

# GEODESIC CARBON NANODOMES AS PRECURSORS TO NEARLY FREE-STANDING GRAPHENE

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The growth of graphene has been attracting tremendous attention ever since its discovery in 2004. Various methods have been employed to fabricate graphene films, such as epitaxial growth on SiC samples, self-assembly procedures, where graphene oxide films are transferred to a substrate and reduced to graphene by chemical reaction or heating, and chemical vapor deposition of hydrocarbons on a hot metal substrate. The latter method allows to produce large, high-quality graphene films on metal surfaces, which can then be transferred intact to other substrates [1,2].

By combining *in-situ* high-resolution photoelectron spectroscopy and *ab initio* calculations, we have shown that carbon nanoislands formed during the growth of a long-range ordered graphene layer on Ir(111), assume a peculiar domelike shape [3], thus producing at the nanometer length scale a morphology that recalls the Eden Project in Cornwall, UK (see Figure 1). The growth mechanism is completely different from all those previously observed for two-dimensional islands on metals.

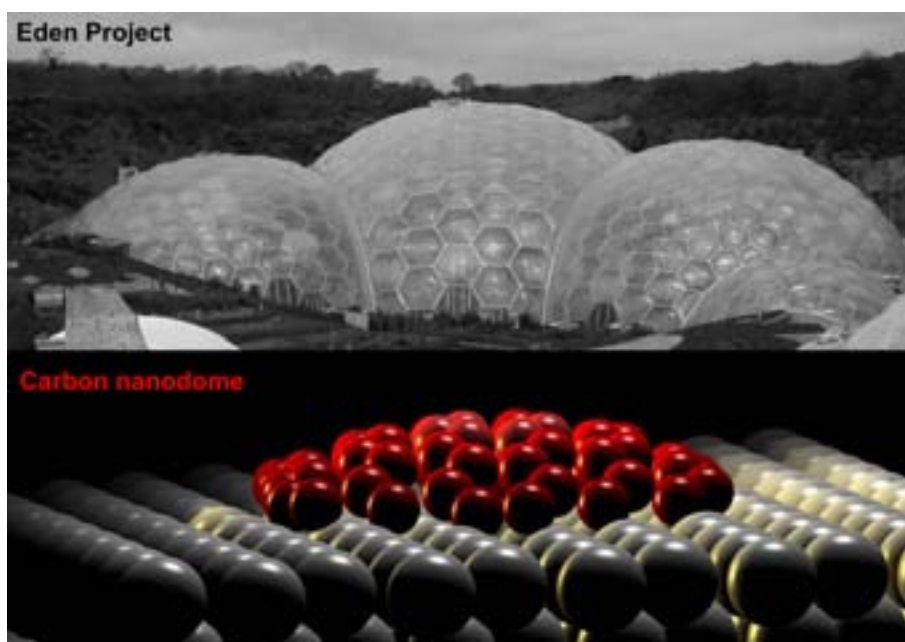
The temperature programmed growth involved the adsorption of ethylene at room temperature, followed by sequential heating to higher temperatures. For temperatures below 1000 K (see Figure 2(a)), the single C 1s peak at 284.12 eV, corresponding to a perfect graphene layer, is split into three components. After heating to higher temperatures, two of the components ( $C_A$  and  $C_C$ ) gradually shift and disappear, while the third one ( $C_B$ ) grows and, after heating to 1270 K, only one peak remains. At the same time, an additional peak appears in the Ir  $4f_{7/2}$  spectrum for the low-temperature anneals, but gradually disappears as the temperature is increased. After heating

to high temperature, the Ir  $4f_{7/2}$  spectrum corresponding to a well ordered graphene layer is practically unchanged with respect to that of the clean Ir(111) surface, a direct indication that the quasi-free standing graphene layer is weakly interacting with the iridium surface.

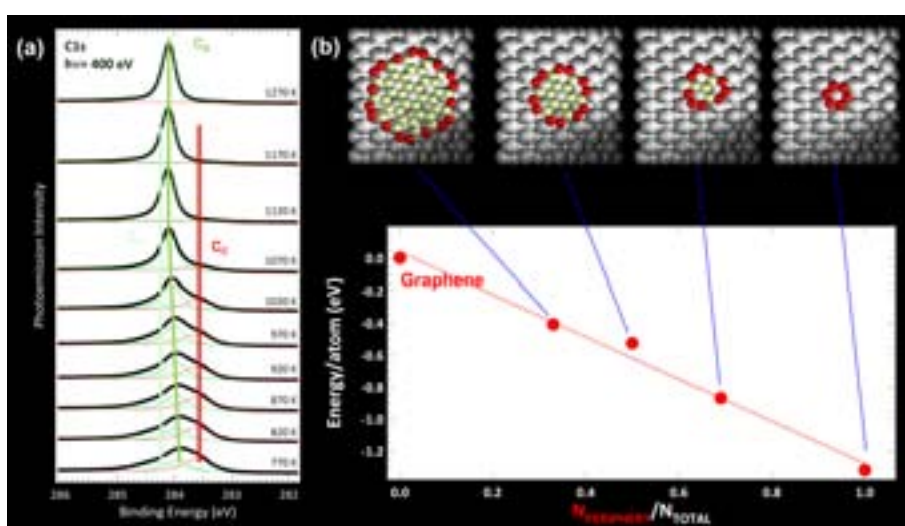
These results were interpreted with the help of density functional theory (DFT) calculations on the morphology of graphene clusters of different sizes on iridium, and by making calculations on the C 1s and Ir  $4f_{7/2}$  core levels. The DFT show that the carbon species resulting in C 1s core level components at lower and higher binding energy with respect to the main peak are due to atoms at the periphery of cluster region ( $C_C$ ) bonded to two carbon atoms, and to carbon atoms ( $C_A$ ) bonded with three carbon atoms and directly bonded to the periphery atoms. The main component ( $C_B$ ) is due to the atoms at the center of the cluster.

Moreover calculations show that the interaction of the carbon atoms with the iridium substrate is much larger at the edges of the island than in the center. As the islands grow larger, the central carbons detach and move away from the substrate, thus creating a dome-shaped island. For very large islands, almost all of the carbon atoms are in this nearly free-standing state, and only those at the perimeter of the islands are strongly bound to the surface as a result of the C 2p hybridization with the first-layer Ir d band.

Further support to our interpretation arises from the evolution of the calculated binding energy/atom in the cluster as a function of  $N_p/N_T$  ( $N_p$  is the number of atoms at the periphery,  $N_T$  is the total number of atoms in the cluster) for different cluster sizes. The graph, shown in Figure 2(b), displays a remarkably



**Figure 1.** The modern architectural structures of the Eden Project in Cornwall (top) compared to the morphology of the carbon nanodomains grown on Ir(111) (bottom).



**Figure 2.** (a) C 1s spectra after annealing at different temperatures of the Ir(111) surface saturated with  $C_2H_4$  at 300 K. The spectra were measured at 300 K. The different components represent nonequivalent C and Ir atoms, as explained in the text. (b) Evolution of the binding energy per atom as a function of the ratio of C atoms at the periphery  $N_p$  and the total number  $N_T$  in each C cluster.

linear behavior and indicates that the islands are bonded to the substrate mainly with the C atoms at the edges.

This scenario matches the experimental findings, indicating an evolution, as a function of the heating temperature, from small graphene islands in which carbon atoms have several different chemical environments, to very large islands that approach free-standing graphene. These results show that the size of these geodesic carbon nanodomains depends on the temperature of the metallic substrate, suggesting a number of possible ways to control the size of graphene sheets at the nanoscale.

## References

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