

Supporting Information: Graphene on Rh(111): a template for growing ordered arrays of metal nanoparticles with different periodicities.

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Geometry of an Ir nanoparticle comprising 7 Ir atoms on the RD0_{11×11}moiré of graphene/Rh(111):

Figure S1 shows the optimized geometry of a nanoparticle composed of 7 Ir adatoms on the hcp subdivision of the RD0_{11×11}moiré. The Ir-C bonding lengths are of 2.08 Å for all atoms at the nanoparticle edges and of 2.22 Å for the Ir adatom placed at the center. The first neighbor distances between Ir adatoms range from 2.52 to 2.54 Å. C atoms below the nanoparticle present a sp^3 hybridization according to the alternate bonding scheme described in the main manuscript. Hence, nanoparticle adsorption induces changes in the bonding landscape of the graphene/Rh(111) interface associated to the breakdown of bonds and the formation of new ones. As a result, after nanoparticle adsorption, graphene corrugation is increased by 11 pm, from 1.21 to 1.32 Å.

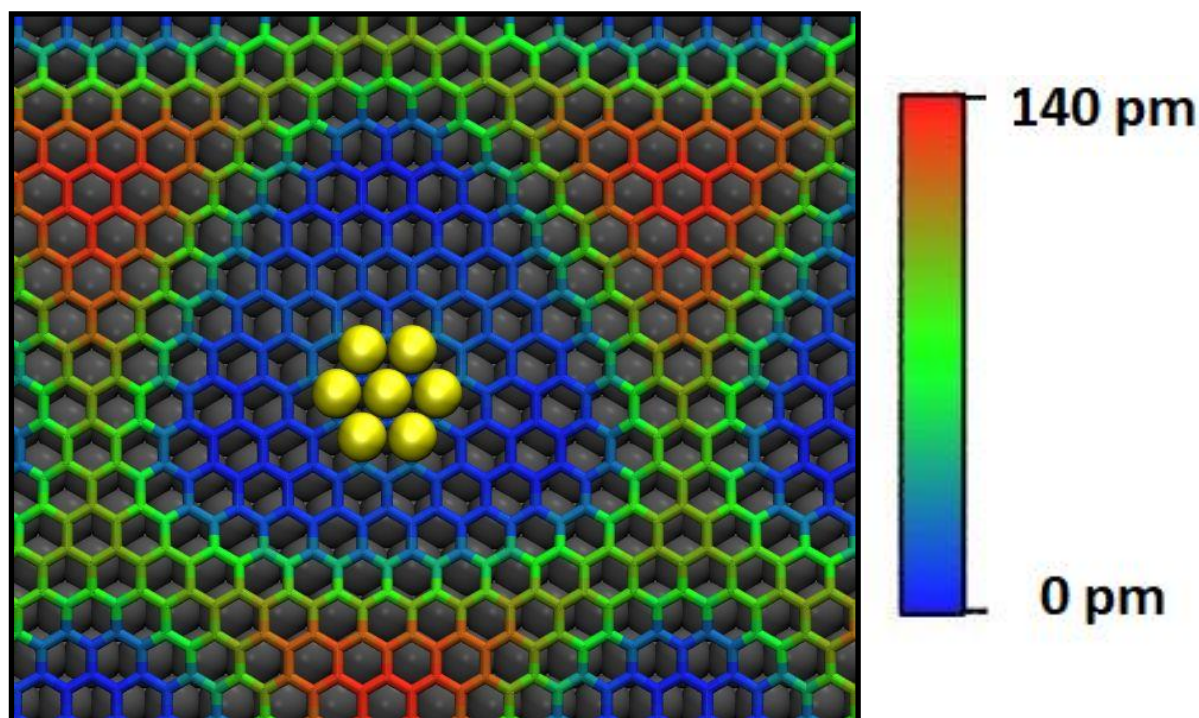


Figure S1.Optimized geometry for a nanoparticle comprising 7 Ir adatoms adsorbed on the hcp subdivision of the RD0_{11×11}moiré of the graphene/Rh(111) surface.

Geometry of an Ir nanoparticle comprising 19 Ir atoms on the RD0_{11×11} moiré of graphene/Rh(111):

The optimized geometry of a nanoparticle composed of 19 Ir adatoms on the hcp subdivision of the RD0_{11×11} moiré is shown in Figure 2h in the main text. In this case, nanoparticle adsorption also gives rise to changes in the bonding landscape at the graphene/Rh(111) interface, which induce local variations of the distance between the 2D material and the metal substrate along the moiré supercell. As a result, the corrugation of the graphene layer is increased by only 14 pm, 3 pm more than for the nanoparticle composed of 7 Ir adatoms.

The bonding distances between Ir atoms in the nanoparticle and C atoms placed nearly below them range between 2.06 and 2.21 Å, being those adatoms with shorter Ir-C bonds the ones located at the corners of the hexagonally shaped cluster. Interestingly, the distances between first neighbors Ir adatoms are in the range 2.45 - 2.57 Å, which are 9.8 - 5.3 % smaller than the corresponding interatomic spacing within the (111) plane of Ir.

Geometry of an Ir nanoparticle comprising 19 Ir atoms on the RD0_{6×6} moiré of graphene/Rh(111):

The DFT analysis performed here has demonstrated that nanoparticle adsorption on the RD0_{6×6} moiré pattern is not stable, at variance with the case of the RD0_{11×11} supercell. The potential energy hypersurface of this case is so complex that convergence has been achieved only at ~0.05 eV/Å forces. The structure presented in Figure 4e in the main text has been obtained after fixing the in-plane coordinates of the Ir adatoms. Otherwise, the Ir clusters composed of 19 Ir atoms do not reach a full convergence but move along the “low” areas of the surface. The present structure does not present the sp^3 re-hybridization of C atoms according to an alternate bonding scheme, in which they bind to either an Ir adatom of the

aggregate or a Rh substrate atom. In contrast, the bonding landscape was found to be rather complex. For instance, for the case of a nanoparticle comprising 19 adatoms, some Ir atoms are found to be chemisorbed to C ones located nearly below, whereas others are placed at distances in the range 3.30 - 4.58 Å from atoms of the graphene layer. Figure 4e shows the obtained geometry, with imposed constraints, for the adsorption of a nanoparticle composed of 19 Ir adatoms on the hcp subdivision of the RD0_{6×6} moiré. A side view of this geometry showing the differences in the Ir-C bonding lengths along the supercell is shown in the inset of Figure 4e. The resulting vertical variations in the positions of the Ir adatoms within the aggregate are much higher than for the case of the nanoparticle on the RD0_{11×11} moiré. The Ir-Ir first neighbor distances, obtained for the nanoparticle composed of 19 adatoms on the RD0_{6×6} moiré, range from 2.44 to 2.87 Å. This scatter in Ir-Ir bonding lengths is too high as to consider the aggregate as a nanocrystal.

Influence of the moiré pattern at the graphene/Rh(111) interface on the Ir nanoparticle spatial distribution:

Figure S2a,c,e show examples of boundaries between regions, where nanoparticles are adsorbed on the moiré RD0_{11×11}, and areas where they are placed over other rotational domain. In particular, Figure S2a,c are the STM images shown in Figure 3a,b of the main manuscript. Figure S2e shows a topography including the area displayed in Figure 3f of the main manuscript. The removal of the Ir nanoparticles with the STM tip following the manipulation procedure described in the main manuscript allows us to uncover the graphene surface below, which can be observed in subsequently acquired STM images. In the main manuscript, it was stated that after nanoparticle removal, it was found that, the moiré periodicities (L_M) below the nanoparticles in the regions of Figures 3a,b,f, placed at the other side of the boundary with an area of the RD0_{11×11} pattern, were respectively, 2.9, 2.8 and 1.6 nm. To support that

statement, Figure S2b,d,f shows STM images acquired, respectively, in the square dotted areas of Figure S2a,c,e after nanoparticle removal. As discussed in the main manuscript, from Figure S2 b,d, or equivalently Figure 3a,b, it is inferred that there are various graphene rotational domains with different moiré periodicities (L_M), giving rise to well-ordered nanoparticle lattices. In contrast, Figure S2e,f demonstrates that for the case, in which nanoparticles are adsorbed on a moiré pattern with smaller periodicity (1.6 nm), they exhibit larger sizes and are randomly dispersed, leaving uncovered a significant fraction of the graphene surface.

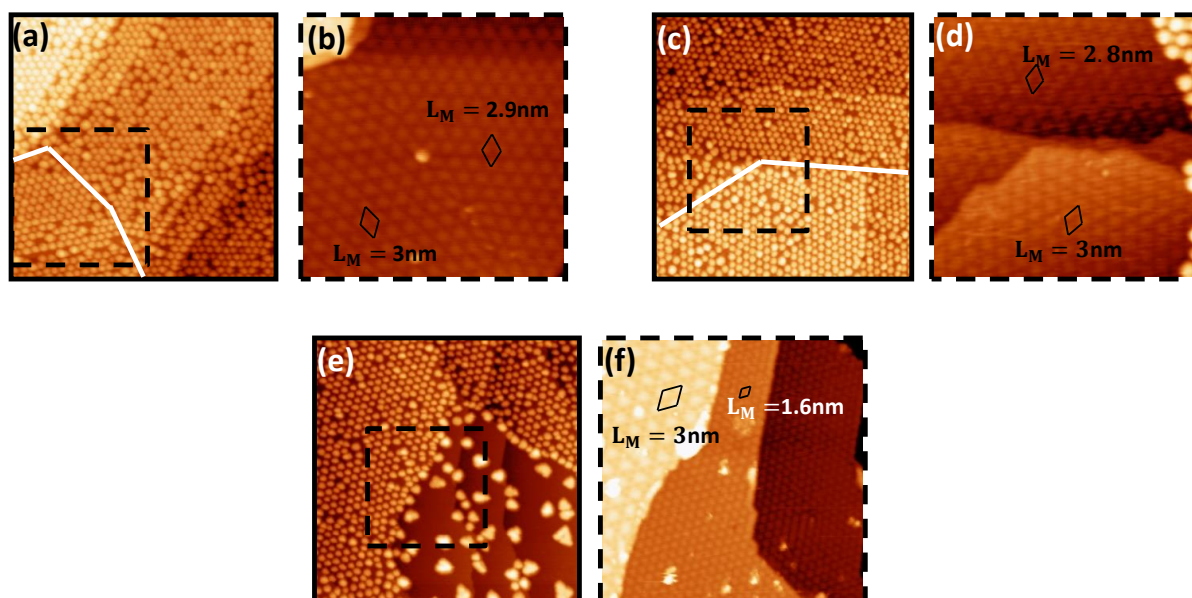


Figure S2. a), c) and e) Large scale STM images showing boundaries between regions exhibiting different nanoparticles arrangements. b), d) and f) STM images after aggregates removal within the dotted squares of a), c) and e). Tunneling parameters: a) and b) $V_s = -2.0 \text{ V}$, $I_T = 0.2 \text{ nA}$; c) and d) $V_s = 2.0 \text{ V}$, $I_T = 70 \text{ pA}$; e) and f) $V_s = +2.2 \text{ V}$, $I_T = 30 \text{ pA}$; Sizes: a), c) and e) $100 \times 100 \text{ nm}^2$; b),d) and f) $45 \times 45 \text{ nm}^2$.