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**TRANSFORMATION OF STRUCTURE AT THE NANOSCALE:  
THEORY AND ATOMIC IMAGING**

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Our *in situ* aberration-corrected high-resolution transmission electron microscope (AC-HRTEM) experiments correlated with quantum chemical modelling demonstrate that a direct transformation of structure of carbon nanomaterials is possible under the electron beam (e-beam) radiation. In this talk, we will overview and discuss two examples of such transformations: a process of fullerene formation from a finite graphene sheet [1]; and reactions of the concave surface of carbon nanotubes leading to the formation of hollow nano-protrusions [2].

Etching of edge carbon atoms of a finite graphene flake by the e-beam facilitates the formation of curved fragments, which continue being etched until a closed fullerene cage is formed. A piece of graphene of limited size may not be the most stable allotrope of carbon, particularly under the e-beam radiation, so that the latter stages of this thermodynamically driven process should happen with the similar ease to the formation of C<sub>60</sub> from carefully designed polyaromatic molecules. Once the edges are sealed, no further carbon atoms can be lost, and the newly created fullerene remains intact under the e-beam.

Figure 1 presents experimental AC-TEM images [1] showing stages of fullerene formation directly from graphene: (a) black arrow indicates a double layer of graphene, which serves as substrate; white arrow points at a strip of graphene (monolayer) adsorbed on this substrate; the dashed white line outlines a more extended island of graphene mono- or bi-layer, which has its edges slightly curved on the left side; (b) final product of graphene wrapping a fullerene molecule on the surface of graphene monolayer (carbon atoms appear as black dots); (c-h) consecutive steps of gradual transformation of a small graphene flake (c) into fullerene (g,h). The graphene lattice is filtered out from images (c)-(h) for clarity.

Quantum chemical modelling [1] elucidates four critical steps in a "top-down" mechanism of fullerene formation: (i) the loss of carbon atoms at the edge of graphene leading to (ii) the formation of pentagons that triggers (iii) the curving of graphene into a bowl-shaped structure, which (iv) subsequently zips up its open edges to form a closed fullerene structure.

The interior surface of carbon nanotubes is known to be chemically inert and typically remains unaffected by reactive species. We inserted catalytically active atoms of transition metal Rhenium (Re) into nanotubes and demonstrated that in the presence of Re the nanotube sidewall can be engaged in chemical reactions [2]. The energy of the e-beam of AC-HRTEM set at 80 kV ensures no direct effects caused by the e-beam on the nanotube

structure and visualizes formation of nanometre-sized hollow protrusions on the nanotube sidewall in real time. Direct space AC-HRTEM images and theoretical modelling demonstrate that the nano-protrusions are always formed *via* three key stages: (i) a bulging nanotube sidewall followed by its rupture, (ii) a fast formation of a metastable asymmetric nano-protrusion with an open edge and (iii) a slow symmetrisation process leading to a stable closed nano-protrusion. Control experiments and theoretical calculation confirm the importance of the atomic catalytic centres of Re that interacting with carbon fragments create highly active intermediates able to react with the nanotube inner surface. Thus, our study uncovers the endohedral reactivity of carbon nanotube, which up to date was believed to be non-existent.

The future development of ultra-fast imaging techniques for AC-HRTEM may help to capture chemical transformation in more detail and enable deeper understanding of this and other reactions in nanotubes.

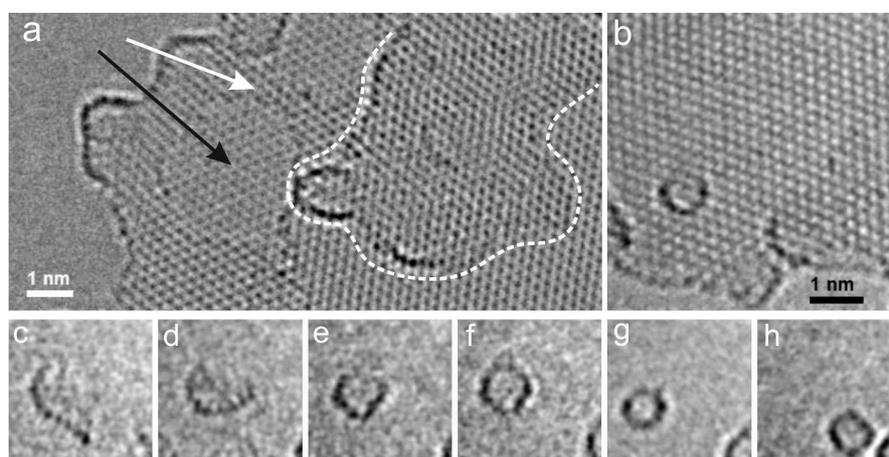


Figure 1: AC-TEM images showing stages of fullerene formation directly from graphene.

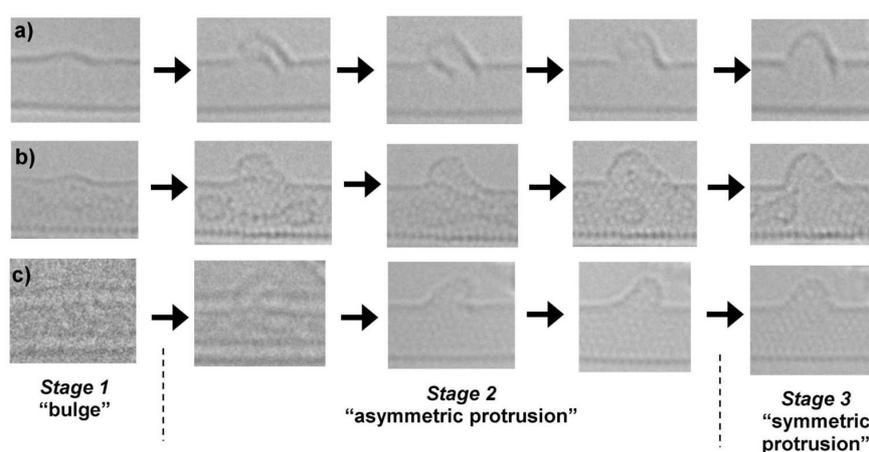


Figure 2: 80 kV AC-HRTEM time series images of different stages of nano-protrusions formation on nanotube.

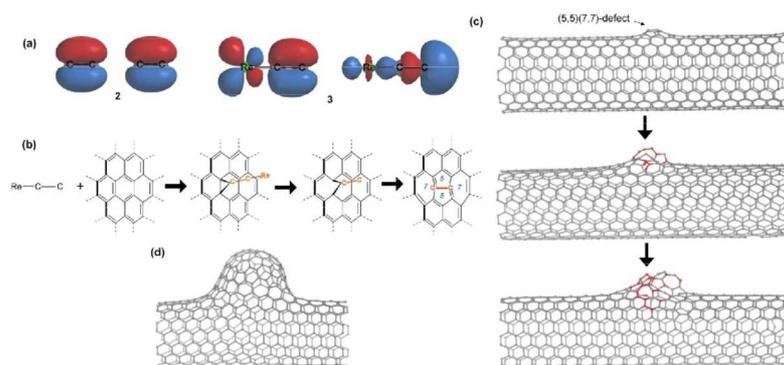


Figure 3: (a) the HOMO of alpha-spin electrons. The bonding of Re to the bi-radical C<sub>2</sub> fragment **2** generated under the e-beam from decomposing fullerene molecules, alters the beta-spin HOMO so it is localized mainly on the terminal carbon, thus increasing the reactivity of intermediate **3** towards the nanotube interior. While the C<sub>2</sub> bi-radical alone does not react with the nanotube sidewall, when activated by Re it can either be inserted into the nanotube sidewall to create a (5,5)(7,7)-defect, as shown in 3(b), or rupture the nanotube. Figure 3(c) presents MD calculations showing that the (5,5)(7,7)-defect can react readily with additional molecules of C<sub>2</sub>; carbon atoms incorporated into the structure of the nanotube sidewall are shown in red. Closure and symmetrisation of the nano-protrusion (d) is dictated by the nanotube structure. Nano-protrusion shown in (d) is constructed to match the shape/size of those observed in the experiments; the stabilisation energy of this protrusion is very close in value to that of a closed protrusion formed in the MD simulations.

## References

- [1] A. Chuvilin *et al.*, Nature Chemistry, 2 (2010) 450.
- [2] T. W. Chamberlain *et al.*, Nature Chemistry (2011), editor decision awaiting.
- [3] This research was supported the EPSRC (Career Acceleration Fellowship to EB), the DFG (German Research Foundation) and the State Baden-Württemberg within the SALVE project (KA-1295/10-1).