Adatoms and nanoengineering of carbon

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Abstract

We present a new and general mechanism for inter-conversion of carbon structures via a catalytic exchange process, which operates under conditions of Frenkel pair generation. The mechanism typically lowers reaction barriers by a factor of four compared to equivalent uncatalysed reactions. We examine the relevance of this mechanism for fullerene growth, carbon onions and nanotubes, and dislocations in irradiated graphite.

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Nanotechnology with carbon is made possible by the myriad metastable structures afforded by three fold coordinated carbon. The quintessential fullerene structure: hexagonal rings with 12 pentagons, comprises but a small subset of possible metastable structures of different ring statistics and properties[1]. Any arbitrary shape of surface may be engineered from a hexagonal net modified to include rings of different sizes [2]. Quasi-spherical carbon onions[3,4] are observed after $> 100$ keV electron irradiation of polyhedral carbon particles[5] and under some CVD conditions[6]. They shrink under sustained irradiation[7], suffer self-compression and, through surface tension, adopt nearly spherical shape. The phenomenon arises from Frenkel pair creation, migration and annihilation[8] and it appears to be a radial analogue of the c axis expansion (or “plating out”), observed in graphites under neutron irradiation [9]. One of the structural models which appears to mimic well experimental HRTEM onion images, achieves spherical shape through insertion of pentagon/heptagon pairs or pentagon-pentagon-octagon triads into the ground state, icosahedral, faceted fullerene shell[10].

In order to discuss shape changes, it is instructive to map a flat graphite sheet to a general shape by the introduction of topological defects. Pentagons and heptagons are, respectively, positive and negative 60° wedge disclinations. Their disposition is the main determinant of shape. They can be moved by the
absorption and emission of edge dislocations, which themselves are identified as wedge disclination dipoles and appear as pentagon-heptagon pairs.

If such processes occur in even-numbered systems through the Stone-Wales (SW) route\textsuperscript{[11]}, high barriers must be overcome (\(> 6 \text{ eV}\))\textsuperscript{[12]}. This may be theoretically possible within the thermal spike of an irradiation event or under the extreme conditions of a carbon arc, but is unlikely to contribute as strongly as a mechanism which operates more homogeneously and is modestly thermally activated at typical substrate and annealing temperatures.

Carbon dimers afford an intuitively simple basis for interpretation of growth and attrition of fullerenes (observed as stable, even \(n\) clusters \(C_n\)). Addition of a \(C_2\) dimer to a fullerene or a graphite sheet followed by bond reconstruction (as invoked in the “Pentagon Road” of fullerene growth) leads to replacement of a hexagon by a pair of pentagons. Removal of such a pair (as might be invoked in onion formation) yields, in the case of graphite, two pentagons and an octagon. Each such addition/removal step must be accompanied by rearrangement to lower energy and stabilise the growth or shrinkage process.

Carbon dimers are known to be ejected during thermal decomposition of fullerenes\textsuperscript{[13]} and \(C_2\) is a substantial component of a carbon gas\textsuperscript{[14]}. However, odd numbered species principally \(C\) and \(C_3\) also exist in the gas phase and may be ejected under irradiation above the displacement threshold.

These observations led to the proposal that the SW transformations occurring during growth be auto-catalysed — catalysed by the presence of additional carbon atoms \textit{i.e.} in locally odd-numbered systems. Here we explore further this possibility, first discussed by Eggen \textit{et al.}\textsuperscript{[12]} in the case of the last in the sequence of transformations \textsuperscript{[15]} which convert an arbitrary \(C_{60}\) fullerene into icosahedral \(C_{60}\) or buckminsterfullerene (BF). In that first study, a carbon adatom was shown to reduce the barrier for this last transformation step (from a \(C_{2v}\) isomer to BF) from 4.7 to 2.9 \text{ eV}. Whereas there has been much work on the topology and sequence of transformations, including a detailed study of the energy landscape\textsuperscript{[16]}, there is still a need to establish energetically viable transformation paths of the kind we propose here.

As before, we apply Local Spin Density Functional Theory code AIMPRO\textsuperscript{[17]}, using the Ceperley-Alder functional\textsuperscript{[18]} and norm-conserving pseudo-potentials\textsuperscript{[19]}. A real-space \(sp\) basis of 16 Gaussians per atom is used for the wavefunction and 4 Gaussians per atom for the valence charge density. Analytic atomic forces are used within the conjugate gradient method to optimise structures until forces were negligible.

In this way we have examined the final annealing transformation in \(C_{60}\) when the adatom is not in the lowest energy state and we have considered generalised transformations that create and move dislocations and disclinations.
(i.e. pentagons and heptagons) in graphene sheets. The result is a general and low energy route for nano-engineering carbon structures.

The SW transformation in BF involves the bond linking two pentagons rotating through 90° about its centre, effectively causing pairs of pentagons and hexagons to swap sites (Fig 1a). The new auto-catalytic exchange mechanism we find (Fig 1b) achieves the same end, while at the same time the adatom is incorporated into the ball and a host atom is ejected. The route and its activation barrier were obtained by optimisation, removing degrees of freedom corresponding to atomic movements which simultaneously break one bond while making another. For the catalysed exchange process the degree of freedom removed is the difference in squares of AB and AC bond lengths, i.e. 

\[ r_{A-B}^2 - r_{A-C}^2 = C_0 \] (see Fig 1b). (Note that in the non-catalysed case another degree of freedom is also removed \( r_{A-D}^2 - r_{B-C}^2 = C_1 \), see Fig 1a) and an energy surface as a function of \( C_0, C_1 \) found.

In this mechanism the SW barrier to BF formation from the nearby \( C_{2v} \) isomer is decreased from 4.7 eV to 1.1 eV. Only one bond is broken and one formed, as opposed to non-catalysed SW where there are two such bond pairs. Another perspective is that the ad-atom has already dilated the pentagon, part-transforming it to the hexagon required in the product.

In the starting structure the adatom B sits proud of the BF cage above a pentagon-hexagon bond. It rotates about this bond, flattening into the BF cage and beginning to form a bond with host atom A. While it does this, the bond from A to host atom C breaks and C lifts proud to become the new adatom.

Overall the reaction is exothermic by 1.2 eV compared with 1.5 eV without the adatom. The increased stability of the adatom on the \( C_{2v} \) paired pentagon system and the metastability of the final \( C_{61} \) state accounts for the difference. This metastable state of the adatom, where it sits above a bond shared between a pentagon and a hexagon (the 'homo' isomer of \( C_{61} \)), is 0.26 eV above its ground state above a hexagon-hexagon bond (the 'methano' isomer of \( C_{61} \)). This metastability is one reason why the mechanism was previously overlooked. Positive charging and high spin (e.g. triplet) states cause only marginal increases in the activation barriers.

It is known that DFT(LSDA) calculations can underestimate reaction barriers however this is typically of the order of 0.2 eV[20] and thus will not qualitatively affect these results. In addition any error will systematically affect all calculated barriers including the uncatalysed.

The mechanism, with its concomitant interstitialcy diffusion, is entirely consistent with experiments in which a beam of \( ^{13} \text{C} \) ions impinging on \( ^{12} \text{C} \) \( C_{60} \) molecules led to an output atom beam of isotopic ratio of 1:60 \( ^{13} \text{C} : ^{12} \text{C} \) atoms[21].
The observation that the adatom sits preferentially on defective regions still applies [22]. We note that similar mechanisms with vacant sites, rather than adatoms, can apply, but vacancies are unlikely to migrate as easily.

Addressing the generalisation to other carbon structures, we considered the annihilation of incipient glide dipole loops in graphite and the motion of prismatic dislocations. In the polycyclic aromatic hydrocarbon \( C_{62}H_{20} \) we converted four hexagons into two pentagon/heptagon pairs (a glide dislocation dipole, see Fig 2b). The dislocations are characterised by line directions \( \pm \langle 0001 \rangle \) and Burgers vector \( \langle 2\bar{1}10 \rangle \). The SW barrier to annihilation was found to be 5.6 eV and 0.7 eV, respectively for the uncatalysed and adatom catalysed reactions (see Fig 3). The incipient dipole loop had formation energies of 3.4 eV and 1.6 eV respectively. What is striking is that the adatom catalysed barrier to remove the defective region is very low and that there is a pronounced pull on the adatom to this region.

Experience with the original autocatalysis suggests that the activation barriers broadly scale with local curvature [22] and thus these transformations within the shells of carbon onions (and nanotubes) are expected to lie in the range of barriers calculated for BF and graphite. Thus, since carbon onions are produced under irradiation conditions, the mechanism explains the facility with which spherical shape can be assumed, through changes in ring statistics [23].

Interestingly, dimer addition to a nanotube followed by high uniaxial tension has been proposed theoretically[24] as a means of facilitating dislocation glide. In the region through which glide has occurred, the bonding topology, and hence semiconducting properties, of the nanotube are altered giving rise to metal:semiconductor junctions (and hence the possibility of a single nanotube device). Our mechanism lends credence to this possibility - although we note that these authors did not find the reaction path we propose here.

Edge dislocations with \( l = \langle 0001 \rangle \) and \( b = \langle 2\bar{1}10 \rangle \) have glide planes defined by \( b \times l \) which may lie between atoms closely spaced in this direction or between atoms separated by a full bond length. These two parallel planes we label the 'glide' and 'shuffle' planes, respectively, because of their broad similarity with these planes in the diamond structure in \( \langle 110 \rangle \) projection[25].

In the case of a graphene sheet, creation of a glide dislocation may be accompanied by complete reconstruction of its core (Fig 2a), (yielding a pentagon/heptagon pair) and the shuffle dislocation has an extra atom inserted between this pair (Fig 2b). This atom is bound by 2.29 eV to the core and is not differentiable from our adatom models. Moving the glide dislocation is extremely difficult due to its strong reconstruction (barrier 7.64 eV, applying a small correction for edge effects). However the shuffle dislocation
Fig. 1. Reaction pathway for Stone-Wales transformation (a) uncatalyed and (b) adatom catalysed. Pentagons are marked with dotted lines.

(glide+adatom) moves by the 'new' mechanism and has a much lower barrier of 2.22 eV. Interestingly, this migration barrier is comparable with that in a covalent semiconductor such as silicon, which is ductile above approximately 700°C: the temperature at which carbon onions achieve near spherical shape under irradiation [7].

In conclusion, we have demonstrated a general mechanism by which carbon structures evolve at moderate homologous temperatures in the presence of a flux of adatoms. The new reaction pathway presented here gives activation barriers within the range 0.7 to 2.3 eV. This is around a factor of four smaller than equivalent uncatalysed barriers and leads to qualitatively different behaviour. In the case of dislocations this may be lowered further by applied stress.

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Fig. 2. Basal plane dislocations in graphite, (a) glide and (b) shuffle dislocation, equivalent to the glide with an adatom bound at the core. A,B,C show atoms involved in motion as in Figure 1.

Fig. 3. Activation barrier (eV) for forming a glide dislocation dipole in graphene, with and without adatom catalysis.

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