Controlled growth-reversal of catalytic carbon nanotubes under electron beam irradiation.

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ABSTRACT

The growth of carbon nanotubes from Ni catalysts is reversed and observed in *real-time* in a transmission electron microscope, at room temperature. The Ni catalyst is found to be Ni₃C and remains attached to the nanotube throughout the irradiation sequence, indicating that C diffuses most likely on the surface of the catalyst to form nanotubes. We calculate that the energy barrier for saturating the Ni₃C (2-13) surface with C is 0.14eV, thus providing a low energy surface for the formation of graphene planes.

KEYWORDS reverse growth, carbon nanotube, surface growth model.

The catalytic growth of carbon nanotubes is currently the method of choice for growing vertically-aligned patterned arrays for a wide range of electronic, gas sensing and biological applications¹⁻³. Significant advances in the understanding of the growth processes have generally been linked to their *in-situ* observation⁴⁻⁸, usually in specially-modified electron microscopes. The successful incorporation of carbon nanotubes into electronic devices, by exploiting their high-aspect ratios, their electronic structure and their conduction properties, requires control over the growth process and the resulting diameter, length and chirality of the nanotubes. The diameter can be controlled through the initial size of the catalyst^{2,9} and the current extent of the control over the growth is to deposit regular arrays of vertically-aligned carbon nanotubes^{2, 9-11}, through the patterning of the catalyst and the use of chemical vapour deposition, thus producing excellent candidates for electron field-emission applications.

The growth models for obtaining carbon nanostructures from catalysts such as Ni, Co and Fe can be largely categorised into two general groups: bulk diffusion and surface diffusion of carbon through the catalyst. The bulk diffusion model was proposed by Baker⁴, and explains the growth of the nanostructures as being driven by temperature and carbon solute concentration gradients within the catalyst. More importantly, the observations of Baker are based on direct observation of the growth process in a Controlled-Atmosphere Electron Microscope (CAEM)^{4,5}, a transmission electron microscope (TEM) where the growth reaction can be observed in real time⁶⁻⁸. At the core of this model is the observation that the activation energies, derived from the measured growth rates, relate directly to the bulk diffusion of carbon into the respective catalyst (Ni, Co, Fe). However, this also implies that the catalyst is at the eutectic temperature, which is unlikely when the growth results from an endothermic reaction¹², and is also unlikely in recently observed growth at temperatures from room to 300°C¹³⁻¹⁴. The group of surface diffusion models is based on the higher mobility of carbon atoms on the catalyst's surface, leading to carbon nanostructure growth. However, some bulk diffusion will occur, as the catalytic behavior of Ni, for example, depends on the crystalline orientation of the particular surface studied¹², with some surfaces allowing bulk diffusion of carbon easily and others saturating with a layer

of carbon. Again, crucial evidence has been provided recently^{6,7} as a result of the direct observation of the growth process, with significantly higher spatial resolution. These showed a significant reorganization of the catalyst's surface at the initial stages of growth and the fact that the catalyst remained crystalline throughout the growth process⁶. The improvement of the existing models is complicated by a number of factors, amongst which most important are the two modes of catalytic growth (tip-based, where the catalyst is transported away from the substrate, and base-growth, where the catalyst remains firmly attached to the substrate) and the conflicting reports, about the chemical state of the catalyst (i.e. whether it is a carbide or not)^{13,15}. There are a number of direct and indirect reported observations of the catalyst being a pure metal, a carbide, a pure metal with a carbide-organized surface layer or even a carbide/metal/metal oxide polycrystal^{12, 15, 16}. At least in some of the cases, only the (111) lattice fringes of Ni have been presented as evidence of pure catalyst, separated by 2.02Å. However, this reflection is present in Ni₃C(101) and Ni₂O₃(200) with maximum intensity, and in NiO((012)-2.09Å) and graphite((101)-2.02Å) with a quarter of the strongest reflected intensity. Hence, in the particular study of Helveg et al.⁶, further high resolution analysis is needed to definitely conclude that the catalyst remains as pure Ni during and after the growth process.

It is clear though that significant understanding of the growth process has resulted following *in-situ* observation of the growth process. The growth process itself has been proven and observed in the CAEM to be reversible⁵, using a hydrogen etching plasma, at the same temperature used during the growth. Furthermore, carbon nanotubes have been shown to be controllably thinned, cut and closed by electrons accelerated above ~140keV¹⁷⁻¹⁹, a process driven by the knock-on sputtering of the carbon atoms by the fast electrons.

Experiments were carried out on a Philips CM200 TEM (200kV accelerating voltage, LaB₆ source) fitted with a Gatan Imaging Filter (GIF2000). The current density, as recorded at the GIF, was ~75A/cm² (2.3pA in a 2nm diameter probe). The microscope was spatially calibrated immediately prior to the irradiation experiment. Changes in the microscope lenses were kept to a minimum when

switching to the nanotubes and it was re-checked against the graphite 002, resulting in a measurement error of $\pm 0.05 \text{ \AA}$. Images were acquired every 5s, with 0.5s exposures.

Carbon nanotubes were grown using thermal chemical vapor deposition, with polycrystalline Ni wires used as the catalyst. The growth was carried out at 650°C using acetylene and hydrogen as the reactant and carrier gas for 20mins at 10 torr. The nanotube powder is ultrasonicated in methanol and filtered through TEM holey carbon grids.

The DFT calculations were carried out using the CASTEP Code. The energy barrier associated with the insertion of a carbon atom in Ni_3C was estimated using the LST/QST scheme (linear synchronous transit refined by a quadratic synchronous transit²⁰). Exchange and correlation effects were taken into account through the functional developed by Perdew, Burke and Ernzerhof within the generalized-gradient approximation (GGA-PBE)²¹, ultrasoft pseudopotentials with a cut-off energy of 300eV were used to describe the electronic states. A sampling of 15 k-points in the irreducible Brillouin zone was used. The calculation had converged once the total energies of two consecutive iterations are different by less than 10^{-6} eV .

In figure 1, we show that the irradiation process can be controlled so that the growth of carbon nanotubes can be reversed and observed at high resolution by irradiating the catalyst with an intense electron beam. The process observed here is the reverse of the constant-rate part of nanotube growth, after the initial activation stage of the catalyst, when carbon arrives on the surface of the catalyst and diffuses to the rapidly forming layers of the nanotube. The entire set of stills taken through the irradiation process is presented in movie format as Supplementary Information. Figure 1a shows an image of a Ni catalyst at the tip of a carbon nanotube prior to irradiation, whilst Figure 1b shows the same catalyst at the end of the irradiation sequence, with Figure 2 showing some of the stills taken during the irradiation sequence (see Supplementary Movie). The insets in Figure 2 describe schematically the movement of crystal particle throughout the irradiation process. Using Fourier analysis (inset of Figures 1a, b) and spatial filtering we analyse lattice fringes associated solely with the catalyst

and we show that it is Ni_3C before and after irradiation, having rotated from a viewing direction normal to (100) to one normal to (002). This rotation is sudden and occurs ~170s into the growth reversal process (~20nm into the tube), which coincides with the kink in the nanotube indicated in Fig.1a, suggesting that there is a strong link between this rotation and the crystallinity. The rotation of the catalyst particle during the growth reversal is possibly driven by the different activities of the catalyst's surfaces. This indicates that the control of the catalyst's faceting may be linked to the chirality of single-walled nanotubes and consequently to their dielectric nature (metallic or semi-conducting).

The particles attached to the catalyst (indicated by arrows in Fig 2) are a product of the growth process, and appear to remain almost unchanged and attached throughout the irradiation sequence. Firstly, this demonstrates that the 'consumed' carbon from nanotube is sputtered away by the energetic electrons and does not re-deposit or reform as more graphite particles. Secondly, as no significant change in shape or volume occurs, it confirms that the loss of material from the nanotube is directly linked to phenomena at the catalyst/nanotube interface and not to the direct removal of material from the nanotube by the beam.

The catalyst remains attached to the tube throughout, with the only possible reason being that the carbon is sputtered away at the catalyst-nanotube interface, followed by a rapid re-arrangement of carbon atoms from the nanotube at the interface with the catalyst; otherwise, the catalyst would have dropped off. If the irradiation process is not controlled, it can lead to the nanotube disintegrating and the catalyst particle dropping off, or it could lead to the 'poisoning' of the catalyst through encapsulation with concentric graphene shells. This shows that both carbon diffusion through the bulk (i.e. the formation of nickel carbide) and on the surface of the catalyst are possible, but that, at least once a carbide is formed, the surface diffusion of carbon is the likely driving mechanism for carbon nanotube growth. More importantly, it shows that the surface diffusion model for the growth of nanotubes is valid even when carbon diffuses into the catalyst.

Returning to the issue of beam interaction with the sample, the other damage mechanism possible is through heating induced by the beam of electrons. In the case of 200kV-accelerated electrons, for a beam intensity of $500\text{A}/\text{cm}^2$ (here we used $75\text{ A}/\text{cm}^2$), this can account for a $1\text{-}2^\circ\text{C}$ increase in the temperature of an amorphous carbon film, considering radial heat diffusion¹⁹. In the case of a nanotube, the heating due to the energy lost by the beam to the sample would be higher, due to the low-dimensionality of the structure, but still well below the temperatures at which growth has been observed. This is also confirmed indirectly by comparing the overall growth-reversal rate with the reversal rate towards the end of the irradiation series; they are both equal to $7.2\text{nm}/\text{min}$, within experimental errors, so we believe that sputtering, and not induced heating, is the main driving mechanism.

The growth reversal of carbon nanotubes under electron irradiation shows directly that the growth is a surface-diffusion-driven phenomenon. Bulk diffusion of carbon through the catalyst and the formation of metal-carbides are not excluded, particularly as some of the catalyst's surfaces diffuse carbon differently, depending on the particular gases used in the growth process. The transformation of a metal catalyst into carbide, or the establishment of a carbide surface layer may actually enhance the surface diffusion by blocking further diffusion of carbon into the catalyst. Using the growth-reversal rate and the current density, we can calculate an approximate isotropic sputtering energy of 0.04eV ¹⁹. This is likely to be more representative of the order of magnitude of the energy, as it does not account for the anisotropy of graphene or channelling of the electron beam by the crystal. However, it shows that carbon on the catalyst surface is highly mobile. To explore this possibility, we have used Density Functional Theory (CASTEP)²² to calculate that energy barrier corresponding to the super-saturation with carbon of the (2-13) surface in Ni_3C is 0.14eV (Figure 3). This surface is equivalent¹⁵ to the (111) Ni surface of carbon, whose role in the growth of carbon nanotubes has been emphasized by Helveg et al⁶. The carbon-terminated super-saturated carbide surface now offers a pathway on which carbon can attach to graphene structures almost instantaneously, due to the energy gain per carbon atom incorporation^{6,13} (inset Figure 3).

Bulk diffusion is not the main driving mechanism for the growth, at least to a first order of magnitude. It remains to be seen though if, when increasing the current density of the electron beam by a factor of 10, we can also start to observe phenomena that are attributable to a volume diffusion of carbon through the catalyst.

The growth reversal of catalytically-grown carbon nanotubes is a first step towards the reverse-engineering of carbon nanotubes, as it can show the processes and energetics involved in the steady-state part of the growth process (but not the initial stages of catalyst activation and the onset of the carbon nanotube). This offers a unique insight into the growth process, allowing for the high spatial resolution study of the nature and geometry of the catalyst and its relationship with the resulting nanotube. It has revealed that the growth process is driven by surface diffusion, and that changes in the orientation of the catalyst during growth are related to changes in the direction of the nanotube's symmetry axis. As different catalyst facets have different carbon activities, this could open the way to a systematic investigation of the link between the nanotube's crystalline structure and the orientation of the catalyst, as well as its movement during growth .

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SUPPORTING INFORMATION PARAGRAPH The whole sequence of stills taken through the irradiation series are compiled into the movie: "reverse engineering CNT growth.wmv". The images were taken at 980,000x magnification; as a result of the high magnification, the shrinkage of the nanotube becomes evident towards the end of the movie, where the holey-carbon support can be used as a spatial reference.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE CAPTIONS

FIGURE 1 **a)** Bright field image of the carbon nanotube and the catalyst particle before irradiation. The drawn line on the nanotube indicates the place where catalyst rotates. **b)** Diffractogram is taken from the high-resolution image shown in Fig.2 at 0s, which reveals the catalyst to be Ni_3C . The arrows point to the 101 and 002 reflections of Ni_3C , which also correspond to the two outermost drawn circles respectively. The third smallest circle represents the 100 reflection of Ni_3C (absent) and the smallest circle represents the 002 graphite reflection. **c)** Diffractogram (taken from the corresponding high-resolution image in Fig.2 at 463s) showing the catalyst to have rotated, with the drawn circles representing the same reflections as at Fig. 1b. **d)** The bright field image of the catalyst and nanotube after electron irradiation. Taking the catalyst as an ellipsoid, its volume is $\sim 440\text{nm}^3$ and surface area $\sim 290\text{nm}^2$, whilst the volume of consumed carbon is estimated at $\sim 2430\text{nm}^3$.

FIGURE 2 A selection of high-resolution stills taken at the indicated times throughout the irradiation series. The catalyst does not change shape and remains attached to the nanotube throughout the irradiation. Insets show the relative positions of the catalyst in the tube shown in Figure 1, as a function of time. At around 170s into the irradiation sequence, corresponding to the kink in the nanotube, the catalyst suffers a sudden rotation, possibly as a result of the different catalytic activities of the Ni particle's surfaces. The arrows point to a particle that remains attached to the catalyst throughout the irradiation sequence.

FIGURE 3. The (2-13) surface of nickel carbide was modelled by a slab containing three layers of nickel atoms (18 atoms) (light-yellow spheres) with six carbon atoms (dark-black spheres). Two consecutive slabs are separated by $\sim 10\text{\AA}$ of vacuum. The "super-saturation" is accounted by an extra carbon atom located at sites indicated by arrows. We calculated that the energy barrier corresponding to the insertion of a carbon atom initially located in site 2 (at $\sim 6\text{\AA}$ from the surface) into site 1 is 0.14 eV. Inset: A schematic of the proposed carbon nanotube growth model, showing a super-saturated carbide surface and some carbon diffusion into the bulk, with the catalyst core being either carbide or pure metal (yellow-Ni, black-C, grey- Ni_3C). The carbon terminated surface provides a very low-energy pathway for further carbon to migrate and form carbon nanotubes.

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