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Key roles of carbon solubility in single-walled carbon nanotube nucleation and growth[†]

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Elucidating the roles played by carbon solubility in catalyst nanoparticles is required to better understand the growth mechanisms of single-walled carbon nanotubes (SWNTs). Here, we highlight that controlling the level of dissolved carbon is of key importance to enable nucleation and growth. We first performed tight binding based atomistic computer simulations to study carbon incorporation in metal nanoparticles with low solubilities. For such metals, carbon incorporation strongly depends on their structures (face centered cubic or icosahedral), leading to different amounts of carbon close to the nanoparticle surface. Following this idea, we then show experimentally that Au nanoparticles effectively catalyze SWNT growth when in a face centered cubic structure, and fail to do so when icosahedral. Both approaches emphasize that the presence of subsurface carbon in the nanoparticles is necessary to enable the cap lift-off, making the nucleation of SWNTs possible.

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Introduction

Single-walled carbon nanotubes (SWNTs) hold enormous potential applications¹ because of their superior electrical, optical and chemical properties. However, their applications, particularly in electronic devices are greatly impeded by the inability to control the tube's structure (diameter, chirality, defects and length) during the growth.² This lack of control at the synthesis stage largely stems from the insufficient knowledge of SWNT nucleation and growth mechanisms which remain ill-understood.

Due to its higher degree of control and scalability, the catalytic chemical vapor deposition (CVD) process is now the standard synthesis method of carbon nanotubes. In the CVD technique, the nanotube grows from a nanoparticle (NP) that is either supported by a substrate or floating in a gas phase reactor. The process is complex but it is basically accepted that the metal NP acts as a catalyst to favor the decomposition of the carbon-bearing precursor. According to Deck and Vecchio,³ efficient catalysts for CVD should have non-zero but limited (0.5–1.5 wt%) carbon solubility in the solid bulk

^aLaboratoire d'Étude des Microstructures, ONERA-CNRS, BP 72, 92322 Châtillon CEDEX, France. E-mail: hemaoshuai@gmail.com, annick.loiseau@onera.fr ^bDepartment of Applied Physics, Aalto University School of Science, P.O. Box 15100, FI-00076 Aalto, Finland limited to Fe group metals (Fe, Co, Ni) and their alloys.^{4–9} Over the past few years, SWNT growth was reported from metal carbides,¹⁰ noble metals¹¹⁻¹⁴ and even non-metallic NPs¹⁵ having extremely low carbon solubility. However, the key roles played by carbon solubility for catalyzing SWNT growth have never been clearly established. This is because the roles of carbon solubility are covered by the numerous factors involved in CVD synthesis (temperature, pressure, metal-support interactions, etc.) when applying different catalysts. From theoretical point of view, it has been discussed how carbon solubility, depending on temperature and size of the NPs, can affect the growth.16-18 Grand Canonical Monte Carlo (GCMC) simulations¹⁹ have shown that the wetting properties of Ni NPs, controlled by carbon solubility, are of fundamental importance to enable the nanotube growth. Nevertheless, how the incorporated carbon atoms distribute inside the NPs is still unknown. Moreover, experimental evidence on the relationship between carbon solubility and carbon nanotube nucleation remains a relatively uncharted territory.20 Using carbon fibers with a different graphitic character as the support, Rinaldi et al.20 revealed that Ni particles could exhibit different carbon solubilities, resulting in the growth of either carbon fibers or multiwalled carbon nanotubes. To date, the experimental support for the importance of carbon solubility in nucleating single-walled nanotubes remains lacking. Therefore, this creates a research challenge for a more precise understanding of how the carbon solubility in metal NPs affects the nucleation of SWNTs.

phase. For a long time, the catalyst composition has been

In this paper, the roles of carbon solubility are investigated using two complementary approaches. We start with GCMC



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calculations on metal NPs with different carbon solubilities, and study the carbon incorporation in NPs of icosahedral (Ih) and face centered cubic (FCC) structures. Then, we experimentally demonstrate that Au NPs, that usually display an Ih structure, can be transformed into FCC after proper heat treatment. Attempts to grow nanotubes from these two different allotropes lead to contrasting results: the former does not trigger nanotube growth, while the latter systematically enables the nucleation and growth of tubes. On the basis of our computer simulation results, we assign these differences to the lack of carbon solubility in Ih Au NPs that does not allow the lift-off of the tube nucleus. In FCC NPs on the contrary, the presence of subsurface carbon lowers the adhesion energy of the sp² C layer formed on the NP surface, thus enabling the SWNT nucleation. Consequently, several aspects of the key roles of carbon solubility in nucleating SWNTs will be clarified.

Materials and methods

Calculation methods

To simulate carbon dissolution in NPs, a tight binding (TB) model was implemented in a MC code using a grand canonical algorithm with a fixed volume, temperature, number of metal atoms and carbon chemical potential ($\mu_{\rm C}$). The carbon chemical potential is referred to a fictitious ideal monoatomic gas, to explain that it has values of a similar order to the cohesive energies of the various carbon phases (*e.g.*, -7.41 eV per atom for a graphene layer in the model). Applications of this model to the catalytic growth of carbon tubes on Ni have already been demonstrated.²¹

To model a metal with reduced carbon solubility, we therefore keep the relative values of the hopping integrals derived for NiC.²¹ The position of the atomic d level on the other hand obviously varies with the nature of the element considered. $\varepsilon_{\rm d}$ decreases when increasing the number of electrons along a transition series (about 1 eV per element); but since this level is an effective quantity, which is adjustable to some extent, it is useful to see how it is related to the carbon solubility for modeling the gold case. A quantity of great interest is the heat of solution ΔH_{sol} of a carbon interstitial atom in a crystalline transition metal (M) which is calculated according to the formula: $\Delta H_{sol} = E_{M+C} - E_M - E_C$, where E_{M+C} is the total energy of the interstitial M + C system, E_M is the energy of the M system without carbon, and $E_{\rm C}$ is the energy per carbon atom in graphene. To decrease the carbon solubility, the contribution of the pd hybridization has to be reduced. This can be done through a 1.50 eV shift of the p (C) and d (M) atomic levels, leading to a ΔH_{sol} around +0.93 eV. More details are presented in the ESI.†

Experimental methods

The Au NP colloids of 1.4 nm and 10 nm were purchased from Nanoprobes and Sigma-Aldrich, respectively. The Au NP colloid of 3.0 nm was prepared according to the method proposed by Zheng *et al.*²² The Au colloids were dispersed either on a SiO₂/Si ($t_{ox} = 800$ nm) substrate or on a Si₃N₄ TEM grid (DuraSiNTM mesh) for carbon nanotube growth. Pre-growth annealing of the supported Au NPs was performed in air at different temperatures (450 °C or 800 °C) for 2 h. After cooling down, the substrate-supported Au NPs were loaded into a horizontal reactor (inner tube diameter: 40 mm) for the CVD growth of carbon nanotubes. After being stabilized at the desired temperature in a helium gas sphere, CO (200 cm³ min⁻¹) was introduced to replace the helium and the carbon feeding lasted for 1 h. The system was finally cooled down to room temperature under helium.

To track the evolution of Au NPs upon annealing, the Au NPs were dispersed onto a Si_3N_4 grid for TEM (JEOL JEM-2200FS double Cs corrector) characterization with an accelerating voltage of either 80 kV or 200 kV. A number of individual Au NPs were carefully indexed for further observations after annealing in open air at 800 °C for 2 h. Scanning electron microscopy (JEOL JSM-7500FA) and atomic force microscopy (Veeco Dimension 5000) were applied to characterize the morphology of the carbon nanotubes grown on the SiO_2/Si substrate. The structures of the Au NPs and the SWNTs were analyzed by TEM.

Results and discussion

As a first step, we investigated the NP activation mechanisms using atomistic computer simulations based on a tightbinding model developed for the Ni-C system.²¹ Indeed, density functional theory calculations of the stability of carbon atoms or dimers located on the surface, in the subsurface or in the bulk interstitial sites indicate that for noble metals (Cu, Ag, Au), surface addimers are clearly favored on certain metal facets.16 For single carbon atoms, surface adatoms and subsurface sites are almost equivalent, with a positive adsorption energy of about 3 to 4 eV per atom. This is about four times the adsorption energy of the atomic carbon in the subsurface sites of Ni, indicating a stronger tendency for carbon segregation although the lattice parameter of noble metals, especially Au (4.08 Å) and Ag (4.09 Å), is significantly larger than that of Ni (3.52 Å) where the size of the interstitial sites hardly allows carbon incorporation. The segregation tendency of carbon towards the noble metal surface thus results from their electronic bonding scheme rather than from steric hindrance. Such an electronic structure based effect can be easily incorporated in a TB model. In our TB model, changing carbon solubility in a metal can be achieved by shifting the carbon p and metal d energy levels, keeping all other parameters constant. GCMC simulations based on this modified TB model were thus performed to calculate carbon incorporation in Ih and FCC NPs. In the calculations, the total number of metal atoms, carbon chemical potential, volume and temperature (T) were kept constant. Once equilibrium was reached, the numbers of carbon atoms adsorbed outside and possibly inside the cluster were recorded. By varying $\mu_{\rm C}$ and *T*, carbon sorption isotherms on the metal NPs were readily determined.

Fig. 1 depicts the carbon adsorption isotherms of the NPs with different solubilities, sizes and structures. Initially Ih with 309 atoms, and FCC, Wulff shaped clusters with 201 and 405 atoms were considered (Fig. 1a). The clusters have sizes around 1.8-2.5 nm which are close to the sizes of the NPs used experimentally.^{11,13,23} Starting from a pure NP for each run, GCMC calculations were performed with $\mu_{\rm C}$ varying between -7.60 and -4.50 eV per atom, by steps of 0.20 eV per atom. Fig. 1b presents the average mole fraction of carbon dissolved inside the NPs as a function of $\mu_{\rm C}$ at 1000 K where catalysts with different carbon solubilities have been investigated. At a given temperature, beyond a certain $\mu_{\rm C}$ threshold, an increasing number of carbon atoms are adsorbed inside the cluster starting from the subsurface interstitial sites. The carbon fraction then gradually grows until the carbon solubility limit is reached. This limit is defined here as the carbon fraction beyond which carbon species (dimers, chains, etc.) begin to appear on the surface of the NPs. The maximum solubility of carbon in low-carbon-solubility metal NPs is around 15%, which is reasonably lower than the carbon solubility in the Ni NPs (around 25% as seen in Fig. 1b).^{21,24} Obviously, the threshold chemical potential for carbon incorporation is much higher for such a metal NP than for a Ni NP. For example, the threshold carbon chemical potential of Wulff 201 NPs is -6.6 eV and -7.6 eV respectively for a low-carbon-solubility metal and Ni. This means that a higher reaction temperature or a higher pressure is usually required to activate the low-



Icosahedral 309

Fig. 1 (a) Schematic representation of Wulff and Ih structures where the different facets are presented. (b) Carbon adsorption isotherms calculated at T = 1000 K on the basis of GCMC simulations for NPs (with 201, 309 and 405 atoms) of high (top) and low (bottom) carbon solubility. The NP with 309 atoms is Ih when pure, the others are FCC, with their Wulff equilibrium shape.

carbon-solubility metal NPs. Indeed, the low temperature growth of SWNTs by thermal CVD was mainly achieved on Fegroup metal based catalysts^{5,9} instead of low-carbon-solubility metal catalysts. In addition, for both cases, the threshold for carbon incorporation is lower for FCC-Wulff structured NPs than for Ih NPs. This is due to the structural differences between both kinds of NPs. First, the Ih NPs only present densely packed (111) facets which are known to make carbon incorporation less favorable than on the (100) facets present on the Wulff-shaped FCC NPs. Second, their structure consists of a distorted tetrahedral packing giving rise to a radial compressive stress, destabilizing carbon incorporation even more, due to the lack of suitable interstitial sites. The difference between the adsorption thresholds $(\Delta \mu_{\rm C})$ depends on the nature of the catalyst. As indicated by our calculations, the difference in carbon adsorption thresholds ($\Delta \mu_{\rm C}$) between FCC and Ih NPs is much larger for low-carbon-solubility metals $(\Delta \mu_{\rm C} \sim 1.00 \text{ eV per atom, Fig. 1b bottom})$ than for Ni with high carbon solubility ($\Delta \mu_{\rm C} \sim 0.40$ eV per atom, Fig. 1b top). According to our results, we can understand that there is a $\mu_{\rm C}$ window, between the two carbon-incorporation thresholds, within which the carbon nanotubes can grow only from FCC NPs, because no carbon is incorporated in the Ih one. We also see that this $\mu_{\rm C}$ window becomes larger when the carbon solubility decreases in the metallic NPs. Indeed, assuming an ideal behavior of the gas phase, the pressure is related to $\mu_{\rm C}$ by: $\Delta \mu_{\rm C} = k_B T \ln(p_1/p_2)$. Following this equation, a value of $\Delta \mu_{\rm C}$ around 1.00 eV per atom at 1000 K would correspond to ${\sim}5$ orders of magnitude pressure difference. It is thus understandable that the FCC NPs can become active for nanotube growth in a large pressure range where the Ih ones are still inactive.

How carbon atoms are distributed inside the NPs with low solubility for both structures was further investigated by calculating the pair correlation functions centered on the metal atom closest to the barycenter of the NP, for metal-metal and metal-C correlations. Fig. 2 presents two situations. Fig. 2a corresponds to a chemical potential just above the carbon



Fig. 2 Unweighted pair distribution functions (metal–metal, orange and metal–C, black) centered on the atom closest to the center for (a) low carbon chemical potential (beginning of the isotherm) and (b) close to the solubility limit. The metal–C distributions have been multiplied by 2 for legibility. (c) Typical configuration of a Wulff NP (top) and Ih NP (bottom). It clearly shows that the Wulff NP is molten due to interstitial carbon incorporation while the Ih is still crystalline.

Nanoscale

adsorption threshold, and Fig. 2b is close to the solubility limit. Since Ih and FCC Wulff-shaped NPs have different sizes and thresholds, the carbon chemical potentials considered here for both the structures are not similar. At low $\mu_{\rm C}$, very few carbon atoms are incorporated and the crystalline structure of the low-carbon-solubility NPs is well preserved. In the case of FCC structures, the dissolved carbon atoms are located in the subsurface positions while only the carbon atoms on the surface of Ih clusters are observed (Fig. 2a). With increasing $\mu_{\rm C}$, the differences between both the structures are more significant. Indeed, the Ih 309 cluster always presents a pure crystalline core as shown in Fig. 2b, while its outer shell is disordered because it contains a significant amount of carbon. In contrast, a visual inspection of a FCC Wulff-shaped NP shows that increasing $\mu_{\rm C}$ induces the melting of the NPs (Fig. 2c). As a result, a more homogeneous carbon distribution in the whole catalyst destabilizes the crystalline structure. However, Fig. 2 indicates that, as far as the nucleation and growth of SWNTs are concerned, the key difference between the FCC and Ih NPs is the presence of more subsurface carbon atoms in the former, that enable the cap lift-off, while the lack of these tends to favor a stronger adhesion of the sp² layer on the catalyst surface, resulting in a possible encapsulation of the NPs. In the case of graphene growth on a Ni (111) surface, our TB calculations²⁵ have indeed recently demonstrated the weaker adhesion of the graphene layer resulting from the presence of carbon atoms dissolved in Ni, close to the surface.

Our calculations suggest very different abilities to dissolve carbon and hence grow SWNTs for Ih and FCC NPs with low carbon solubility. Since carbon solubility in Au is even lower than in the low-carbon-solubility metal used for calculation, carbon incorporation should be practically impossible in Ih Au under carbon nanotube growth conditions. In order to experimentally confirm this idea, CVD experiments were undertaken to grow carbon nanotubes using Au NPs as the catalyst. Fig. 3a depicts an overview TEM image of the as-received Au NPs, with sizes ranging from 6 to 11 nm. High-resolution TEM images (inset of Fig. 3a, S1 of the ESI†) demonstrate that the Au particles appear as multi-twinned particles with triangular facets arranged along a five-fold symmetry, which is typical of the Ih structure. The observation is in agreement with previous studies where mainly Ih NPs are observed in the as prepared Au NPs.^{26,27} This is because the tiny Ih seed is the minimum-free-energy structure at the initial growth stage, growing kinetically larger Au NPs following a shell-by-shell mode.²⁸

The CVD growth of the carbon nanotubes was carried out at a reaction temperature of 800 °C using CO as the carbon source. No carbon nanotubes were observed to grow on untreated Au NPs (Fig. 3b). The inability of the Au NPs to nucleate SWNTs could be well interpreted by the limited carbon content in such Ih Au particles, as suggested by the isotherms shown in Fig. 1b. With the purpose of ruling out the deactivation of Au NPs by other factors, such as particle diameter and carbon contamination, a series of controlled experiments was carried out. First, Ih Au NPs with different diameters (1.4 nm and 3 nm, Fig. S2 of the ESI[†]) were subjected to CVD growth. These small size Ih Au NPs are still inactive for growing carbon nanotubes, indicating that the size of the Au particles is not the cause for the unsuccessful synthesis of carbon nanotubes. Second, the Au NPs (10 nm) preheated at 450 °C in air were tested for CVD growth of carbon nanotubes. Annealing at 450 °C was chosen because all organic impurities (like thiol) or other carbon contaminants can be removed at this temperature.^{29,30} Still, the 450 °C-annealed 10 nm Au NPs are inactive for growing carbon nanotubes (Fig. S3 of the ESI[†]). These results imply that the carbon contaminant is not responsible for the inactivity of the Au NPs, in agreement with the experimental findings by Schünemann et al.,³¹ who found that amorphous carbon and carbon tar did not poison catalyst particles. Together with our theoretical calculation results, the above experimental phenomena suggest that Ih Au NPs are not favorable for carbon dissolution, responsible for the failure in catalyzing carbon nanotube growth.

Such Ih Au particles could be transformed into FCC single crystalline particles by high temperature calcination, as demonstrated by TEM characterization which had been performed to track the evolution of Au NPs. Fig. 4a and 4b show the TEM images of two untreated Au NPs supported on a Si_3N_4 grid. Both Au NPs present a faceted morphology and planar defects such as contact twins and intrinsic/extrinsic stacking faults. The Au particle shown in Fig. 4a displays a "ring" pattern, a typical feature of an Ih particle.²⁷ While the particle shown in Fig. 4b displays a much weaker "ring" feature and a remarkable "lattice" feature compared to the Au NPs shown in Fig. 4a. The particle is also ascribed to an Ih particle. The differences in the features of the two Ih Au NPs are attributed to their different orientations relative to the TEM observed direction.²⁷

Air calcination was carried out at 800 °C for 2 h to transfer Ih Au to FCC single crystal Au particles. Fig. 4c presents the Au particle shown in Fig. 4a after high temperature calcination. Both the TEM image and the corresponding fast Fourier transform (FFT) pattern (Fig. 4e) indicate that the Au NPs evolved into an FCC single-crystal phase after heat treatment. Similarly, the Au NPs shown in Fig. 4b were also transformed into a single-crystal phase after air calcination at 800 °C, as confirmed by their high resolution TEM image (Fig. 4d) and the



Fig. 3 (a) TEM image of the as-received 10 nm Au NPs. (b) SEM image of 10 nm Au NPs after CO CVD growth at 800 $^\circ C$ for 1 h.



Fig. 4 (a) and (b) TEM images of two untreated Au NPs on a Si₃N₄ grid. (c) and (d) TEM images of the same two Au NPs after annealing at 800 °C in air for 2 h. (e) and (f) The respective FFT patterns of Au NPs shown in (c) and (d).

corresponding FFT pattern (Fig. 4f). The findings are consistent with a previous report²⁶ where Ih to FCC Au transformation was observed by annealing. However, it is noted that during the calcination process, the presence of oxygen greatly enhances the metal-support interaction,³² resulting in the wetting of Au on the surface. In contrast, heating under an inert atmosphere (like helium) does not improve the adhesion of Au on the support. Therefore, it is postulated that the increased Au-support adhesion upon calcination in air causes the spreading of the Au NPs, facilitating the recrystallization of Au from Ih to FCC.

Only FCC Au NPs were demonstrated to grow SWNTs under our CVD growth conditions. Fig. 5a and 5b depict the scanning electron microscopy and atomic force microscopy images of the carbon nanotubes grown on Au NPs calcined at 800 °C, showing that the annealed Au NPs are active for growing SWNTs, in agreement with previous experimental observations.11,13,33 Similarly, carbon nanotubes were also observed to grow on the 800 °C-annealed Au NPs with small diameters (Fig. S4 of the ESI[†]). In order to further verify that FCC Au is the active phase for carbon nanotube growth, TEM characterization was conducted on the Au NPs that had catalyzed the growth of carbon nanotubes. Fig. 5c and d present two such Au NPs. Clearly, both Au NPs exhibit single-crystal structures with an interplanar lattice spacing of 0.20 nm, corresponding to the (200) lattice of FCC Au NPs. Our results thus confirm that the role of annealing at high temperature is to transform the inactive Ih Au NPs to the FCC single-crystal phase and that as expected from our calculations the FCC phase only is enabling the catalysis of carbon nanotube synthesis.

Conclusions

In conclusion, by combining GCMC atomistic computer simulations and experimental work through the use of the pro-



Fig. 5 (a) Scanning electron microscopy and (b) atomic force microscopy images of carbon nanotubes grown on 800 °C-annealed 10 nm Au NPs using CO as the carbon precursor. (c) and (d) TEM images of Au NPs which catalyzed the CVD growth of SWNTs. Both Au particles adopt an FCC single-crystal structure.

perties of Au NPs, the chemistry of the catalyst metal NPs, in particular their ability to dissolve carbon in seeding the nucleation and growth of SWNTs is uniquely identified. Three major conclusions are reached. First, the chemical potential required to incorporate carbon into low-carbon-solubility metal NPs is much higher than that required for incorporating carbon into Fe-group metal NPs, like Ni. This explains why SWNT growth can be easily achieved on Fe-group metal NPs even at a low reaction temperature and the CVD conditions are harsh for synthesizing SWNTs on low-carbon-solubility metals. Second, for metals with low carbon solubility, carbon incorporation is found to strongly depend on their structures (FCC or Ih), leading to different amounts of carbon close to the NP surface. The lower the carbon solubility in the metal NP, the stronger the influence of the atomic structure on the carbon incorporation. We expect that the findings are also of potential interest for the application of metal NPs in other catalysis reactions (for example, graphene synthesis). Finally, the importance of subsurface carbon in NPs is further highlighted for carbon cap "lift off" and nucleation of SWNTs. NPs without subsurface carbon tend to favor a stronger adhesion of the sp² layer on the catalyst surface, leading to the deactivation of catalysts by carbon encapsulation. In contrast, NPs with incorporated subsurface carbon could dewet the carbon cap formed on the metal surface, facilitating the nanotube embryo formation and their subsequent prolongation. This offers new possibilities to tune the catalytic activities of metal NPs by improving its abilities to dissolve carbon and contributes to a better understanding of SWNT growth mechanisms, paving the way to a rational search for better catalysts for controlled synthesis of SWNTs.

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