Channeling of graphene in environmental TEM: towards zero-disorder nanolithography

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Catalytic channeling of graphene by metallic nanoparticles is unique due to the tendency of the trenches to follow the graphene lattice orientations, and the possibility of forming long trenches in graphene with a width of a few nanometers, sub-nanometer edge roughness and consistent lattice orientation. We have studied the rich and complex microscopic behaviour of silver nanoparticle gasification in in-situ environmental transmission electron microscopy and account for some of the observed trends and phenomena, including the “shot-noise”-like discrete removal of carbon atoms from the graphene lattice resulting in Poisson distributed temperature dependent instantaneous measured particle velocities [1], and the fact that nearly all edges have zig-zag orientation.

With the support of DFT calculations, we identify the rate limiting step to be the removal of carbon atoms from zig-zag edges. Other phenomena remain to be explained, such as the curious fact that the characteristic shape of even large silver particles appear to be determined by the 1D graphene-silver interface involving just a few hundred atoms. In the light of these findings, the scientific challenges and technological opportunities involved in turning this process into a zero-disorder nanolithographic technique are discussed.

References

[1] Tim J. Booth, Filippo Pizzocchero, Henrik Andersen, Thomas W. Hansen, Jakob B. Wagner, Joerg R. Jinschek, Rafal E. Dunin-Borkowski, Ole Hansen and Peter Bøggild, Nano Letters **11** (2011) 2689
[2] Filippo Pizzocchero, manuscript in preparation.

Figures

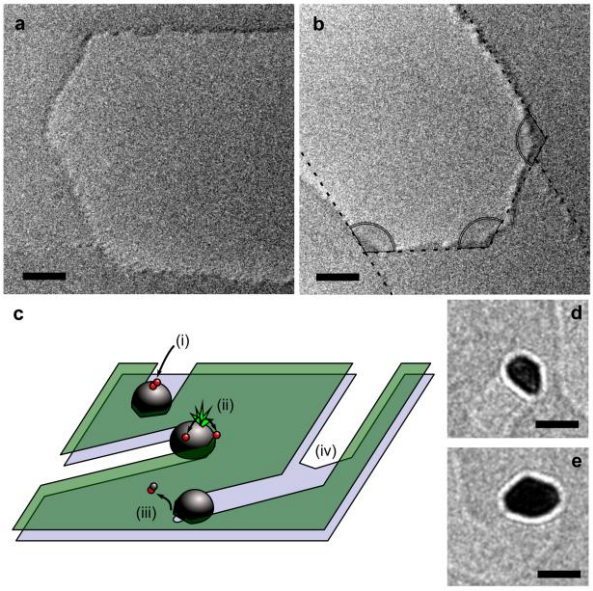

Figure 1: TEM images of the transition between monolayer and bilayer etching (and vice versa) within a single channel. These footprints of the interface of the silver particles in the graphene are triangular in shape with <100> orientated edges, parallel to the zigzag direction of the graphene lattice. Highlighted angles in (b) 120^{o}. Scale bars 5nm. ***c)*** *A schematic representation of the catalytic etching process. (i) The oxygen molecules interact with the silver nanoparticles. (ii) After being adsorbed, the oxygen may dissociate. The atomic oxygen formed diffuses on the surface of the particle, possibly reaching the silver-graphene interface where it interacts with the carbon edge atoms. (iii) Carbon at the edge reacts with the oxygen at the interface and is gasified in the molecular form CO_x leaving a void which the catalyst particle moves to fill. (iv) Schematic representation of changes in the number of layers removed, c.f. (a,b)* ***d-e)*** *The triangular front of etching particles is clearly visible in these images. Scale bars 25 nm and 20 nm respectively.*

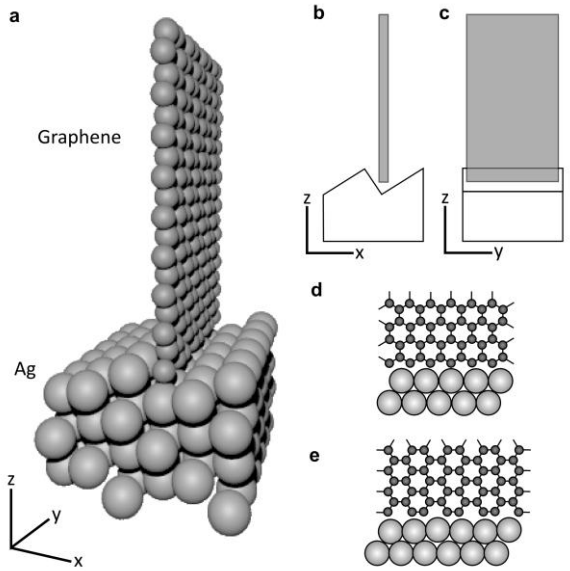

Figure 2: ***a)*** *A three dimensional representation of the structure used in the DFT calculation.* ***b-c)*** *Schematic 2D projections of the structure shown in (a). In particular, in (b) the shape of the step is clear, while in (c) the position of the graphene flake with respect to the silver edge is exemplified.* ***d-e)*** *Scale representations in the ZY plane of the actual DFT relaxed graphene-silver interfaces for the armchair and zigzag edges respectively. In (d) two unit cells are shown, with one in (e).*