How an ordered nanoparticle array can grow on a "featureless" surface

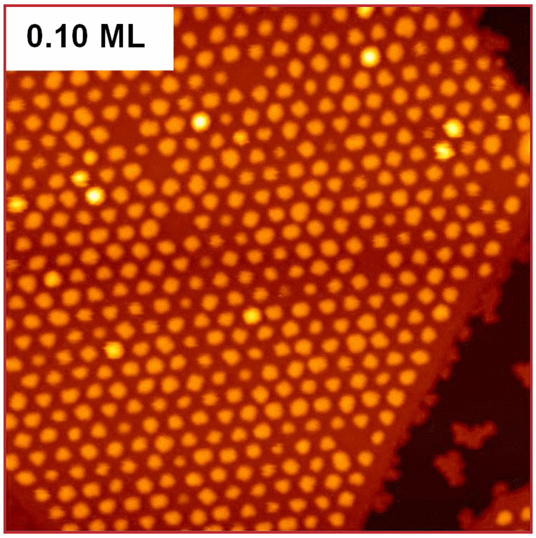

Figure 1: STM image of a periodic array of iridium clusters formed by depositing 1/10 monolayer iridium on a graphene flake (prepared by pyrolysis of ethylene) on an iridium surface (after Ref. 1).

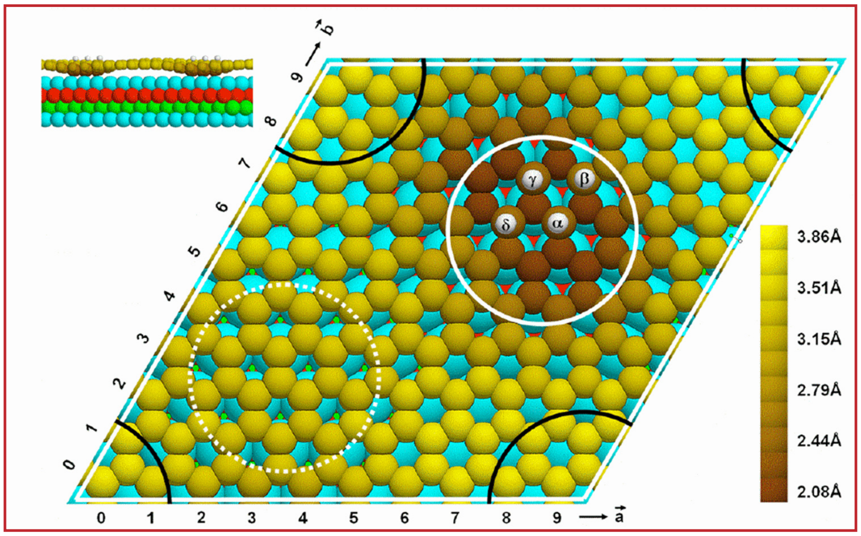

Figure 2: Computed atom arrangement for a cluster in a region where the carbon flake can buckle (after Ref. 2). Carbon atoms are color coded according to their heights above the iridium surface atoms (cyan). In the "bad" regions surrounded by black arcs, no carbon atoms lie directly above surface iridium atoms. The iridium atoms of the cluster (α, β, γ and δ) are colored white and drawn as small balls to show where they sit on the carbon sheet.

By buckling, a carbon-atom sheet both attaches firmly to an iridium crystal, and organizes iridium atoms deposited on it into a periodic cluster array.

Periodic arrangements of transition-metal clusters on surfaces offer exciting prospects for catalysis, information storage and quantum computing. Periodicity may result from cluster-cluster interactions, but a thermally stable array is likelier if a surface presents a periodic arrangement of exceptionally attractive sites to deposited atoms.

Sandia research has explained a subtle example, the iridium cluster array grown, and stable to 400 - 500K, on a single, carbon-atom layer (a "graphene" flake) on the smoothest of iridium metal's crystal surfaces (see Fig. 1). This advance was the fruit of an ongoing collaboration with university researchers in Germany. A new idea was needed because a graphene layer is essentially flat, and, as one knows from the low friction of graphite (which is a stack of graphene layers), typically interacts weakly with its surroundings. What could enable a flat graphene flake on a seemingly featureless iridium surface to organize deposited atoms into a periodic cluster array?

Our answer traces back to the differing radii of carbon and iridium atoms, which imply that carbon atoms only lie directly above iridium atoms in certain regions of a graphene flake on the iridium surface – regions that form a periodic array (Fig. 2). Computational simulations show that these regions are favorable for a buckling of the flake, which bonds it strongly to the underlying metal, and at the same time to iridium atoms deposited on top of it. The carbon atoms lying directly above iridium atoms of the metal surface move downward to form strong bonds to them. Alternate carbon atoms move upward, capturing deposited iridium atoms into a cluster.

The remarkable pinning effect is shown in Fig. 3. Before any iridium is deposited on it (upper panel), the carbon flake is virtually flat, and weakly attached to the underlying metal. Around clusters at favorable sites, the carbon flake is depressed into contact with the metal, and binds strongly to it. Moving clusters to unfavorable regions (cf. Fig. 2), their attachment to the flake, and the flake's attachment to the metal become weak, as the flake no longer buckles. For this reason, experimentally, clusters are not observed in the unfavorable sites.

The mechanism that gives rise to cluster arrays in the iridium on graphene on iridium metal system is sufficiently general that one can expect similar 'templating' to occur if different elements are substituted for the underlying metal and the clusters. This suggests that graphene supported cluster arrays will afford the possibility of wide ranging, highly controlled studies of catalytic chemistry. With magnetic clusters substituted for iridium, one also contemplates the possibility of novel data storage and perhaps quantum computational applications.

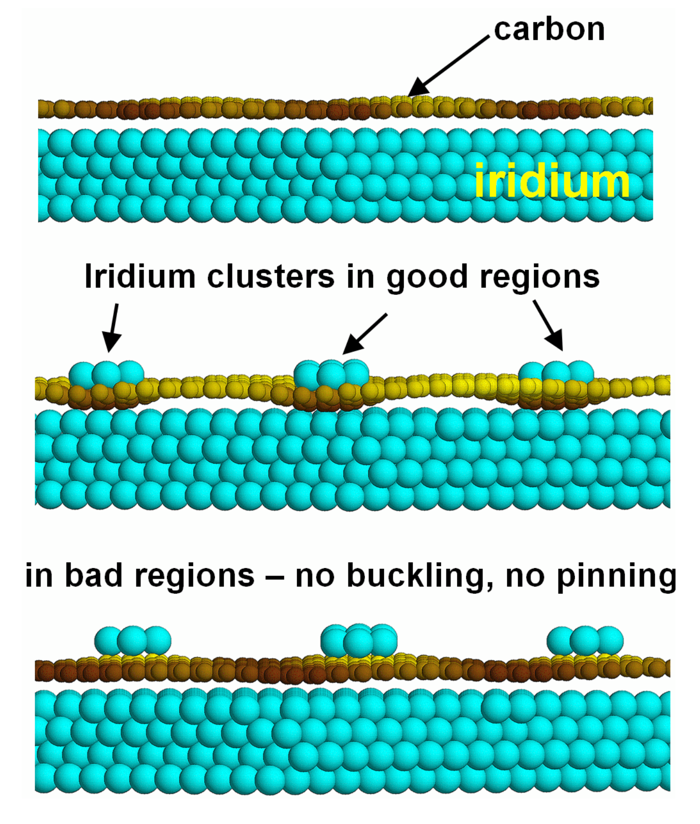

Figure 3: With the sizes of the balls representing carbon and iridium atoms sized proportionately to their radii, and balls, side views show: a carbon flake "floating" above the metal (upper panel), a buckled carbon flake pinned to the metal, with an array of iridium clusters strongly attached to it (middle panel), and a floating carbon flake, with iridium clusters sited in unfavorable regions (bottom panel).

References:

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2. P. J. Feibelman, Physical Review **B77**, 165419(2008).

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