

Metal Atom Catalyzed Enlargement of Fullerenes

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A metal catalyzed enlargement of fullerenes has been demonstrated by *in situ* high-resolution transmission electron microscopy. It was found that carbon atoms and clusters can be continuously incorporated into a closed fullerene cage at a high temperature, leading to an increase in the diameter and consequently the formation of giant fullerene with the assist of adsorbed metal atoms. Density functional theoretical simulations indeed suggest that the activation energy for the carbon incorporation and the associated Stone-Wales transformation can be substantially reduced due to the presence of metal atoms, which should be of key importance for the fullerene growth.

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Fullerene molecules are generally produced from carbon-rich vapor without any catalyst. It is intrinsically difficult to synthesize solely one type of fullerene because a mixture of different kinds of stable fullerenes (C_{60} , C_{70} , ...) are always formed simultaneously, and a separation of the fullerenes with unique mass and specific isomers requires further physical and chemical treatments [1]. Therefore a way to modify the structures of as-formed fullerene molecules by adding or removing carbon atoms has long been anticipated for the controllable synthesis of fullerenes with the desired mass and isomer. Many efforts have been made along the “top-down” pathway, i.e., via the shrinkage of fullerene cages. By photoexcitation [2], energetic bombardment [3], or thermal evaporation [4], a higher fullerene cage was transformed into a lower one by losing carbon atoms or clusters. On the other hand, a few theoretical pathways have been proposed for growing a higher fullerene from a lower one via an insertion of carbon atoms into a closed fullerene cage in the absence of catalyst, and have been used to explain the formation mechanism of giant fullerenes [5–7], while no direct experimental evidence has been reported so far.

In the present Letter, we reconsider the fullerene growth in analogy to that for the synthesis of single-walled carbon nanotubes (SWNTs) [8], where metal catalysts were normally required. By means of *in situ* high-resolution transmission electron microscopy (HR-TEM), it was found that, with the assistance of adsorbed tungsten (W) metal, the as-formed closed fullerene cage can further grow into a larger one, leading to the formation of a giant fullerene at a high temperature. This experimental observation was also well supported by a density functional theoretical (DFT) calculation.

Experiments were carried out using a specimen holder (Nanofactory) inside a JEOL 2010F TEM (120 kV) which is equipped with a CEOS post-specimen aberration corrector. In order to fabricate a suitable environment for the

reactions, we chose to use individual multiwall carbon nanotube (MWNT) with a large inner diameter (around 3–4 nm), where the hollow core acts as a reaction cell for the fullerene growth. First, fullerene molecules were formed inside the MWNT through a thermally activated shrinkage of the inner shells [4]. Then metal catalysts (we used W in the present experiment) were introduced into the MWNTs via a vacuum arc induced sputtering process between two electrodes [9]. As schemed in Fig. 1(a), with the assistance of a piezo-stage, we were able to drive a sharp W tip (made by electrochemically etching) to move in 3-D with a precision better than 0.1 nm, and to manipulate the selected MWNT containing fullerenes and metal clusters under TEM observations. In the meanwhile, a voltage between the W tip and opposite metal electrode can be applied and monitored to induce a current through the MWNT. Therefore, thermal energy can be introduced via joule heating to elevate temperatures of the whole system [10]. Sequential HR-TEM images were recorded by a CCD camera (Gatan 894), and the exposure time was set as short as 0.5 s.

Figures 1(b)–1(d) show a sequence of HR-TEM images of a MWNT containing two small fullerene molecules. Two fullerenes have slightly different diameters: ~ 0.8 nm for the left one and ~ 0.9 nm for the right. Even though we were unable to precisely determine the atomic structures and uniquely assign the species of these two fullerenes here [11], we might roughly assign the smaller fullerene as $C_{80\pm 4}$ and the larger one as $C_{84\pm 4}$ according to their apparent shapes and sizes. Two fullerenes were separated with a distance of ~ 7.0 nm. This distance is much larger than that in the so-called peapod structure (~ 1.0 nm) [12]; therefore, the risk for the irradiation-initiated polymerization and coalescence of nearby fullerene molecules was effectively reduced. Besides this, a weak coupling between the fullerenes and the surrounding nanotube walls was expected due to a large

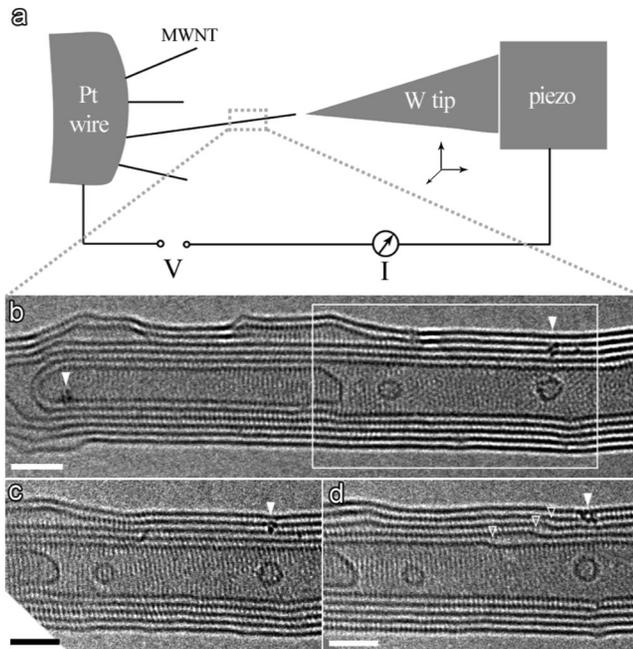


FIG. 1. (a) A schematic image for the experimental setup: a single MWNT was bridged between a W tip and a Pt wire. (b) A five-wall MWNT containing two fullerenes in the hollow core was chosen. A few W clusters were observed (indicated with white arrowheads) in the MWNT. The white rectangular marked the regions of interest for (c) and (d). (c) Under a small voltage (ca. 0.2 V and 4 μ A), no obvious structural change was found. (d) When the applied voltage reached 1.6 V (a current of ~ 45 μ A), a few kinks (indicated with unfilled white arrowheads) were found to form and migrate along the walls. Scale bar is 2 nm.

separation, and the fullerenes were found to frequently undergo an irregular self-rotation and translation inside the MWNT. The introduced W metal was found to preferably form clusters consisting of three or more atoms among the MWNT (see white arrowheads in Fig. 1).

After driving the W tip to make contact with the free end of this MWNT, we gradually increased the applied voltage. Under a small voltage [i.e., 0.2 V and 4.0 μ A in Fig. 1(c)], no obvious structural change was observed on the system. When the voltage was further increased to a higher value [1.6 V and 45 μ A in Fig. 1(d)], a few kinks formed and migrated along the walls of the MWNT, which were attributed to the formation of active topological defects and their subsequent migrations with the carbon evaporation process from the kinks at a high temperature [13,14].

When the voltage reached ~ 1.7 V (a current of ~ 50 μ A), a W cluster (indicated with a white arrowhead) suddenly jumped onto the larger fullerene after penetrating a few walls as shown in Fig. 2(a) (see also movie S1 [15]) [16]. Upon the adsorption of this W cluster, the fullerene immediately started to grow as shown in Figs. 2(b)–2(e). The W cluster was found to migrate continuously on the fullerene cage, and induced a local deformation on the cage around its adsorption site. Formation and annihilation of

sharp edges (which may correspond to pentagons or abutting pentagons) on the fullerene cage were also frequently observed during the growth. The whole fullerene cage developed asymmetrically: in particularly those regions close to the W cluster seemed to grow first, and a local protrusion was formed. After the W cluster moved to the next adsorption site on the same fullerene cage, further growth would be activated. During the whole process, the fullerene cage grew radially (with inflation in diameter), instead of being elongated, confirming that the fullerene energetically prefers to keep a round shape. Finally, as shown in Fig. 2(f), after the W cluster detached and moved back to the MWNT, the fullerene did not grow any more, even though the applied voltage was further increased. The ultimate diameter of the fullerene reached ~ 1.1 nm, which might be roughly assigned as $C_{136\pm 8}$, corresponding to an average growth speed of about 0.5 atom/s (The whole growth time is about 1.1×10^2 s).

The main carbon source for the fullerene growth should be the surrounding nanotube. As reported earlier [4,13,14], a high temperature (up to 2000 K or even higher) can be reached via joule heating on a similar system; therefore, carbon atoms and clusters (mainly in the form of C_2 [17]) are sublimated from the shells of the MWNT. The energetic electron irradiation [18] and electromigration [9] associated with a high current density here may have further facilitated the carbon evaporation. These radical and free carbon clusters migrated into the nanotube's hollow core, and then they were captured and incorporated into the fullerene cage, contributing to the growth.

Here the W metal should play a key role on the fullerene growth, evidenced by the following two important facts: (i) the nearby smaller fullerene molecule never grew, even though it stayed in the same or similar environment (temperature and carbon source) as its growing neighbor, (ii) for the larger fullerene, the growth started only after the adsorption of W metal and stopped just after its desorption.

In order to understand the growth mechanism, particularly the effect of W atoms, we performed DFT calcula-

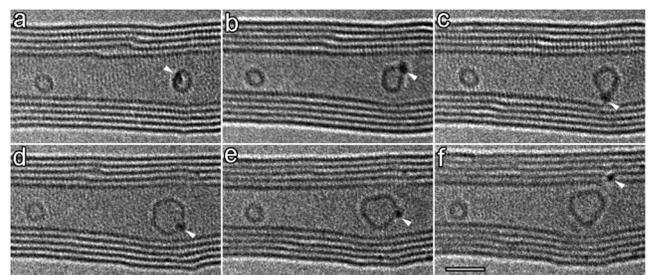


FIG. 2. Serial HR-TEM images showing the W metal assisted enlargement of fullerene: (a) The W cluster jumped onto larger fullerene's cage (white arrowheads). (b)–(e) The fullerene started to grow and obviously inflated. The W cluster was found to be highly mobile on the fullerene cage. (f) After the W cluster detached, the fullerene growth stopped. During the whole process, the applied voltage and current were kept unchanged as about 1.7 V & 50 μ A. Scale bar is 2 nm.

tions using the DMol³ program package. A C₈₄ fullerene with *D*₂ symmetry was chosen as the initial configuration, corresponding to the larger fullerene molecule in Fig. 2. To reduce computation time, we considered the simplest case where only 1 W atom was adsorbed onto the fullerene. The geometry was optimized without symmetry constraints imposed until the system energy converged to 10⁻⁵ Ha, and the maximum force on each atom was less than 0.001 Ha/Å. The nudged elastic band method [19] was employed to determine the minimum-energy pathway for the structure transformations.

We first calculated the binding energy of a W atom on different adsorption sites. The results showed that the W atom has the strongest binding energy of about -2.5 eV when it sits at the center of the hexagon (out-of-plane). This binding energy is about 0.7 eV higher than that of the bridge and pentagon sites [15]. The activation energy for the diffusion of W atom on the fullerene cage was also calculated. It has a small value of ~0.6 eV. On the other hand, the activation energy for the diffusion of carbon atom is much higher (~1.5 eV). As a result, W atoms are more mobile on the surface of the fullerene cage at high temperature than C atoms do on the same surface.

Next we examined the possible initial configurations whereby the W atom could effectively assist the incorporation of C₂ into the fullerene cage. Two possible pathways for the insertion of a C₂ into the carbon network without any catalyst were chosen as the starting configurations for our calculations [shown in Figs. 3(a) and 3(b)], which were previously proposed [5–7]. Energetically, the insertion of a C₂ unit into the C₈₄ fullerene is an exothermic process with an energy gain of ~7.8 eV. While in the absence of catalyst, the potential barrier for the C₂ incorporation is very high (about 4.3 and 5.1 eV for the cases shown in Figs. 3(a) and 3(b) on C₈₄ respectively). Then a W atom was introduced into each configuration. Two of the most stable configurations among the numerous possible situations were shown in Figs. 3(c) and 3(d), where the W atom binds with one end of C₂ to form a “handle” like structure. The energies of these structures are about 0.5–0.8 eV lower than any other examined configurations. The activation energy for C₂ incorporation is reduced by more than 2 eV and becomes about 2.1–2.3 eV, clearly indicating

that the adsorption of W metal can effectively assist the carbon incorporation. In a realistic situation, more than 1 W atom may be involved which may reduce further the activation energy.

After the incorporation of C₂, a few local topological defects were introduced onto the fullerene cage, where abutting pentagons and pentagon-heptagon pairs were formed, as shown in Fig. 3. In order to reduce the strain energy, these defects need to be annealed. A key factor for the reduction of the strain energy of the system should be the Stone-Wales (SW) transformation [20], which seems to be one of the lowest energy pathways for the structural transformation and growth of fullerenes [1,5–7]. As shown in Fig. 4, a typical SW defect has two pentagons and two heptagons coupled in a pair, which can be transformed into four hexagons by a 90° rotation of a C-C bond at its center. However this transformation has a high energy barrier of about 5–7 eV [21,22], fortunately, our calculations show that this energy barrier can be substantially reduced to about 3.15 eV, after the adsorption of a W atom close to the SW defect. This barrier might also be further reduced due to the so-called autocatalytic mechanism [21]. Therefore the adsorption of W metal is also very important for the defects healing and structure transformation of the fullerene, and the carbon incorporation as well.

Now we could make a rough estimation about the reaction kinetics following the method in Refs. [22,23]. The reaction rate is known to be determined by $(1/\nu) \times \exp(-\Delta E/k_B T)$, where ν is the attempt frequency, ΔE is the apparent reaction barrier, k_B is the Boltzmann constant, and the reaction temperature T is about 2000 K here. If the SW transformations (with a barrier of ~3.15 eV and an attempt frequency of 10¹³ Hz) dominates the overall reaction rate, the reaction should be completed in ~10⁻⁵ s, which is much shorter than the experimental value (~1.1 × 10² s); therefore, some other processes, e.g., the capture and incorporation of carbon should determine the reaction rate.

As well as W metal, other metals like Fe, Co, and Ni, well known as the catalyst for the growth of SWNTs, should have a similar effect, even though the number of W atoms for the most effective catalytic clusters cannot be known neither from our experiments nor simulations.

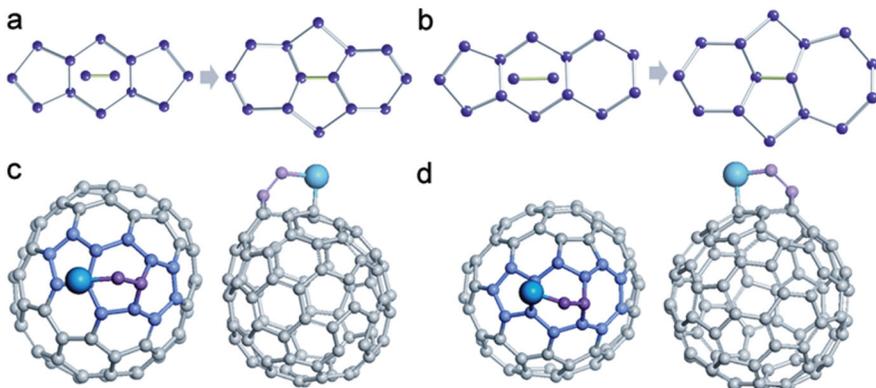


FIG. 3 (color). Schemes for two different pathways proposed for the incorporation of a C₂ into the carbon network (a) without and (b) with the anticipation of heptagon. (c),(d) Two initial configurations considered for the W atom to assist insertion of C₂ into the fullerene cage. The models (c) and (d) correspond to the pathways (a) and (b), respectively.

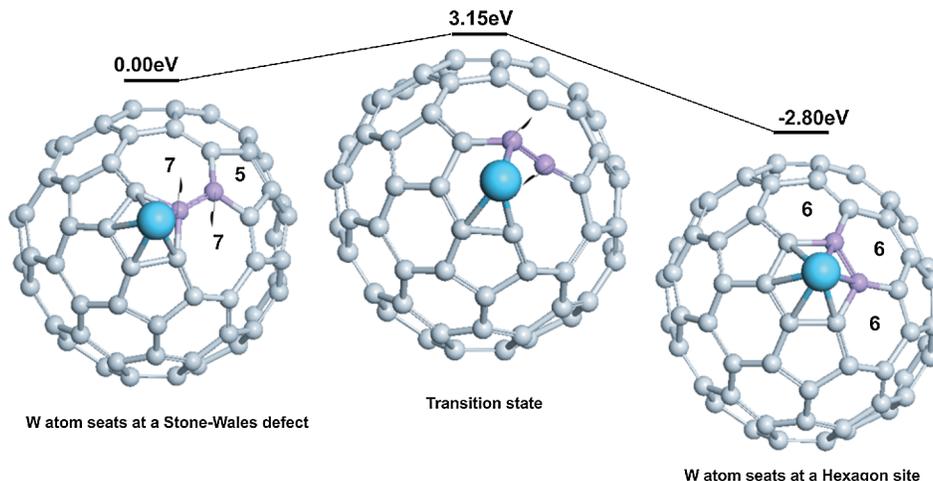


FIG. 4 (color). Transition energy barrier for a SW defect into four hexagons by a simple 90° rotation of a C-C dimer (in purple) with the adsorption of a W atom (in blue).

To conclude, the *in situ* HR-TEM experiments and the DFT calculations demonstrated the adsorbed W metal effectively catalyze the growth of as-formed fullerene molecules at high temperature. This behavior can be regarded as an alternative to achieve a desired fullerene with the tailored structure. Also this work gives a new insight into the understanding of the formation and growth mechanism of fullerenes including the giant fullerenes.

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