

MECHANISM OF DIRECT TRANSFORMATION OF GRAPHENE TO FULLERENE

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Introduction

Over the past two decades, many different models of fullerene formation from graphite have been proposed. Generally accepted mechanisms fall into four groups according to the exact route leading to fullerenes: Pentagon Road [1, 2], Fullerene Road [3], Ring Coalescence [4] and Shrinking Hot Giant model [5]. All of these routes can be classified as “bottom-up” mechanisms because fullerene cages are formed from atomic carbon or small clusters of carbon atoms, which subsequently coalesce to form fullerene cages through a series of intermediates. Although there is a large body of experimental evidence supporting the “bottom-up” mechanisms, it is almost entirely based on mass spectrometry and its variants that analyze only species present in the gas phase. These experiments provide no direct structural information about the precursors of fullerenes and do not allow following fullerene formation *in situ*.

In this work [6], aberration corrected transmission electron microscopy (AC-TEM) visualizes directly in real time a process of fullerene formation from a graphene sheet. Quantum chemical modeling 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.

Experimental

Graphene represents an ideal viewing platform for molecular structures using AC-TEM because it provides a robust and low contrast support for molecules and other nanoscale species adsorbed on the surface. Under AC-TEM observation with exposure to the 80 keV electron beam (e-beam), the edges of the graphene sheet appear to be continuously changing their shape (Figure 1a). The high energy of the e-beam transferred to the carbon atoms of graphene can cause fragmentation of large sheets of graphene into smaller flake-like structures (Figure 1c). The flakes adsorbed on a graphene substrate can be visualized, and their further transformations can be observed readily in AC-TEM.

The final product of these transformations is often a perfect fullerene molecule (Figure 1b).

The sequence in Figure 1c-h shows a typical transformation route for an individual graphene flake that changes its shape under the influence of the e-beam becoming increasingly round (Figures 1c to 1e). The contrast of its edges gradually increases (Figure 1f) indicating that the edges of the flake come progressively out of plane and rearrange into the spheroid shape of a fullerene (Figure 1g).

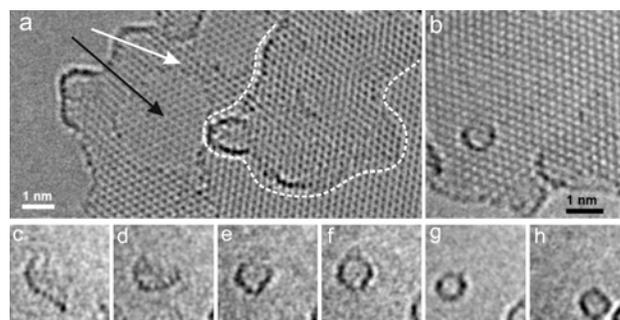


Fig. 1 Experimental AC-TEM images showing stages of fullerene formation directly from graphene. (a) black arrow indicates a double layer of graphene, which serves as substrate; white arrow points at a strip of graphene (monolayer) adsorbed on this substrate; the dashed white line outlines a more extended 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.

The experimental TEM images provide compelling evidence for the graphene-to-fullerene transformation. However, the formation of fullerene from graphene can be best explained through quantum chemical modeling of the key initial stages of the process.

Quantum chemical modeling

The description of a small graphene flake, which initially contained 117 carbon atoms and subsequently was reduced to 86 and 84 atoms, is based on the DFT formalism using the Q-CHEM quantum chemistry package [7] with the B3LYP exchange-correlation functional and 6-31G* basis set. Dispersive van der Waals interactions between the graphene flake and the underlying graphene sheet contribute to up to ~30% reduction in its stabilization energy, depending on the size and curvature of the fragment. The energy of these non-covalent interactions was estimated using the empirical Girifalco potential[8], which has been successfully applied for describing the interactions between graphitic nanostructures. The structures used for modeling represent one possible flake

that is as close as possible to the experimental observations (Figure 1c-h).

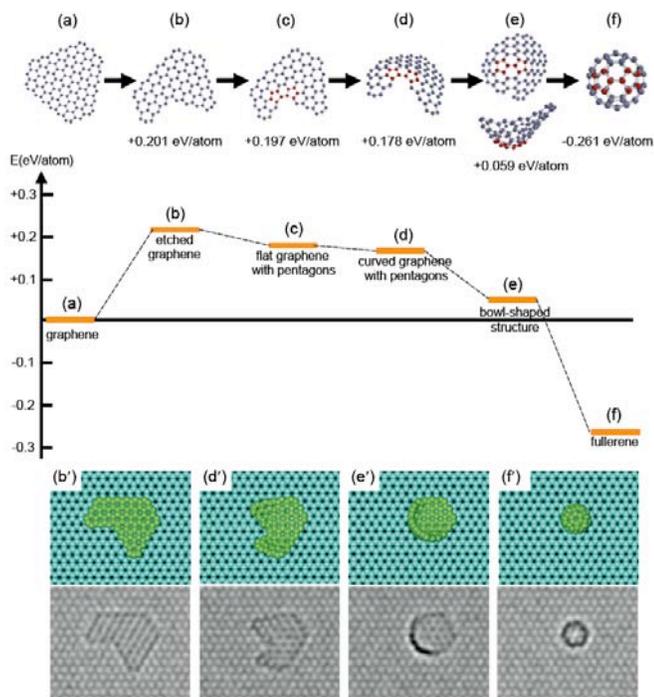


Figure 2. Quantum chemical modeling of the four critical stages of fullerene formation from a small graphene flake: loss of carbon atoms at the edge (a) → (b); formation of pentagons (b) → (c); curving of the flake (c) → (d); formation of new bonds leading to zipping of the flake edges (d) → (e). Figure (e) shows top and side views of a bowl-shaped intermediate structure. Stabilization energies (in eV per carbon-atom) of intermediate structures and resultant fullerene C_{60} , relative to a flat defect-free flake of graphene shown in (a), are presented pictorially and graphically. Top views of graphene flake (b'), curved graphene intermediates (d', e') and fullerene C_{60} molecule (f') adsorbed on underlying graphene substrate and simulated TEM images corresponding to each structure showing how they would appear in TEM experiments.

Induced by the high-energy e-beam, the initial loss of carbon atoms at the edge destabilizes the structure (Figure 2b) because it increases the number of dangling bonds at the edge. Formation of pentagons at the edge (Figure 2c) and subsequent curving of the flake are thermodynamically favorable processes as they bring covalently deficient carbon atoms close to each other (Figure 2d). New carbon-carbon bonds are then formed leading to zipping of the flake edges and reducing the number of dangling bonds. This has a profound stabilizing effect on the structure. In a similar way, the bowl-shaped structure (Figure 2e) can evolve further by losing carbon atoms from its remaining open edge through the e-beam etching, formation of more pentagons and curling

until the structure is sufficiently small to close up into a cage (Figure 2f). Fullerene is the most stable configuration for a finite number of sp^2 -carbon atoms as the molecular cage has no open edges (i.e. etching is prohibited) and all carbon atoms form three carbon bonds. If the structure of the newly formed fullerene does not correspond to the most stable isomer, its structure can “anneal” via a series of Stone-Wales rearrangements [1] that are facilitated by the e-beam in AC-TEM or by an add-atom under the standard fullerene synthesis conditions [9].

The experimentally observed images can be related through AC-TEM image simulation to models of graphene flake (2b'), curved graphene intermediates (2d' and 2e') and the resultant fullerene molecule (2f') adsorbed on graphene substrate. Once fullerene formation is complete, the molecule appears to roll back and forth on the underlying graphene (Figure 1h). This is possible because the energy of van der Waals interaction of a fullerene with the substrate is significantly reduced compared to a flat graphene flake [8] due to the reduced surface area in contact with the substrate.

Conclusions

Our *in situ* TEM experiments correlated with quantum chemical modelling demonstrate that a direct transformation of flat graphene sheets to fullerene cages is possible. Etching of edge carbon atoms by the e-beam facilitates the formation of curved graphene fragments, which continue being etched until it becomes possible for them to zip up into a fullerene. 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_{60} fullerene 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.

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