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On the low-temperature growth mechanism of single walled carbon nanotubes in plasma enhanced chemical vapor deposition

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ABSTRACT

Despite significant progress in single walled carbon nanotube (SWCNT) production by plasma enhanced chemical vapor deposition (PECVD), the growth mechanism in this method is not clearly understood. We employ reactive molecular dynamics simulations to investigate how plasma-based deposition allows growth at low temperature. We first investigate the SWCNT growth mechanism at low and high temperatures under conditions similar to thermal CVD and PECVD. We then show how ion bombardment during the nucleation stage increases the carbon solubility in the catalyst at low temperature. Finally, we demonstrate how moderate energy ions sputter amorphous carbon allowing for SWCNT growth at 500 K.

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1. Introduction

Growth of single walled carbon nanotubes (SWCNTs) continues to attract widespread attention thanks to their specific electrical, mechanical and chemical properties and their envisaged applications in diverse areas, including electronics, energy storage, composite materials and medical industry [1–4]. Since all of these applications depend on the carbon nanotube (CNT) properties (to a varying degree), controlling their size, density, chirality and quality during the growth process is extremely important [5,6]. Moreover, fabrication of the nanotubes with a given set of desired properties under different processing conditions such as different temperatures is highly desirable as well. Indeed, various applications impose boundary conditions precluding certain growth conditions. For instance, CNTs grown on temperature sensitive substrates such as polymers require low temperature conditions.

Various growth systems have been developed, including arc discharge [7], laser vaporization [8] and thermal chemical vapor deposition (CVD) [9,10]. Similarly, various growth mechanisms such as vapor–liquid–solid (VLS) [11,12], scooter [8,13], root-growth [14,15] and vapor–solid–solid (VSS) [16] mechanisms have been proposed to describe the CNT formation mechanism. One of the most well-known mechanisms is the VLS-mechanism which was adopted by Baker et al. [17] to describe the catalytic growth of CNTs and carbon nanofibers (CNFs) at elevated temperatures. In this mechanism, a gas phase carbon precursor adsorbs on the surface of the catalyst, after which it dissociates resulting in carbon

atoms dissolving in the liquid nanoparticle. After saturation of carbon atoms in the catalyst, the carbon atoms segregate and a solid CNTs is produced. This mechanism is typical for thermal CVD growth.

An attractive alternative for thermal CVD is plasma enhanced chemical vapor deposition (PECVD) [18–20]. Important advantages include the growth of freestanding vertically aligned SWCNTs [21,22] and the ability to produce both multiwalled carbon nanotubes (MWCNTs) and SWNTs at reduced temperatures [23,24]. A more detailed account of the various effects and advantages of PECVD can be found in recent reviews [25–27].

A plasma consists of ions, electrons, radicals, molecules and atoms, in addition to metastable (exited) species, photons and electromagnetic fields, and as a result, the occurring physical and chemical processes in the plasma are highly complex. Moreover, all of these factors contribute to the CNT growth mechanism, and thus the growth mechanism in a plasma is typically different from thermal CVD and is not yet known completely. For instance, the plasma ions can cause local heating of the catalyst surface which leads to an enhanced absorption and diffusion of carbon atoms on and in the catalyst [28].

Due to the fact that the catalyst at low temperature is in the solid or quasi solid phase, temperature is one of the key factors affecting the growth mechanism. Hofmann et al. achieved the production of CNFs at low temperatures. They found that at low temperature, the transport of carbon atoms occurs by surface diffusion on the solid surface of the nanoparticles (rather than by bulk diffusion) [24,29].

Computer simulations allow to study the microscopic processes underlying the growth process, and consequently both classical

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MD and MD/MC simulations [30–36] as well as ab initio and semi ab initio modeling [37–43] have been widely used to investigate the growth mechanisms at the atomic scale. It should be noted that the most of these simulations, however, investigate the CVD method. Only a few studies up to now consider the growth mechanism in PECVD [44–46].

In view of the multitude of process parameters in PECVD-based SWCNT growth, it is very difficult to combine all these parameters in a single growth simulation. Therefore, the effects of the various parameters are separately investigated in PECVD. Neyts et al. recently studied the electric field and argon ion bombardment effects on SWCNT growth in plasma [44,45]. The effects of ion bombardment are determined by the ion type, energy, flux and angle of impact, as well as the surface material and temperature [27]. It was shown that Ar ion bombardment in an energy window of 10–25 eV leads to better nucleation and defect healing of the SWCNT cap [44]. Recently, we succeeded in simulating SWCNT growth from both C-ions and thermal C-atoms for the first time at low temperature, resembling a plasma environment [46]. We found that ion bombardment, leading to sputtering of amorphous carbon that covers the catalyst surface, facilitates the growth of SWCNTs [46].

In this Letter, the effect of ions on the carbon solubility in the catalyst at low temperature is studied, demonstrating that the diffusion of carbon atoms in the catalyst increase with increasing ion energy. Also the effect of this solubility on the growth mechanism of CNTs by plasma-deposition is investigated. Finally, the growth mechanisms under CVD and PECVD conditions are compared.

2. Methodology

We use reactive molecular dynamics simulations to simulate the growth of SWCNTs under CVD and PECVD conditions. The interatomic potential that we use is identical to the potential used in our previous study [46]. In our simulations, the catalytic particle is a Fe-cluster containing 48 atoms. In the CVD simulations, the temperature was set to 1100 K employing the Berendsen thermostat with a relaxation time of 0.01 ps. Thermal carbon atoms are allowed to impinge on the cluster every 30 ps. The trajectories were integrated by the Verlet Velocity algorithm using a time step of 0.5 fs.

In the PECVD simulations, both thermal carbon atoms as well as energetic carbon ions are considered as growth species. The ions are assumed to be neutralized by Auger emission before their actual impact with the surface and thus carry no charge. These 'ions' are given a higher velocity as if they were accelerated by an electric field in the plasma sheath. Carbon atoms that are added to the cluster with thermal velocity correspond to carbon atoms originating from surface-decomposition of the hydrocarbon gas.

It is also assumed that the flux of thermal carbon atoms to the catalyst surface is four times higher than that of the carbon ions. Thus, each fifth carbon species added to the cluster is a carbon ion, while the other four are thermal carbon atoms. The impingement rate is set identical to the CVD case, i.e., $1/30$ ps^{-1}. The simulated PECVD growth is carried out at low temperature (500 K), again controlled by the Berendsen thermostat using a relaxation time of $\tau = 0.01$ ps. As the goal of the present simulations is to investigate low-temperature growth, we have chosen this small τ-value to impose a strong heat dissipation. Indeed, this ensures that in the simulation, the growth process is not facilitated or enhanced by the catalyst heating due to the ion bombardment. The time step for the initial stages of the impact is 0.05 fs, increasing up to 0.5 fs with decreasing maximum ion velocity.

In our simulations, the number of metallic nearest neighbors (MNN) of the carbon atoms added to the cluster is calculated every time step. A metal atom is counted as a metallic nearest neighbor

of a carbon atom if the distance between the Fe-atom and the C-atom is smaller than 2.3 A. Therefore, two types of carbon atoms can be discerned in the graphitic structure (graphitic encapsulation or nanotube): (1) 'bulk diffusion' carbon atoms that were previously dissolved in the metal cluster (MNN $\geqslant$ 5) and resided in the cluster for at least 20 ps; and (2) 'surface diffusion' carbon atoms that were not previously dissolved in the metal cluster (MNN < 5). This definition corresponds to the definition used by Gomez-Gualdron et al. [47,48] for surface and bulk diffusion atoms. Finally, we also compute the maximum number of metallic nearest neighbors (MMNN) for every carbon atom in the SWCNT.

3. Results and discussion

3.1. The growth mechanisms of SWCNTs by CVD and PECVD

The distribution of the percentage of carbon atoms forming the SWCNTs, versus the maximum metallic nearest neighbors (MMNN) of carbon atoms is shown in Figure 1a. It is clear from the figure that in a low temperature (500 K) CVD process, the carbon solubility in metal cluster is low. Indeed, under this condition, the distribution peaks at MMNN = 4. As the melting point of the catalyst is about 800 K [49], the catalyst is in the solid or quasi solid state in this condition and as a result the added atoms mostly remain on the surface rather than dissolving in the bulk. However, at higher temperature (1100 K), the catalyst is in the liquid state which facilitates the dissolution of the carbon atoms in the nanoparticle.

Figure 1b shows that in the CVD environment in which the gas phase carbon atoms dissolve in the liquid catalyst followed by their segregation on the catalyst surface to contribute to the nanotube's structure or cap (Figure 1e). At low temperature, the atoms do not dissolve in the solid catalyst easily but rather diffuse over the surface. This leads to encapsulation of the nanoparticle (Figure 1d), in agreement with previous findings [31].

Under low-temperature PECVD conditions, the catalyst is in the solid phase and as a result, the solubility of the carbon atoms is low. Nevertheless, a significant number of carbon atoms contributing to the structure were dissolved in the catalyst (Figure 1a, b). This can be attributed to the fact that such small metal nanoclusters becomes more liquid-like with increasing C-concentration [50]. In this condition both bulk diffusion as well as surface diffusion of carbon atoms plays a significant role in the SWCNT growth process (Figure 1c). It should also be noted that the surface diffusion of carbon atoms in the SWCNT formation process in PECVD is more important in comparison with high-temperature CVD (Figure 1b).

3.2. The effects of ion energy on CNT growth

Figure 2 compares SWNT growth at low temperature (500 K) with low (10 eV), moderate (60 eV) and high ion energies (100 eV). The carbon atom percentage with MMNN in the nanotube structure is seen to increase with ion energy (Figure 2a).

When the ion energy is low, the ions hardly affect the growth mechanism and as a result, the growth process is similar to the growth in low-temperature CVD. This implies that the carbon atoms form a graphitic layer on the catalyst surface and tend to encapsulate the nanoparticle (Figure 2c).

In the moderate ion energy regime, the ions increase the solubility of the carbon atoms in the catalyst in spite of the solid phase of the catalyst (Figure 2b). In this energy range, a large number of carbon atoms that finally contribute to the structure of the nanotube are dissolved in the catalyst (their MMNN is more than 5). Therefore, it can be concluded that the ions increase the solubility
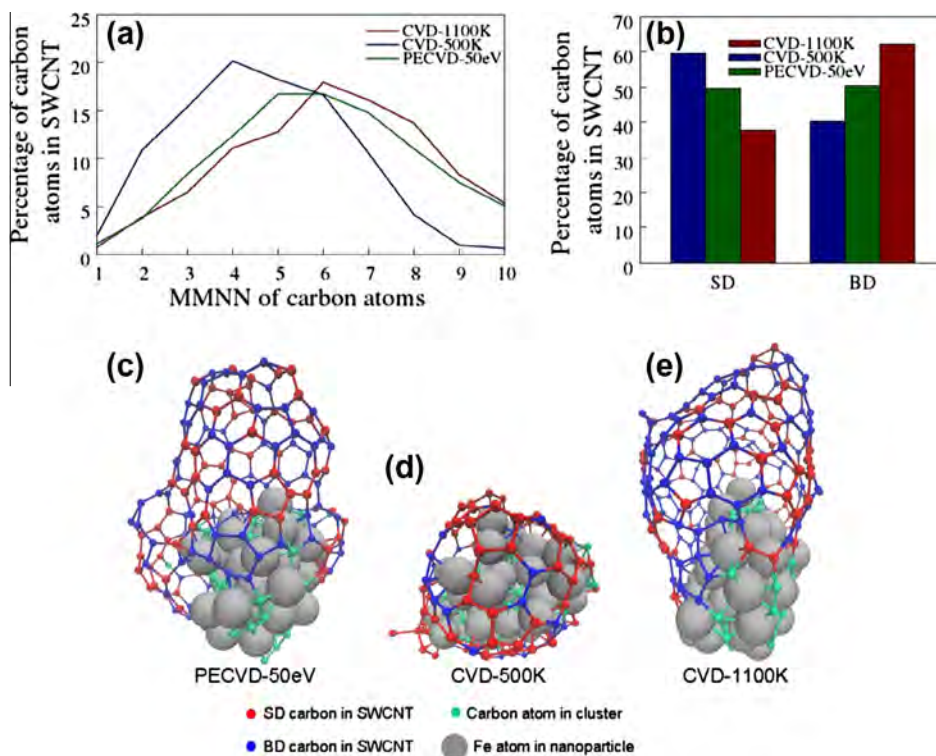
Figure 1. (a) The distribution of the percentage of the carbon atoms forming the carbon network, versus MMNN of carbon atoms. (b) Percentage of carbon atoms forming the carbon network undergoing either surface diffusion (SD) or bulk diffusion (BD). A snapshot of the simulated PECVD and CVD growth of SWCNTs for (c) PECVD conditions including 50 eV ions, (d) thermal growth at 500 K and (e) thermal growth at 1100 K.
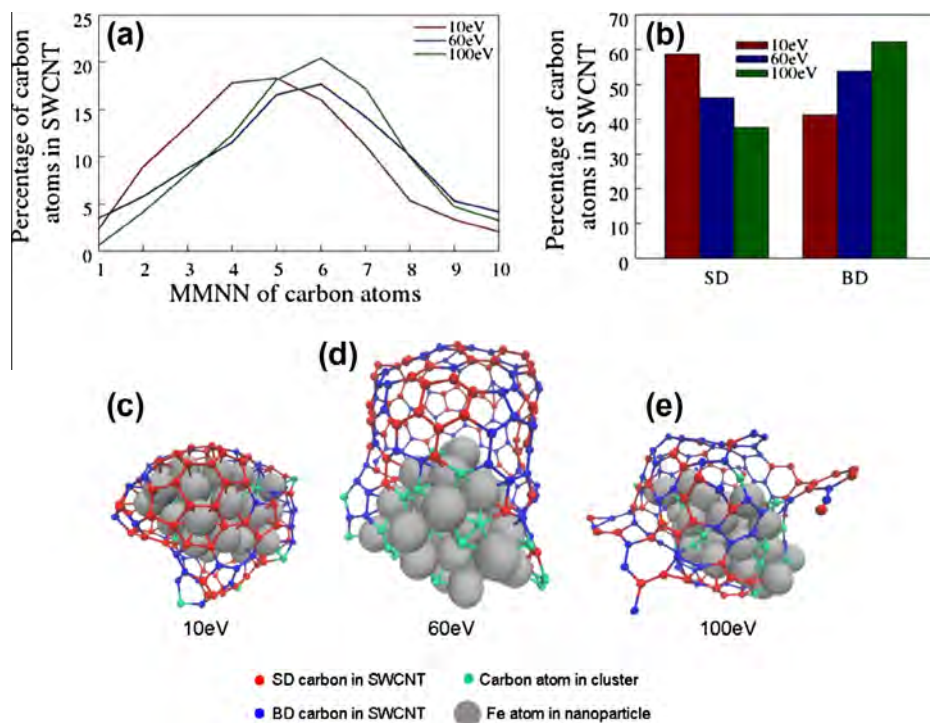

Figure 2. (a) The distribution of the percentage of carbon atoms forming the carbon network versus MMNN of carbon atoms. (b) Percentage of carbon atoms forming the carbon network undergoing either surface diffusion (SD) or bulk diffusion (BD). A snapshot of the simulated PECVD growth at 500 K of SWCNTs using ions having energies of (c) 10 eV, (d) 60 eV and (e) 100 eV.

of the carbon atoms in the catalyst and as a result stimulate the SWCNTs growth at low temperature (Figure 2d).

When the ion energy is high, the ions have enough energy to increase the solubility of the carbon atoms in the metal catalyst and

stimulate growth (Figure 2b). However, due to their high energy, the ions also induce damage to the formed carbon structure (Figure 2e), as well as sputtering of the catalyst itself. This regime is therefore not suitable for growing SWCNTs.
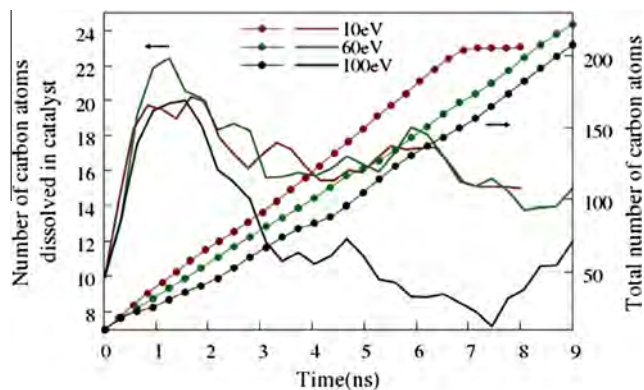
Figure 3. The number of dissolved carbon atoms and the total number of C atoms in the Fe/C cluster during the growth of the graphitic structure in plasma.
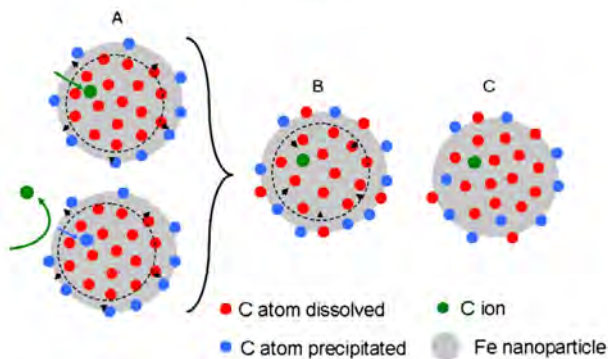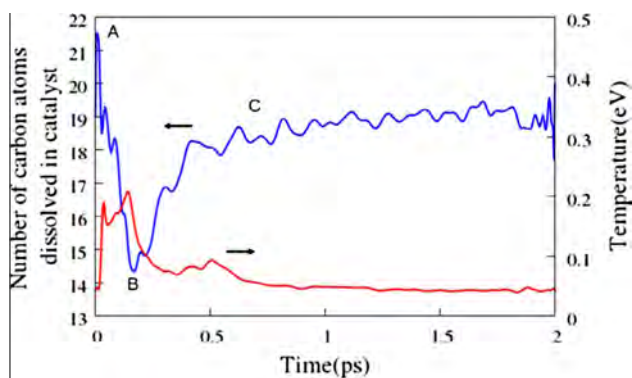

Figure 4. Representative trajectories of dissolved carbon atoms and temperature after the ion collision.

Figure 3 shows the temporal distribution of the number of dissolved carbon atoms as well as the total number of carbon atoms for three energy regimes investigated. In the low energy regime, the number of dissolved carbon atoms and the total number of carbon atoms behave as in the low-temperature CVD condition [46]. This implies that the total number of carbon atoms after formation of a graphitic layer on the nanoparticle surface remains constant which indicates that the growth is suppressed, as can be seen from the stagnation of the red curve at around 7 ns in the figure.

In the moderate energy regime, the number of dissolved carbon atoms after saturation is higher than that in the low energy regime. This implies that the solubility of the carbon atoms increases with ion energy. When the cap formation starts, the number of dissolved carbon atoms decreases followed by a steady state, as can be seen in Figure 3. After reaching steady state, the added carbon atoms allow the continued growth of an SWCNT. Recall that in
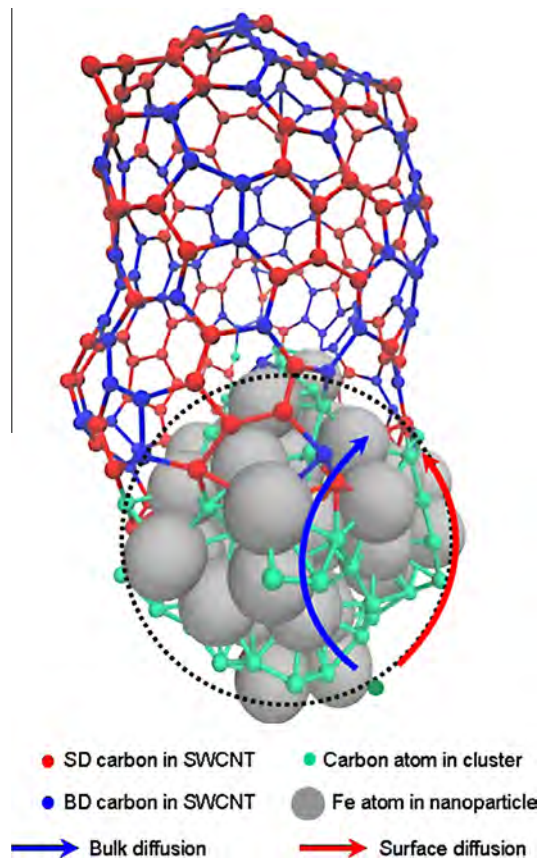

Figure 5. The growth mechanism of carbon nanotubes in the presence of ions as well as a final SWCNT as grown with 60 eV C-ions in addition to the thermal C-atoms.

all energy regimes, the impingment frequency (with a 1-to-4 ions-to-neutrals ratio) was set to $1/30 \, ps^{-1}$; due to the sputtering of the amorphous carbon by ions in the moderate and high ion energy regimes, however, the slope of the total number of carbon atoms in the high energy regime (100 eV) is less than the slope in the low energy regime (10 eV).

In the high energy regime, the Fe cluster is also sputtered which leads to a drastic decrease of the carbon solubility. The total number of carbon atoms due to the sputtering by ions therefore also shows the smallest slope. This implies that growth is not observed under these conditions (see Figure 3).

To further investigate the effect of ions on the nanotube growth, the collision of a C-ion with moderate energy (50 eV) with a $Fe_{48}C_{70}$ cluster is analyzed. Figure 4 shows the temperature of the metal cluster and the number of dissolved C-atoms in the catalyst as a function of time. It can be seen that the number of dissolved C-atoms in the catalyst initially decreases drastically (whereas the temperature initially increases after the ion collision) and subsequently increases again (while the temperature decreases again). However, the number of dissolved carbon atoms in the final state may be less than that in the initial state: The ion is directly or indirectly (by collision with surface carbon atoms) inserted to the catalyst, which locally increases the carbon atom density in the catalyst. As a result, the dissolved carbon atoms in that local volume are displaced towards the surface which is facilitated by the (temporary) increase in temperature. By displacing the carbon atoms to the surface, the carbon density in the bulk of the catalyst decreases again while the temperature of catalyst is still high. This process produces a driving force [47] which displaces the carbon atoms back from the surface to the bulk of the catalyst, as graphically represented in Figure 4.

Finally, Figure 5 shows the growth mechanism of carbon nanotubes in a PECVD environment in the presence of ions as well as a final SWCNT as grown with ions having moderate energy (60 eV) in addition to the thermal carbon atoms. In this mechanism, the bombarding carbon ions change the local density of carbon atoms in the cluster and cause carbon atoms to diffuse more easily in the bulk or on the surface of the catalyst at low temperature. The extent of the surface and bulk diffusion in the plasma environment depends on the flux of impinging ions, their energy and the catalyst temperature. In the high ion energy regime, the bulk diffusion of carbon atoms dominates the surface diffusion, similar to the effect of the elevated temperature in thermal CVD. Ions with such high energies in PECVD growth strongly modify the local density of the carbon atoms, but also severely damage the nucleating nanotube cap, and thus do not allow the CNT to grow. Moderate ion energies, however, establish an equilibrium between surface diffusion and bulk diffusion of carbon atoms to be incorporated in the growing SWCNT. By increasing the carbon solubility in the catalyst at low temperature, growth of the CNT is promoted. In agreement with experimental studies on PECVD growth [24,29], we also observe that surface diffusion of carbon atoms dominates bulk diffusion, at least in the modere ion energy regime.

Finally, note that a complete description of the PECVD growth process in principle requires considering all possible radicals, ions, electrons, neutral molecules and atoms as well as photons, in the presence of electromagnetic fields [25–27]. Taking all these factors into account is at present clearly not feasible, and we therefore only focus on the effect of the carbon ions and neutral carbon atoms in these simulations.

5. Conclusion

Employing reactive molecular dynamics simulations, we demonstrate that the growth mechanism in low-temperature PECVD is different from high-temperature CVD and strongly depends on the ion energy. If the ion energy is low ($\sim$10 eV), the mechanism is similar to low-temperature CVD in which the growth is suppressed by encapsulation of the catalyst. If the ion energy is moderate ($\sim$50 eV), the carbon solubility in the catalyst increases. This increase in solubility occurs as a result of the change in the carbon atom density in the catalyst induced by the ion collisions. At high ion energy ($\sim$100 eV) sputtering of the carbon network as well as the metal catalyst increases, leading to damage formation and destruction of the carbon nanotube.

Therefore, it can be concluded that the moderate energy ions have two major roles in nanotubes growth: (a) Sputtering of amorphous carbon which suppresses the encapsulation of the catalyst; and (b) Increasing the carbon solubility in the catalyst which stimulates growth.

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