

Direct Transformation of Graphene to Fullerene

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S1. Effects of carbon atom loss at the edge and middle of graphene sheet.

The calculated energy required to remove a carbon atom from the middle of a graphene sheet varies between 7.4 eV and 7.65 eV [s1-s3]. It is interesting to note that the mechanism of an atom loss at the edge of a small graphene flake differs strikingly from the analogous process in the middle of a graphene sheet. A mono-vacancy in the middle of the sheet undergoes a symmetry preserving Jahn-Teller distortion, which results in a weak reconstructed bond, the formation of a pentagon, and a small out-of-plane displacement of the remaining dangling bond atom. As the geometry of the pentagon is not compatible with the flat structure of graphene, it is formed transiently and has minimal effect on the global structure of the graphene sheet. Meanwhile, our modelling shows that the loss of a carbon atom at the edge of a small graphene flake causes the flake to curve out of plane forming “a bowl” shape and thus aiding the formation of a pentagon at the edge, which is a crucial element of the fullerene structure.

S2. Formation of spheroidal structures from graphene.

Wrapping of small flakes of graphene into spheroidal fullerene-like structures is a phenomenon that commonly occurs under TEM imaging conditions. Figure 1s shows three spheroidal fullerene-like cages formed from graphene flakes in the same area of substrate.

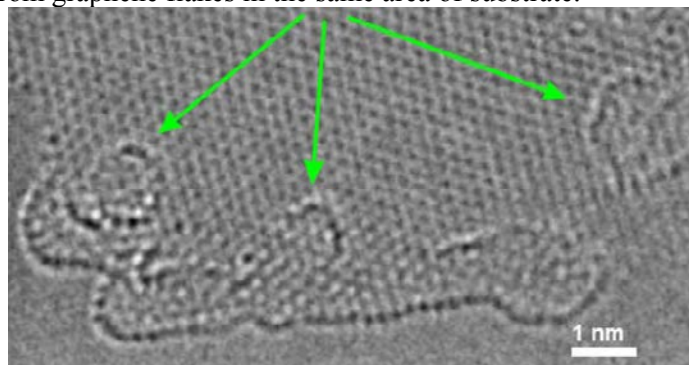


Figure 1s. Experimental TEM images of discrete spheroidal cages at different stages of their formation (indicated by green arrows) adsorbed on thin graphene sheet.

We would like to encourage the readers to view a very striking TEM movie showing the dynamics of transformation of graphene into fullerene as a Supplementary Information video file (Graphene_TEM_movie.avi).

S3. Place of the “top-down” mechanism among currently accepted models of fullerene formation.

Over the years, many different mechanisms of fullerene formation have been suggested, including the “nautilus model”, “accelerating snowball model”, “pentagon road”, “fullerene road”, “party line”, “ring stacking mechanism”, “ring fusion spiral zipper mechanism”, Kvararon model and most recently the “shrinking hot giant model”. The main reason for such profusion of different and sometimes

conflicting models lies in the fact that each of them provides only partial explanation of the experimental observations. At the present time, *there is no single unifying model of fullerene formation giving satisfactory explanation of how the fullerenes are formed.*

Analysing the current understand of the fullerene formation mechanisms, some general points can be made as follows:

- All currently accepted mechanisms can be classified as “bottom-up” models, as in all cases formation of fullerenes starts from atomic carbon or small clusters of carbon atoms.
- In all concepts formation of fullerene is considered to be in the gas phase. All experimental methods analyse the species present in the gas phase, but not on the surface of graphite.
- Experimental evidence supporting the mechanisms is based on mass spectrometry (and related techniques) and HPLC, which do not provide direct information about the structure of intermediates and do not allow following the fullerene formation *in situ*.
- Initial stages of all mechanisms involve three-particle collisions that are highly unlikely in the gas phase.
- Mechanisms currently accepted are highly complex as they proceed *via* series of unstable intermediates, existence of which is often questionable.

With respect to the above points, the “top-down” mechanism of graphene to fullerene transformation proposed in our paper is clearly very distinct from all other existing mechanisms.

It is surprising that the idea of graphene to fullerene transformation has never been considered as a viable mechanism of fullerene formation. None of the reviews on fullerene formation [s4, s5] including the latest feature article [s6] include the “top-down” model as a possible mechanism. There has been only one tentative study that attempted to envisage how a sheet of graphene could transform into a fullerene [s7], which unfortunately did not consider the possibility of carbon atom loss and pentagon formation at the edge of graphene, and therefore concluded that this process requires enormously high activation energy (15eV) and consequently is not feasible under any experimental conditions.

The key reason why the “top-down” model has never been seriously explored is the results of isotope mixing experiments carried out in the early 90’s [s8-s10]. Arc-discharge experiments utilising composite electrodes made from graphite-¹²C and amorphous carbon-¹³C showed that the isotopes are scrambled in fullerenes formed under these conditions. This led to a notion that graphitic sheets *must dissociate to atomic (or near atomic) carbon from which fullerene cages are formed.* However, experiments reported in our study clearly demonstrate that a sheet of *graphene can be transformed directly to fullerenes without dissociation to individual atoms.*

The isotope mixing experiments are compelling, but they also have weaknesses:

- Typically, only 5% of carbon atoms in fullerenes were found to be ¹³C [s8, s9], which means that fullerenes are formed predominantly from graphite, rather than amorphous carbon.
- The isotopic composition of fullerenes formed in the gas phase has been investigated. However, it is known that a significant proportion of fullerenes are formed on a graphite cathode [s11]. The isotopic composition of fullerenes formed directly on the cathode (i.e. on surface of graphite) remains unknown.

The previous evidence of isotope mixing does not rule out the “top-down” model that may coexist with the traditional “bottom-up” mechanisms during the fullerenes production. For example, in arc-discharge some fullerenes may be formed in the gas phase from C₂ fragments and some may form on the surface of graphite electrodes from small flakes of graphene.

S4. References.

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