Supporting Online Material

The nucleation of the smallest fullerene-like carbon cages on metal surfaces

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1. Supplementary videos:

Video1:

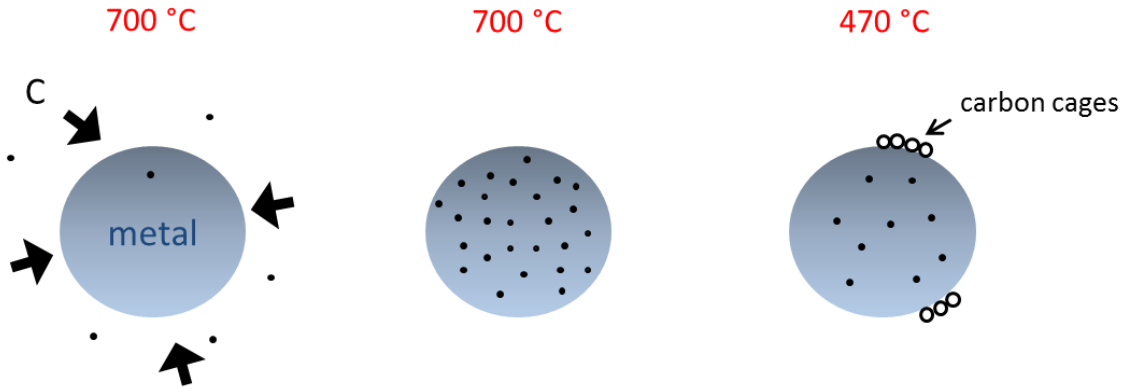
The video shows the appearance of cages at the edge of a Co lamella supported by few-layers graphene. The cages remain on the metal surface during the retraction of the Co lamella. The temperature during the recording was 470°C.

Video2:

The video shows the effect of electron irradiation on carbon cages. The circular features transform into graphitic carbon after two minutes of irradiation with a beam current density of approximately 1 A/cm^2. The temperature during the recording was 480°C.

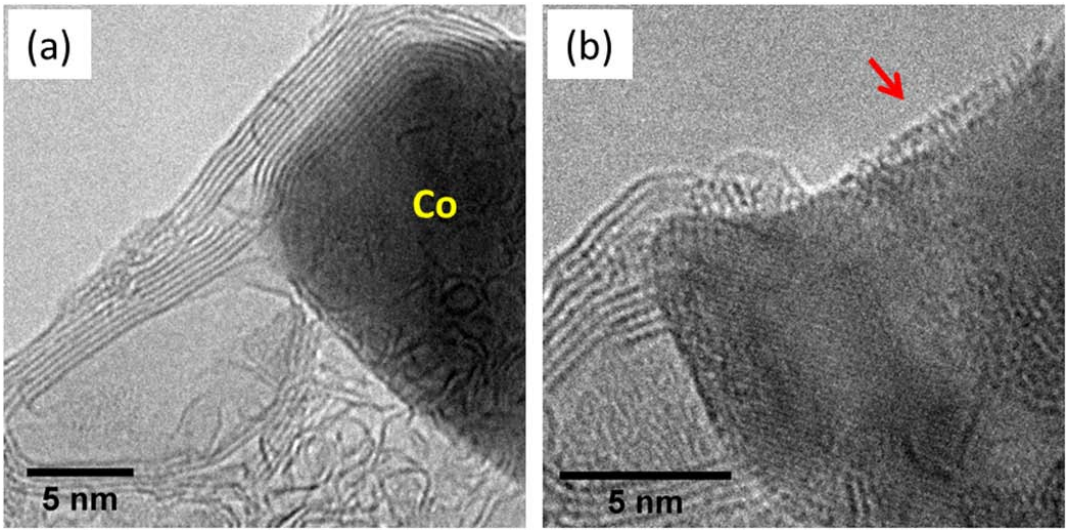
2. Formation of cages by dissolution and segregation:

The following figure shows schematically a possible scenario for the formation of the cages by dissolution of carbon atoms in the metal and segregation at the surface upon cooling. At 700°C, carbon atoms diffuse into the nanoparticle which eventually leads to saturation. Cooling to 470°C leads to supersaturation and the successive nucleation of the cages.



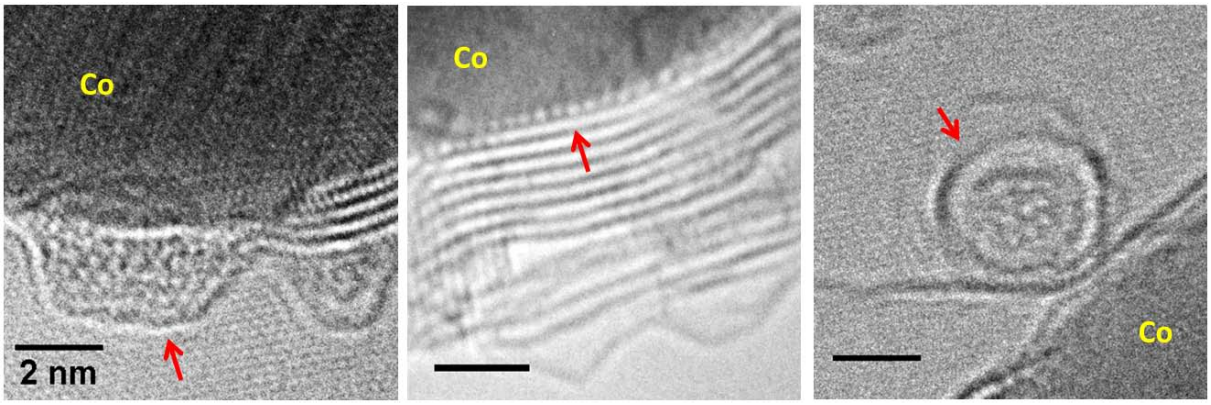
3. Growth of carbon cages on a Co surface after electron-beam sputtering of graphitic material

The prerequisite for the formation of cages is an uncovered metal surface. If this is not the case an intense electron beam can be used for sputtering and removing the graphitic material from the metal surface. This led to the immediate growth of the cages on the bare metal surface once the beam intensity was reduced. The following figures show a Co nanoparticle initially covered with graphitic layers (a). After removing the carbon shell with the electron beam (b), the metal particle transformed its shape, the graphitic material disappeared, and the cages formed on the Co surface.



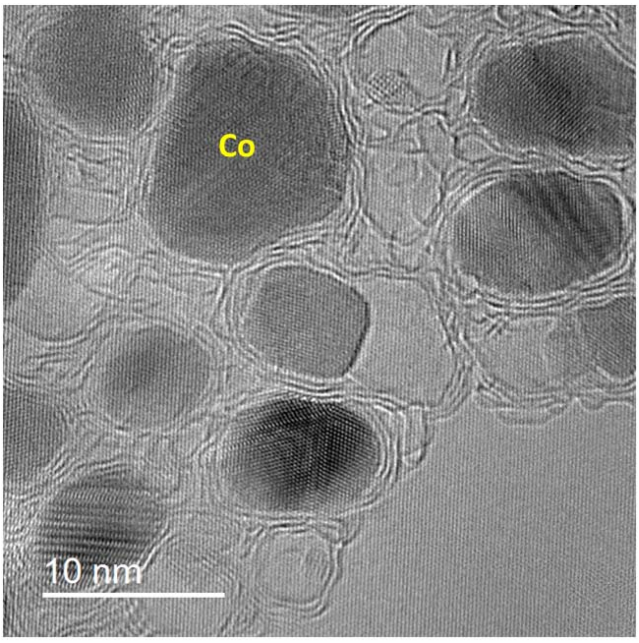
4. Order of the carbon cages under stress applied by a graphitic layer:

The following figures show the effect of stress of spatial confinement on the observed cages. When the encapsulating graphenic layer exerts stress on the arrangement of cages, quasi-crystalline order appears. The stacking of several layers is shown in the left hand image. The middle image shows cages lined up in a monolayer on a Co surface under several graphitic shells.



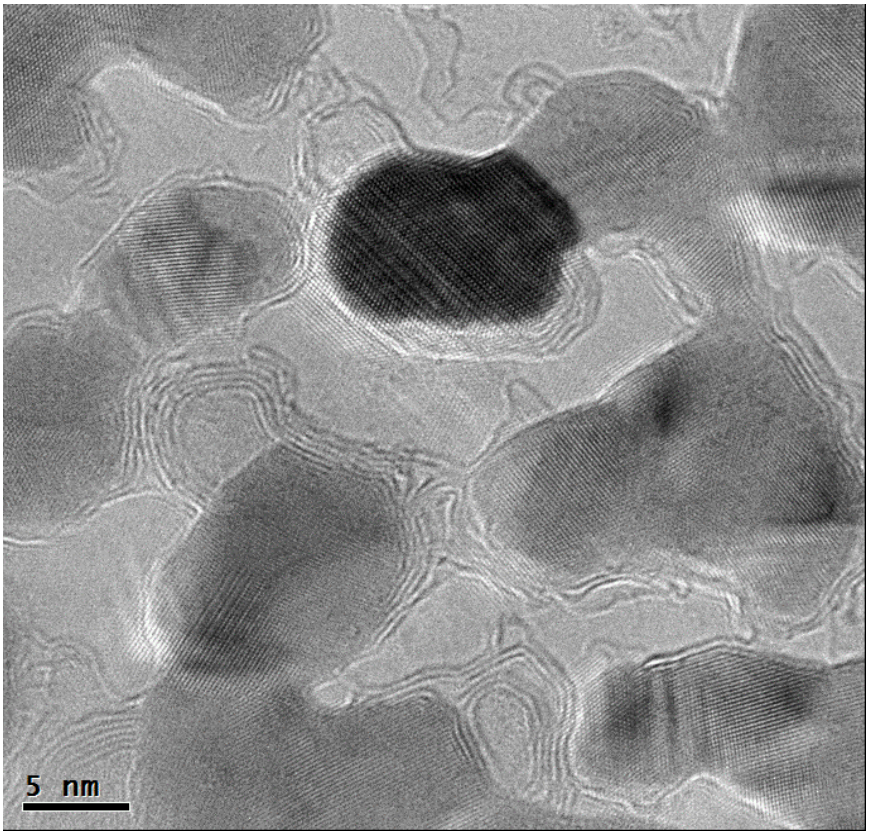
5. Ex-situ study:

A heating cycle was carried out *ex-situ* in a vacuum furnace by varying the temperature more than 10 times between 800°C and 500°C. This leads to an increased density of the observed cages. However, more than 20 heating cycles led to the formation of small metal nanoparticles completely encapsulated by graphitic layers (see following figure). No small cages appear anymore.



6. Rapid encapsulation of Ni crystals with graphitic layers after heating:

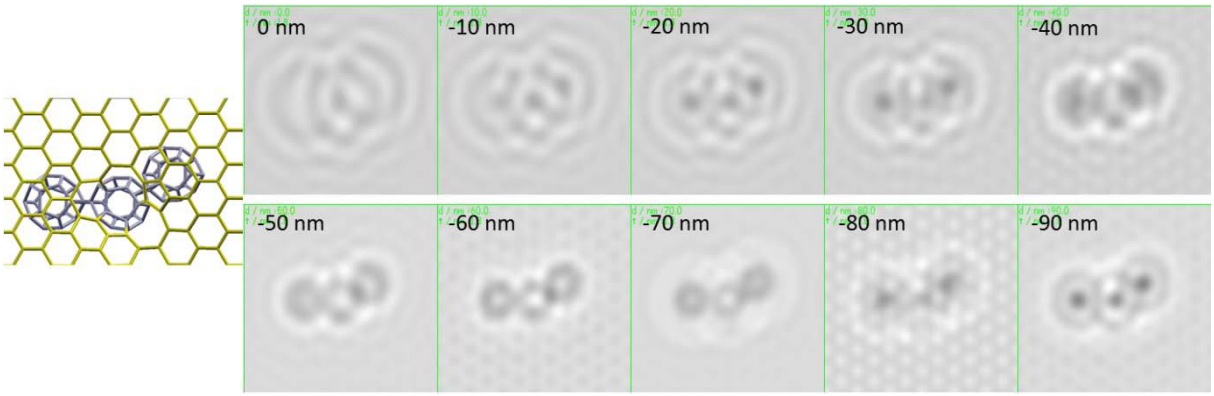
The image shows the encapsulation of Ni crystals under the same experimental conditions as those leading to the formation of small carbon cages on Co, Fe, or Ru. No cages are found on samples with Ni deposits.



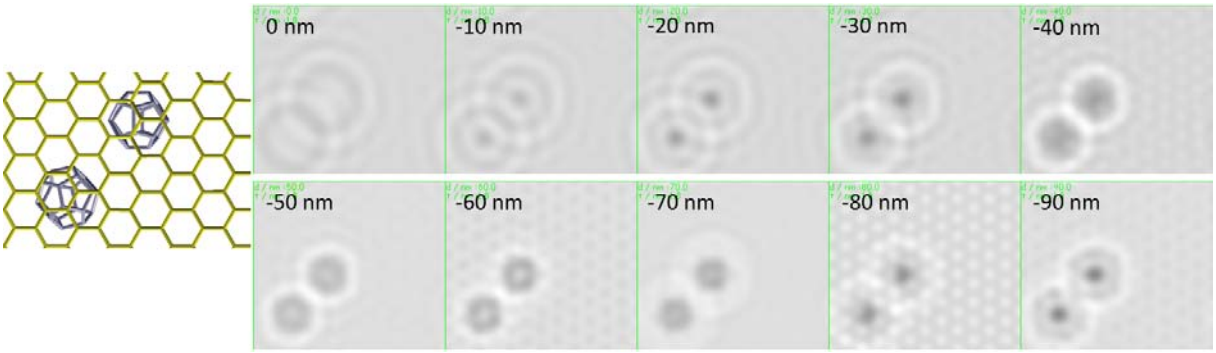
7. Simulation of electron microscopy images:

We performed HRTEM simulations of polymerized and unpolymerized C_{20} using the EMS software (Electron Microscopy Simulator) [P. A. Stadelmann, Ultramicroscopy **21**, 131 (1987)]. We used the multislice approach for modeling the TEM images of the structure. The parameters for a Jeol 2100F (C_s = 1.0 mm) were used. It is apparent that the observed distance of the cages is only conform with the polymerized case (first focal series) and not with isolated cages (second series).

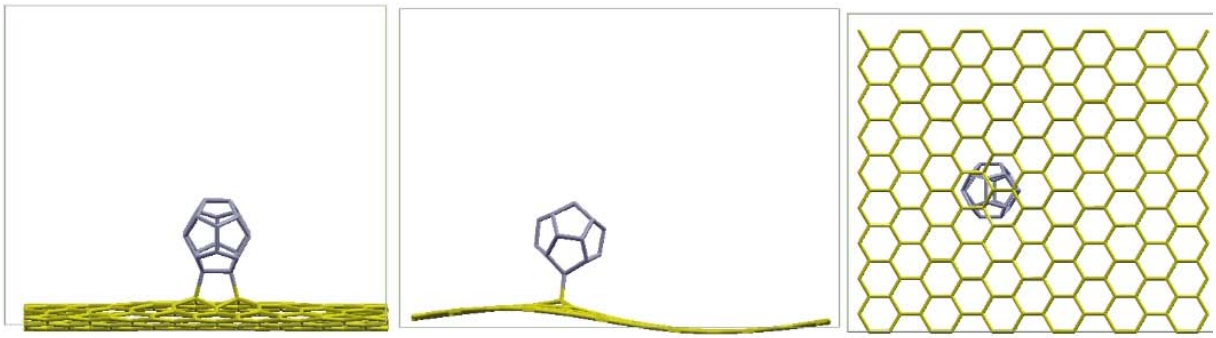
The following figure shows a focal series of three *polymerized* C_{20} on a graphene surface. The C_{20} molecules have been brought together as close as possible to find the limit where bonds start to form. The figure shows a situation with a distance slightly larger than this limit.



The following figure shows the simulation of two *unpolymerized* molecules of C_{20} on a graphene surface.

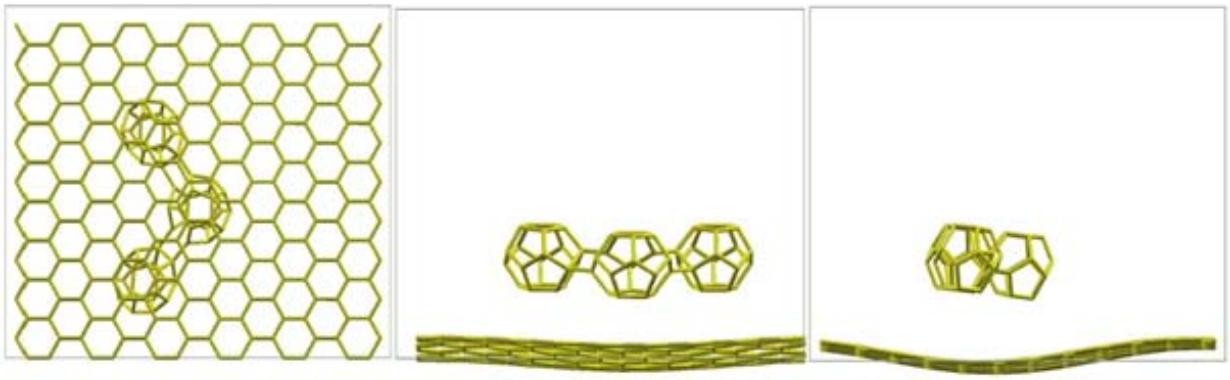


8. Simulation of an isolated C_{20} on graphene (bridge site)



Distance(C20-graphene) = 1.55 Å: formation of bonds.

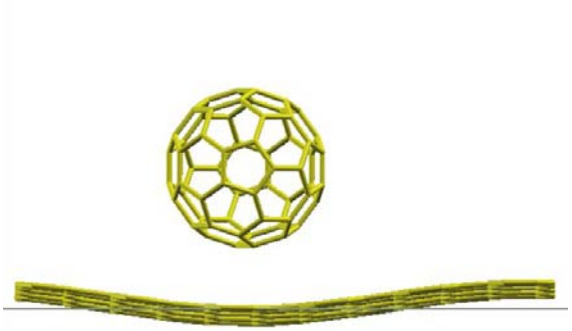
9. Simulation of three polymerized C_{20} on pristine graphene:



Distance (C_{20} - graphene) = 3.7 Å: no bond formation.

The relaxed structure for three polymerized C_{20} shows no bond formation with pristine graphene but conversely a repulsion of the graphene layer. This repulsion is allowed in the calculation since free graphene is considered and not graphene on a metallic substrate as in the experiment.

10. Simulation of C_{60} on pristine graphene



Distance(C_{60} -graphene) = 3.49 Å: no bond formation.

11. Simulation of C_{20} adsorption on a divacancy:

Distance(C_{20} - graphene) = 1.13 Å