performed simulations of the desorption kinetics of O_2 adsorbed on the Au_3/graphene system and compared them with experimental results [3]. The computed energy barrier is in agreement with the experiments. The catalytic properties of the Cu_4/graphene system for carbon reduction reaction are also explored and compared with Cu_3X/graphene (X= Ni, Mn, Fe, Co) systems. The results suggest that the limiting potential of the reaction can be tuned by varying the binding energy of the clusters with graphene, which in turn depends on the cluster size and composition.

References

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