Supporting Information for

Graphene Edges Dictate the Morphology of Nanoparticles During Catalytic Channeling

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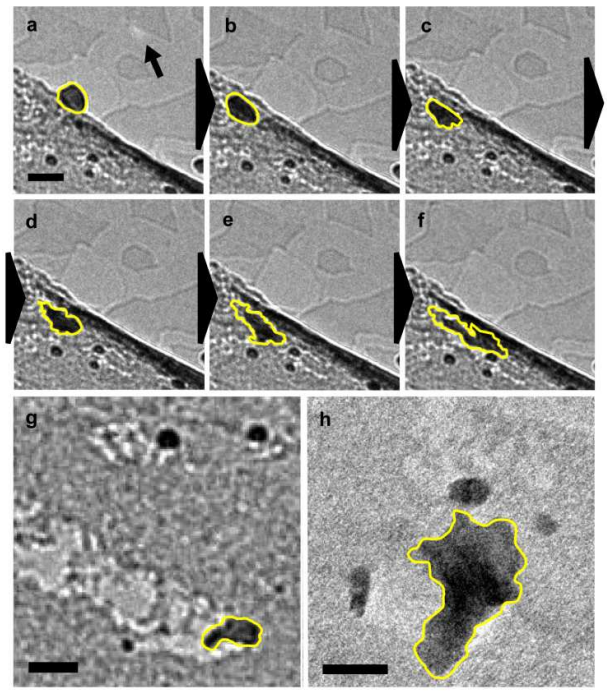

Figure S1 a-f) Sequential TEM images of a particle that changes from channeling graphene to the amorphous carbon of the grid, taken at elevated temperature in oxygen atmosphere (600-800 K, 4-13 Pa). When the particle is etching graphene a Bragg reflection spot is distinguishable (black arrow). Scale bar 25nm. **b)** As soon as the particle reaches the amorphous carbon layer, the spot is not visible anymore. At this point the shape of the particle becomes increasingly irregular. **g-h)** Two further examples of deformed particles etching in the amorphous carbon layer. The yellow lines are a guide for the eye to help distinguish the border of the particles. Scale bars 25 nm and 50 nm respectively.

Computational Details

Density functional theory calculations were performed with the GPAW [1] code, which implements the Projector Augmented Wave (PAW) [2] method for treating the core electrons. The RPBE [3] exchange-correlation functional was employed. In all calculations, the wavefunctions were expanded onto a real space grid, with a grid spacing of 0.2 Å.

The graphene/nanoparticle interface was modelled as a Ag(211) stepped surface with a wide graphene nanoribbon (GNR) perpendicular to it, in contact with the silver atoms at the step (see Fig. S1). The opposite edge is saturated with hydrogen atoms. A 4x4x1 Monkhorst-Pack grid of k-points

was used and the structures were relaxed until the remaining forces were < 0.05 eV/Å. For the Ag surface, only the first layer, i.e. the atoms in contact with graphene, was allowed to relax.

To calculate the binding energy of a carbon adatom on a silver surface, the Ag(111) surface with a carbon adatom was modelled as a 3x3 slab of silver atoms with a thickness of 5 layers. A 8x8x1 Monkhorst-Pack grid of k-points was used and the structures were relaxed until the remaining forces were < 0.05 eV/Å In order to calculate the binding energy of edge carbon atoms for armchair and zigzag edges, we use wide (~ 28 Å) graphene nanoribbons in large supercells (~ 15 Å in the periodic direction) in order for the vacancy to be considered isolated. A 4x1x1 Monkhorst-Pack grid of k-points was used and the structures were relaxed until the remaining forces were < 0.05 eV/Å.

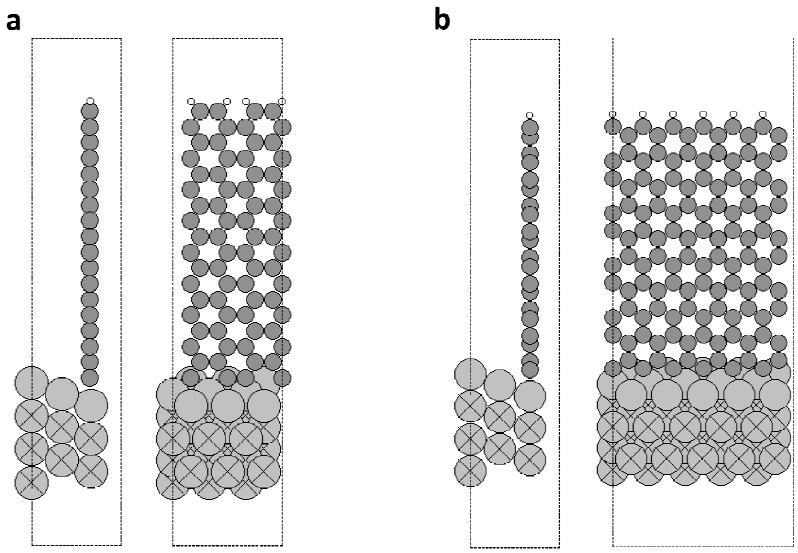

Figure S2: The Ag(211)/graphene interface used as the model for the graphene/nanoparticle interface. The atoms marked with a cross are kept fixed during the geometry optimizations.

Reaction Path

The reaction path of Fig.4 contains stable intermediates that are relevant for the oxygenation and carbon removal of rows of carbon atoms at the interface with the silver nanoparticle. Additional energy barriers (transition-state barriers) might be involved between these stable intermediated and are not taken into account in the present work. In

order to consider transitions state barriers, the detailed atomic mechanism for the removal of each individual carbon atom should be known, or assumed.

The unit cell of the zigzag structure contains 6 carbon atoms at the interface, thus allowing 6 oxygen atoms to bind. Since the oxygenation has to be repeated twice in order to restore a zigzag edge, an entire cycle produces 12 CO molecules per unit cell. The energy levels for the reaction path at the top of Fig. 4 are calculated as:

a) $E_a = E^a_{cell} + 6E_{O_2}$

b) $E_b = E^b_{cell} + 3E_{O_2}$

c) $E_c = E^c_{cell} + 3E_{O_2} + 6E_{CO}$

d) $E_d = E^d_{cell} + 6E_{CO}$

e) $E_e = E^e_{cell} + 12E_{CO}$

where E^i_{cell} is the total energy of the unit cell (graphene and metal surface) at the step *i*, E_{O_2} and E_{CO} are the total energy of gas phase oxygen molecule and CO respectively.

The unit cell of the armchair structure contains 4 edge carbon atoms instead. The gasification of the entire row thus produces 4 CO molecules per unit cell. The energies are calculated as:

g) $E_g = E^g_{cell} + 2E_{O_2}$

h) $E_g = E^h_{cell}$

i) $E_g = E^g_{cell} + 4E_{CO}$

The energies are then normalized on the number of produced CO molecules, i.e. 12 and 4 for zigzag and armchair respectively.

Interface stress

In order to model the interface with periodic boundary conditions, the lattice parameters of graphene and/or the silver slab have to be compressed or expanded slightly. Due to the strength of the C-C bond in graphene, it is likely that the first few layers of silver atoms will be altered. This hypothesis has been tested by calculating the total energy of interfaces where the unit cell has been expanded and compressed. For both armchair and zigzag interfaces, the minimum energy interface is found when graphene has negligible stress or strain. Fig. S2 shows the plot for the zigzag case, for which the optimal interface occurs when the C-C bond length is 1.42 Å, very close to the DFT equilibrium of 1.43 Å calculated with the RPBE functional.

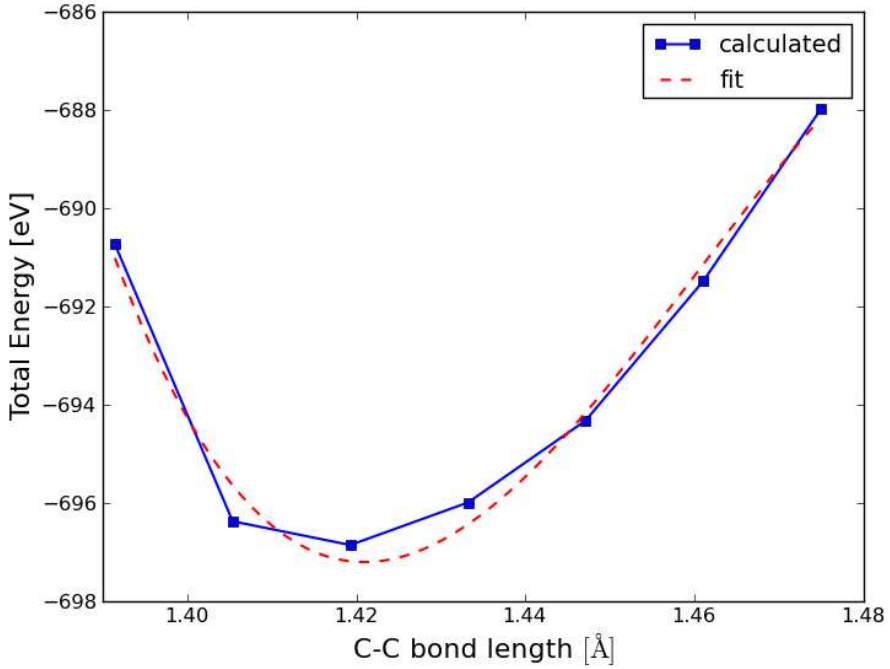

Figure S3: Total energy versus graphene C-C bond length. The C-C bond length is varied by varying the unit cell in all three spatial dimensions.

Carbon adatom on silver

The adsorption energy of carbon adatoms on the silver surface is calculated as:

$$E_{ads} = E_{Ag+C} - E_{Ag} - E_C$$

where E_{Ag+C} is the total energy of the silver slab with the adsorbed carbon, E_{Ag} is the total energy of the slab alone and E_C is the total energy of the isolated carbon atom.

The fcc-hollow site was found to be the most stable adsorption site for a carbon adatom on the Ag(111) surface, with $E_{ads}^{(111)} = 3.26\ eV$. The most stable site for the Ag(100) surface is also the hollow site, with $E_{ads}^{(100)} = 4.10\ eV$.

Carbon binding at the edge

The binding energy of carbon atoms at the graphene edges are calculated as:

$$E_{bind}^{AC/ZZ} = E_{GNR} - E_{GNR-C} - E_C$$

where E_{GNR} is the total energy of the GNR and E_{GNR-C} is the total energy of the ribbon from which an edge carbon atom has been removed.

For an edge atom on the armchair edge, the binding energy is $E_{bind}^{AC} = -7.73\ eV$. This also includes the significant relaxation of the GNR with the formation of pentagons which stabilize the edge, thus decreasing the carbon binding energy. For the zigzag edge, the

binding energy is found to be $E_{bind}^{zz} = -5.94\ eV$, and the energy associated with the relaxation is much smaller in this case compared to the armchair case.

References

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[2] P.E. Blöchl, Phys. Rev B **50**, 17953 (1994)

[3] B. Hammer, L. B. Hansen and J. K. Nørskov, Phys. Rev. B **59**, 7413 (1999)

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