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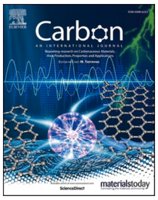

In situ transmission electron microscopy of temperature-dependent carbon nanofiber and carbon nanotube growth from ethanol vapor

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ABSTRACT

Carbon nanofibers (CNFs) and carbon nanotubes (CNTs), which have been known for decades, recently gained significant commercial interests for various applications. However, the controlled synthesis of CNF/CNT has been hindered by the lack of nanoscale experimental evidence on how the growth temperature affects the growth process under real growth environment. We report the *in situ* transmission electron microscopy (TEM) experiments to directly observe Ni catalyzed CNF/CNT growth from alcohol precursor at near atmospheric pressure using a homebuilt bubbler system for the introduction of ethanol vapor. Using real time imaging, we revealed the active state of the Ni catalyst during the temperature-dependent CNF/CNT growth (600–800 °C). We observed the formation of CNFs starting from 600 °C and CNTs were formed at higher temperatures. The lattice parameter measurements pointed to an expansion of the Ni lattice as the temperature was increased, which we attribute to increased carbon solubility. The as-grown CNFs and CNTs were further characterized by XPS, Raman spectroscopy, and EELS, that allowed to have a highly reliable overall view of the structure changes with temperature. Results revealed that the change in structure with temperature was caused by the combined effects of increased carbon solubility and graphitization of the walls of the growing nanostructure. This increased carbon solubility in turn affected carbon diffusion and could be the reason for the change in structure from CNF to CNT at high temperature. Using *in situ* TEM we clearly revealed the effect of growth temperature on the structural changes.

1. Introduction

Due to their extraordinary physical properties and chemical stability, carbon nanofibers (CNFs) and carbon nanotubes (CNTs) find applications in many areas including energy storage, wearable electronics, thermal interfaces, chemical sensors and photonics, among others [1–3]. Nevertheless, it is generally accepted that a precise control of their structure at the nano and micro level is indispensable to enable these applications. Among the different approaches adopted in CNF and CNT synthesis, chemical vapor deposition (CVD) involving the catalytic decomposition of carbonaceous precursors at temperatures in the range 600–1000 °C, is the most widely used, since it allows better control of structure and is scalable in addition to being a low cost process with high yield. Because of the special relationship between the structure and the versatile properties of the nanostructures formed, much research has been dedicated to understanding the growth mechanism of CNFs/CNTs formation by CVD [4–6].

Among the different experimental variables in the CVD synthesis of CNFs/CNTs, such as temperature, pressure, and reactant gas concentration [5,7–9], the growth temperature is the most important parameter that crucially determines the structure of the product obtained, since the state of the catalyst is temperature dependent [10–15]. The growth temperature can control the degree of internal carbon diffusion by changing the amount of dissolved carbon [16]. Furthermore, higher growth temperatures usually led to improved crystallinity of the graphitic walls of CNT [12]. Despite significant progress in process development, currently, an indepth understanding of the effect of temperature on the actual growth process is still not achieved, due to missing information on non equilibrium phenomena occurring at high temperature in the gas-solid reaction.

In this regard, *in situ* characterization techniques have provided valuable information on reaction mechanisms and intermediates. With

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the help of *in situ* X-ray diffraction (XRD) [17,18], *in situ* X-ray photoelectron spectroscopy (XPS) [19–21], and *in situ* Raman spectroscopy [22–24] important insights have been obtained into the state of the catalyst particles and their role in CNF and CNT growth mechanisms at different temperatures. *In situ* XRD experiments confirmed that during CNT growth, a transition from pure Ni metal to the carbide phase occurs due to the increased amount of dissolved carbon [18]. Using *in situ* XPS analysis, it was possible to monitor the increase in Ni carbide fraction during the growth of a CNF at 700 °C [19]. Similarly, CNT growth rate and lifetime were tracked by following the change in G band fraction with temperature using *in situ* Raman spectroscopy [22]. However, these *in situ* techniques do not allow to simultaneously describe the dynamic changes in both structure and bonding of the active phase, and moreover, they provide spatially averaged information from a relatively large area.

In this context, *in situ* transmission electron microscopy (TEM) offers atomic- and nanoscale information on the physical and chemical states of individual catalytic particles through imaging and spectroscopy from which, important clues to the reaction mechanisms under different growth conditions can be obtained [25–27]. Using *in situ* TEM, it has been possible to determine the active state of catalyst particles, which when combined with favored carbon diffusion pathways derived from density functional theory (DFT) calculations, can provide a holistic view of the reaction mechanism [8]. Wang et al. reported that the active phase of the Co catalyst particle during the multiwall CNT growth is Co_3C and proposed that the main diffusion pathway is that between the catalyst surface and the graphitic wall [28]. Fan et al. reported that the active phase of a Ni–Co binary alloy remains a pure metal during CNF growth and that the bulk diffusion is energetically more favorable than interface diffusion [29]. However, these previous *in situ* TEM studies on CNF and CNT growth used gaseous hydrocarbons as carbon precursors, while alcohol carbon sources, which have recently gained great attention due to their high yields, have so far not been studied.

Currently, alcohols (mainly ethanol) are the most used carbon precursors for large scale CNF and CNT growth, both due to economic and ecological concerns. Water molecules and hydroxyl radicals generated from the decomposition of alcohols act as etchant to prevent amorphous carbon formation due to which, the yield of reaction and catalyst lifetime can be significantly increased [1,5,30]. However, introducing a liquid vapor into an *in situ* TEM system with closed cell could be complicated by re-condensation of the vapor, which blocks the gas flow due to the limited available space at the reaction site and the ultra narrow diameter of the supply lines, in addition to the danger of contaminating supply lines, as a result of which, there are only rare studies on using ethanol vapor in an *in situ* TEM system [31,32]. Thus, to the best of our knowledge, there are no reported *in situ* TEM studies on CNF and CNT growth using alcohol as the carbon source at near atmospheric pressure using a closed cell.

In this work, we report *in situ* TEM studies to elucidate the effect of temperature on the growth of CNFs and CNTs with Ni catalyst and ethanol as the carbon source at near atmospheric pressure. Our homebuilt bubbler system allowed to precisely flow ethanol vapor into a micro-electro-mechanical system (MEMS) based closed cell system in a controlled way while maintaining near atmospheric pressure conditions. Using this system, we successfully monitored the growth of CNFs and CNTs from alcohol precursor on a Ni catalyst at different temperatures. We performed *in situ* analysis on growing CNFs/CNTs at three different temperatures (600 °C, 700 °C, and 800 °C) to study the structure changes in real time. To gain a deeper understanding of the growth mechanism in a real growth environment, we also conducted *ex situ* characterization (post-analysis) on the CNFs/CNTs that were grown using the same system and conditions for the comparison. Selected area electron diffraction (SAED) patterns were analyzed both under *in situ* and *ex situ* conditions to understand the active state during growth. Complementary spectroscopic techniques including XPS, Raman spectroscopy, and *in situ* and *ex situ* electron energy loss spectroscopy (EELS) allowed to get detailed information on the obtained structures. Combining *in situ* results with *ex situ* techniques on the same sample allowed to quantitatively estimate the increase in carbon solubility and the crystallinity of the walls (sp^2 carbon fraction and I_{D1}/I_G ratios) with growth temperature in a reliable manner. We surmise that the increased carbon solubility modified carbon diffusion and crucially affected the structure of the growing nanofiber or nanotube.

2. Material and methods

2.1. Preparation of Ni catalyst

3 nm-thick Ni films were deposited onto the surface of closed cells (DENSsolutions gas heating chip) using an electron beam evaporator (WOOSUNG, WC-4000) under high vacuum conditions ($\sim 5 \times 10^{-6}$ torr). The cells were chosen from the same batch to ensure reproducibility in repeated experiments. The Ni deposited closed cells were then loaded into the gas holder (DENSsolutions gas holder). The gas supply lines in the gas holder and in the homebuilt bubbler system were flushed by 4 % H_2 in Ar gas for a short time to remove residual gases. The deposited catalyst on the chip was then annealed at 800 °C to form Ni nanoparticles.

2.2. In situ TEM experiments

A homebuilt bubbler system was used to control the pressure and the gas flow at the reaction site. *In situ* experiments were conducted on an aberration-corrected TEM (FEI, Titan^3 G2 60-300) operated at 200 kV. CNF and CNT growth studies were performed at 600, 700, and 800 °C, with a pressure of 728 mbar and a flow rate of 0.43 ± 0.0029 ml/min. The carrier gas (4 % H_2 in Ar) was saturated with ethanol vapor by bubbling the gas through the inlet vial (theoretically 6.5 % C_2H_6O in Ar at 22 °C), and was directly introduced into the closed cell. For growth kinetics study, sequential images were acquired using a Gatan camera (BM-Ultrascan) at time intervals of 0.16 s with an exposure time of 0.1 s, and the dose rate was 7.92 $e^{-1}/\text{Å}^2 \bullet$ s, under which conditions the growth was not affected by the electron beam. For high resolution imaging, the exposure time was 0.1 s and the dose rate was 1380 $e^{-1}/\text{Å}^2 \bullet$ s; under these conditions, beam-induced artifacts were observed.

2.3. Complementary spectroscopic analysis

Complementary spectroscopic techniques were used to characterize the CNF and CNT obtained from *in situ* TEM experiments. EELS was recorded from the same TEM described above with a Gatan Quantum 965 dual EELS system in STEM mode. During the measurement, we collected data from 100 μm^2 regions (with a step size of 2 μm) through spectrum imaging. The energy dispersion was 0.025 eV/ch and the energy resolution was 1.0 eV under an acceleration voltage of 200 kV. XPS (Thermo Fisher Scientific, ESCALAB 250XI) was performed with monochromatic Al Kα radiation. XPS analysis area was set to 200 μm beam diameter and the step size was 0.1 eV with a base pressure of 1×10^{-10} torr during all measurements. Raman spectra were collected on a Raman Microscope system (WITec, alpha300S) equipped with 532, 633, and 785 nm lasers; in our measurements, we used the 633 nm laser to reduce plural scattering.

2.4. SAED pattern indexing

A 60 μm-size selected-area aperture was used to acquire the SAED patterns, and these were captured from six different positions at each condition. SAED patterns were analyzed using the DiffTools package for Digital Micrograph® software (industry standard software for TEM analysis). Rotationally averaged radial intensity profiles were obtained and the acquired profiles were automatically indexed using the top hat filter (THF) tool in the DiffTools to reduce measurement errors. The *d*-

spacing value of each crystal plane was obtained through auto-indexing, and the *d* values were converted to lattice constants. From these data, the average lattice constant for the entire region was derived.

2.5. *Calculation of activation energies during CNF and CNT growth*

For calculating the energies of activation for CNF and CNT growth (Fig. 4g–i), their growth rates were measured during the growth stage by successively capturing images (Fig. S10 and Fig. S11). The moving

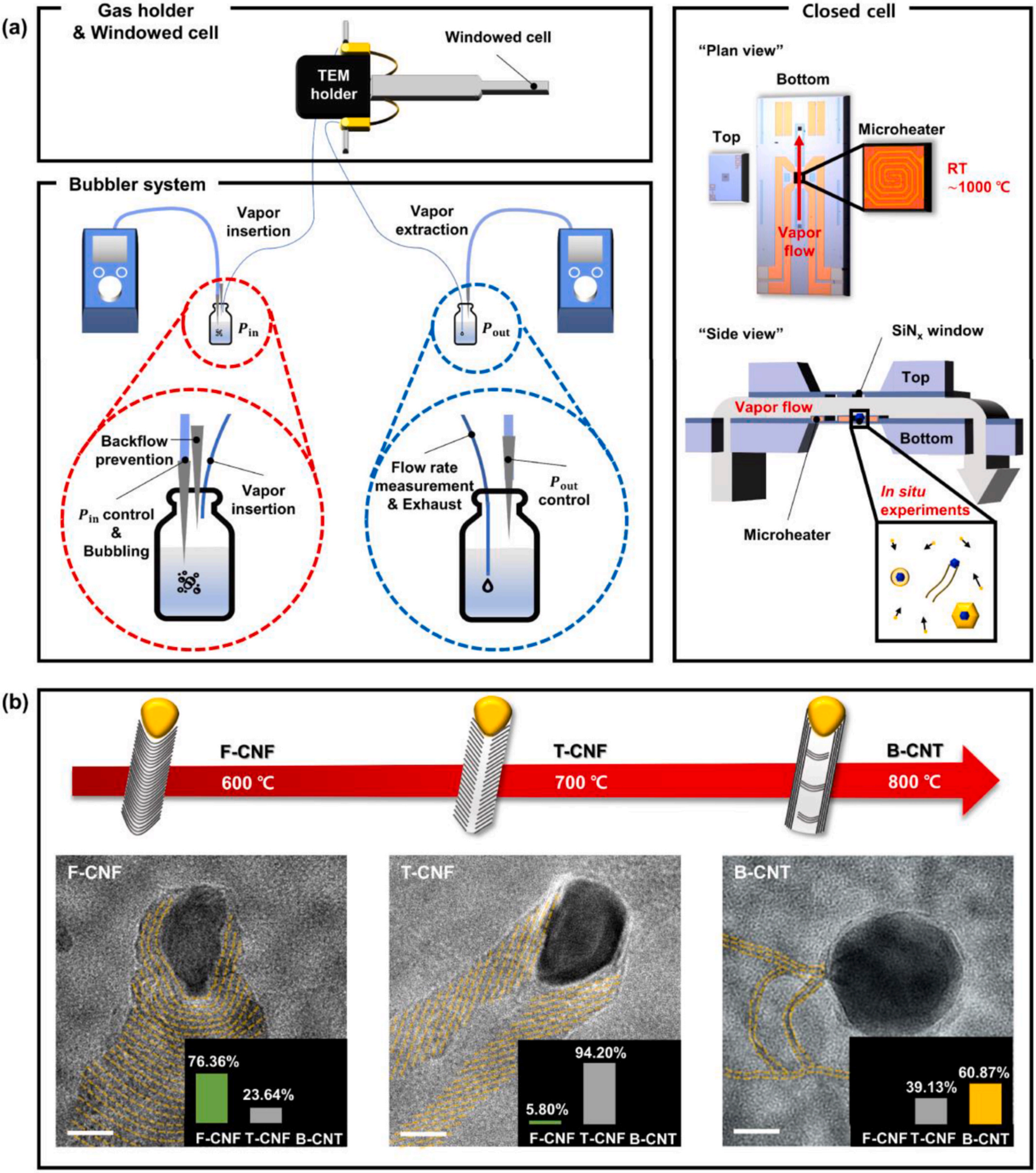

Fig. 1. *In situ* TEM experiments where liquid vapor was introduced into a closed cell using the homebuilt bubbler system. (a) Schematic of the devised bubbler system and the closed cell. (b) Temperature-dependent growth of CNF and CNT with ethanol as carbon source. Scale bars are 10 nm. (A colour version of this figure can be viewed online.)

trajectories of each growing structure were tracked down manually using the Manual Tracking plugin in ImageJ software. Since the growth was accompanied by random orientation, the segments showing constant growth were measured. A sufficient number of growing structures were tracked down for statistical analysis to correctly estimate the effect of temperature on growth rate. The growth rate showed oscillatory behavior during the growth, as also reported in previous works [27–29]. The average growth rate with respect to temperature change was used for the calculation of activation energies. The activation energy (E_a) was calculated according to the modified Arrhenius equation.

$$\ln k = -\frac{E_a}{k_B T} + \ln A$$

Where, k is the growth rate, k_B is the Boltzmann constant, T is the absolute temperature, and A is the pre-exponential factor. The gradient from the plot of $\ln k$ versus T^{-1} was be used to determine the activation energy.

3. Results and discussion

3.1. CNF and CNT synthesis with ethanol vapor

Our *in situ* TEM experiments on CNF and CNT growth with ethanol vapor as the carbon source were conducted using a MEMS-based closed cell connected to a homebuilt bubbler system. We modified the commercial gas distributer system from DENSsolutions to supply ethanol in the vapor state by replacing the gas supply lines with our homebuilt bubbler system. Two vials with pumps were connected to the gas inlet (P_{in}) and outlet (P_{out}) lines, which allowed to precisely control the pressure and flow rate at the reaction site (P_r and F_r) in the closed cell (Fig. 1a and Video S1). The working pressure and flow rate at the reaction site were calculated as described in SI and Tables S1–2 [33]. Thus, our bubbler system enabled as good control of both pressure and flow rate as commercially available gas flow systems (Fig. S1), which allowed to grow CNFs and CNTs at different temperatures with high reproducibility. To precisely understand the effect of temperature on growth, we fixed the internal pressure at the reaction site at near atmospheric pressure and observed the growth and changes in carbon structure as the temperature was increased. Ni nanoparticles were used as the catalyst in view of their high catalytic activity [5,34–36], and ethanol, being weakly oxidizing, was selected as the carbon source to obtain high growth yield [37–41]. Ethanol is known for the carbon precursor suitable for the growth of high-purity single-walled CNTs (SWCNT) [41]. In general, when size of particle is small and the carbon partial pressure is low, SWCNTs tend to predominately form over MWCNTs [4,7–9]. In such situation, the use of environmental transmission electron microscopy (ETEM) can be more suitable for observing SWCNTs growth, because it operates under low-pressure conditions and does not have limitations in spatial resolution due to the lack of SiN_x windows. However, we developed a novel liquid precursor supply system for atmospheric pressure experiments that favor MWCNT growth and conducted the first *in situ* TEM study using ethanol precursor.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.carbon.2024.118843

We identified the formation of a carbonaceous structure upon heating first at 540 °C, and noticeable structural changes were confirmed in the temperature range of 600–800 °C as shown in Fig. 1b and Fig. S2 (at a higher temperature, carbon nano-onions [42] were predominantly formed as described in Fig. S3 rather than CNFs/CNTs).

A fishbone-type CNF (F-CNF) was formed at a relatively low temperature of 600 °C and this structure changed to a tubular CNF (T-CNF) at 700 °C. At 800 °C, the main structure grown was a bamboo-type CNT (B-CNT) [13]. All the three tubular structures were formed by tip-growth mode, but a change in the growth mechanism from the tip-to base--growth also occurred occasionally at 800 °C, ending in a multiwalled CNT (M-CNT). In tip-growth mode, the carbon source decomposes on the exposed surface of the catalyst particle and the carbon atoms diffuse towards the rear side of the catalyst (in proximity to the substrate). The carbon atoms precipitate to form graphitic walls along a direction opposite to the growth direction. A closer look at the images in Fig. 1b reveals the presence of graphitic walls on F-CNF grown by precipitation of carbon atoms at the rear surface (surface opposite to the exposed surface) of the catalyst and stacked almost perpendicularly to the growth direction. T-CNF also has graphitic walls similar to F-CNF, grown by precipitation on the rear surface, but these did not completely cover the particle but left a hollow column as shown in the schematic. B-CNT shows graphitic walls along the growth direction with internal closures (knots) that separate the columns.

3.2. State of the catalyst during the growth

The structure of the growing CNF/CNT is intimately connected to the state of the catalyst. During growth, the amount of dissolved carbon inside the catalyst particle impacts the degree of carbon diffusion and critically affects the structure of the growing CNFs/CNTs [9,16,43–47]. We imaged the active phases of the Ni catalyst during CNF and CNT growth in the temperature range of 600–800 °C. TEM images show that the overall structure remained similar to that of pure Ni (Fig. S4), but measurement of SAED patterns with rotational average intensity profiles revealed a slight increase in lattice constant indicating that the Ni crystal expanded during the growth (Fig. S5 and Table S3). Although we attempted high resolution imaging to accurately determine the state of the catalyst during the reaction, the high electron beam dose (1380 $e^{-1}/Å^2 \bullet s$) under high magnification perturbed the growth (Fig. S6 and Videos S2, S3). Due to the defects induced by the electron beam irradiation, the graphitic walls formed under the high electron beam dose resulted in helical-like growth (Video S2) or sometimes just collapsed without undergoing sustained growth (Video S3). In view of this electron beam effect, we decided to use data taken under relatively lower electron beam dose conditions (7.92 $e^{-1}/Å^2 \bullet s$) and found that analyzing SAED patterns was a more appropriate method than atomic-resolution imaging to understand the exact state of the catalyst during the growth.

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To determine the change in average lattice constant with temperature, we averaged SAED patterns with rotational intensity profiles from Fig. S5 and Table S3 (Fig. 2 and Table S4). We note here that, due to dissolved carbon in the catalyst and the formation of carbonaceous species by the decomposition of ethanol vapor, SAED patterns from *in situ* analysis appear more blurry (Fig. 2a–c) compared to the those obtained in post-analysis of the grown carbon structures (Fig. 2d–f) [48]. A clear increase in the average lattice constant of the catalyst was observed in our *in situ* experiment (Table S4). The lattice constants at 600 °C, 700 °C, and 800 °C were 3.6079 ± 0.0026 Å, 3.6226 ± 0.0043 Å, and 3.7187 ± 0.0052 Å (Fig. 2a–c and Table S4). Comparison of our experimental results with reference thermal expansion data confirmed that the lattice expansion was not due to thermal expansion but was caused by dissolved carbon (Fig. S7) [49,50]. We then calculated the carbon concentrations corresponding to this lattice expansion at 600 °C and 800 °C to be ~7.56 at.% and ~20.38 at.%, respectively (Fig. S8) [18], which incidentally, are much higher than the carbon solubility in bulk Ni [51,52]. Post-analysis of the grown structures (Fig. 2d–f and Table S4), indicated only a very slight lattice expansion and the corresponding carbon concentrations at 600 °C and 800 °C were ~0.50 at.% and s ~4.22 at.%, respectively. We attribute this difference to additional growth during cooling after cutting off the carbon source supply, during which process, a certain amount of dissolved carbon could be consumed by forming additional graphitic walls. The difference in lattice constant changes between *in situ* results and *ex situ* analysis clearly shows the structural changes of Ni catalyst during the growth and allows us to

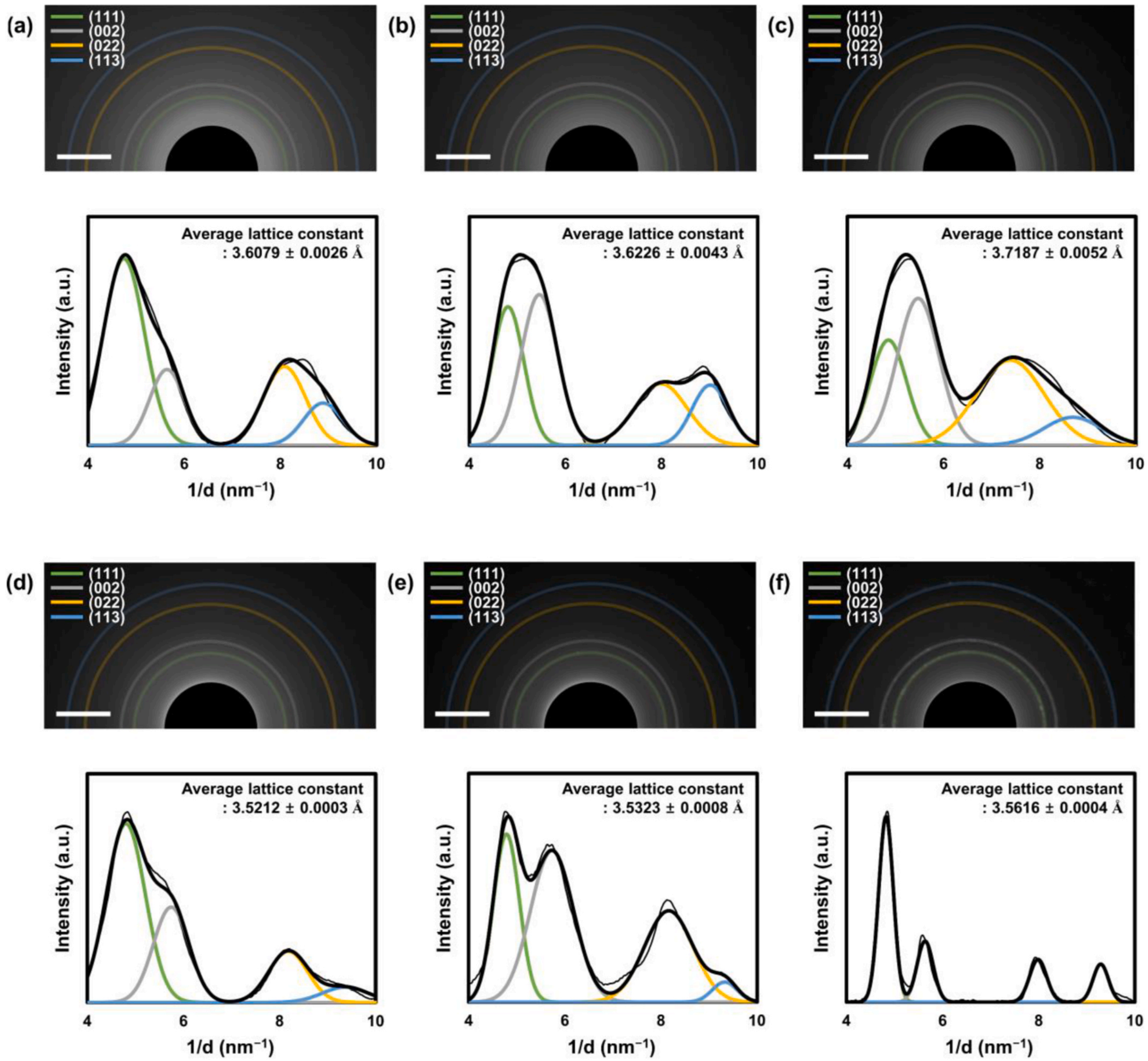

Fig. 2. Averaged SAED patterns of Ni catalyst with the rotational average intensity profiles showing change in d-spacing with growth temperature. (a–c) Diffraction patterns during the reaction at (a) 600 °C, (b) 700 °C, and (c) 800 °C. (d–f) Diffraction patterns from *ex situ* analysis of grown structure at (d) 600 °C, (e) 700 °C, and (f) 800 °C. Scale bars are 2.5 nm^{-1}. (A colour version of this figure can be viewed online.)

better understand the growth mechanism.

It has been known that nickel catalyst has different active phases during the catalytic growth, including Ni_3C at 300 °C, Ni–Ni_3C composite from 400 to 500 °C, and metallic Ni above 600 °C [16,53,54]. Therefore, previous *in situ* TEM studies has suggested that metallic Ni was the active state during the growth at temperatures above 600 °C (Lyu et al. only reported that Ni_3C is temporally observed as active state at 500 °C which can readily degrade to metallic Ni again) [35,43,55,56]. However, this does not necessarily rule out the presence of carbon within the Ni catalyst. In contrast to *in situ* TEM, other *in situ* XRD and XPS studies have shown that the active state is not metallic Ni during the CNF/CNT growth at temperature above 600 °C due to the presence of the intestinally dissolved carbon inside the Ni catalyst which is generally referred to as non-stoichiometric NiC_x since it does not have definite crystalline structure [18,19]. The lattice parameter changes due to the interstitially dissolved carbon is very small and it would be the reason why previous *in situ* TEM studies identified it as a metallic Ni. To address this issue, we conducted SAED analysis with a relatively lower electron beam dose to monitor the evolution of the Ni catalyst during growth, aiming to accurately measure the subtle changes in lattice parameters by superimposing overall signals from Ni catalysts at the reaction site. This approach allowed us to successfully evidence that the nickel carbide is the active phase (Fig. S5 and Table S3). SAED, with its penetration depth of hundreds of nanometers, is suitable for analyzing to lattice parameter changes originated from interstitially dissolved carbon within the bulk and on the surface of Ni nanoparticles [57].

Previous studies have reported that dissolved carbon in a Ni catalyst can weaken the interaction between the graphene and the surface of the catalyst [58], and hence the increased carbon concentration at higher temperatures could lead to a detachment of the graphitic wall with a lower adhesion force. This behavior is expected in our experiments as well, and could be reason for the observed structure changes.

3.3. Temperature-dependent carbon bonding state change

The mechanical, electrical, and optical properties of CNF and CNT can be modulated by changing the ratio of sp^2 to sp^3 bonds, which in turn, is a measure of the degree of graphitization [59,60]. During *in situ* TEM experiments, we also performed electron energy-loss spectroscopy (EELS) analysis of the sample to reveal the changes in the bonding state of carbon at different temperatures. These effects were also investigated using complementary spectroscopic studies, such as XPS and Raman spectroscopy, so as to minimize possible systematic errors and get a clear picture of how the temperature affects the carbon bonding state. Spectroscopic analyses were performed using averaged information of grown CNFs/CNTs structures from reaction sites to minimize potential error. Additionally, to compare the results obtained from the same structures and verify the difference between *in situ* and post-analysis results, the EELS measurement was carried out both *in situ* and *ex situ*.

In the case of EELS, the density of anti-bonding π^* and σ^* states can be used to calculate the fraction sp^2 bonds [61–63]. To accurately quantify this fraction, we adopted the "Five Gaussian Peaks Method" by Mironov et al. [64] This method was developed by adding two additional Gaussian peaks to the "Three Gaussian Peaks" method proposed by Zhang et al. [61] Using this method, we estimated the sp^2 fraction at each temperature (Fig. 3a and b), and the parameters used for fitting are listed in SI and Table S5. The actual sp^2 fraction can be calculated by comparing the peak intensities of π^* and σ^* to those of a 100 % sp^2-hybridized material as shown in SI [63]. Our results show that the sp^2 fraction tends to increase with temperature. Though the sp^2 fraction values obtained from the post-analysis were slightly higher than those from *in situ* analysis, which might be caused by additional crystallization during cooling, a similar overall trend was observed in both cases.

XPS can also be used to estimate the sp^2 and sp^3 fractions. However, an interpretation of XPS C1s could be difficult in the presence of disordered carbons and carbons bonded to other species (such as oxygen) due to binding energy shifts associated with various heteroatoms. Smith et al. proposed a good alternative method based on the 7 peak C1s

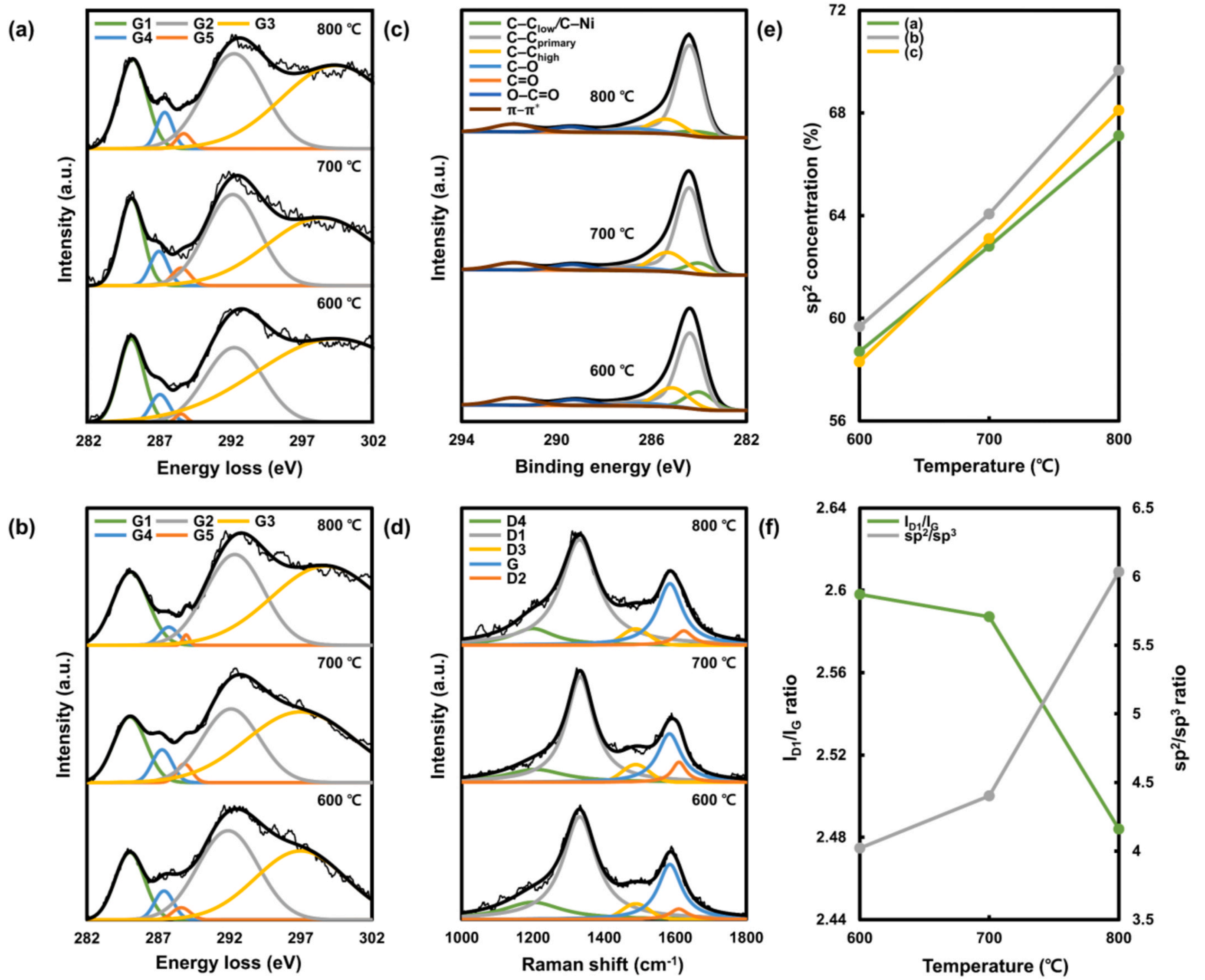

Fig. 3. Complementary spectroscopic analysis to understand the temperature-dependent growth mechanism. EELS obtained through (a) *in situ* analysis during the growth and (b) *ex situ* analysis on the grown CNF and CNT. (c) XPS and (d) Raman spectra obtained from *ex situ* analysis. (e) The comparison of EELS and XPS showing the relative sp^2 fraction change with the temperature. (f) The comparison of I_{D1}/I_G from Raman spectroscopy and sp^2/sp^3 from XPS with temperature. (A colour version of this figure can be viewed online.)

deconvolution (3 C–C peaks, 3 oxygenated peaks, and π–π^* transition peak) [65]. We applied this deconvolution method to our results to identify the sp^2 and sp^3 fractions at each temperature (Fig. 3c); the parameters used for fitting are listed in SI and Table S6. The observed trend in sp^2 fraction at different temperatures obtained from XPS is in good agreement with our EELS analysis (Fig. 3e), confirming increase in sp^2 bonds fraction with temperature [66–68]. Furthermore, our findings align well with XPS data from Yang et al. and Park et al. [69,70]. These studies indicate that as the synthesis temperature of CNT growth increases by 200 °C within the range of 500–800 °C, the sp^2 fraction of the sample increases by 12 % and 8 %, respectively. The increases in the sp^2 fraction observed in our experiment well matched with these previous studies. We confirmed this result by performing additional EELS deconvolution using the "Sum of Decaying Gaussian Peaks Method", where we assigned the asymmetric $C{=}C$ π^* peak (we chose this peak because of its asymmetric nature; SI, Fig. S9 and Table S7) [71]. The calculated sp^2 fractions using this method were a little higher but still in good agreement with the trend shown in Fig. 3e.

The structures of CNF and CNT were further analyzed using Raman spectroscopy [72,73]. Though Raman analysis cannot directly give information on sp^2 and sp^3 fractions, the ratio of the intensities of the D1 and the G band is related to impurities, defects, and disorder in CNF and CNT [74,75]. Sadezky et al. proposed a combination of four Lorentzian peaks (G, D1, D2, and D4) and one Gaussian peak (D3) for the Raman spectral investigation of carbon materials [76]. We used this deconvolution method (SI, Fig. 3d and Table S8) to calculate the I_{D1}/I_G ratios. The I_{D1}/I_G ratio and the sp^2/sp^3 ratio, both indicative of the degree of graphitization of carbon networks, are known to correlate with each other [77–79]. The measured I_{D1}/I_G ratio decreases with increasing temperature, implying increased graphitization with temperature, which correlates with the increasing sp^2/sp^3 ratio obtained from XPS analysis (Fig. 3f). Thus, results from complementary spectroscopic studies sRow consistency over EELS, XPS, and Raman spectroscopy.

To sum up the overall spectroscopic analysis results, the effect of

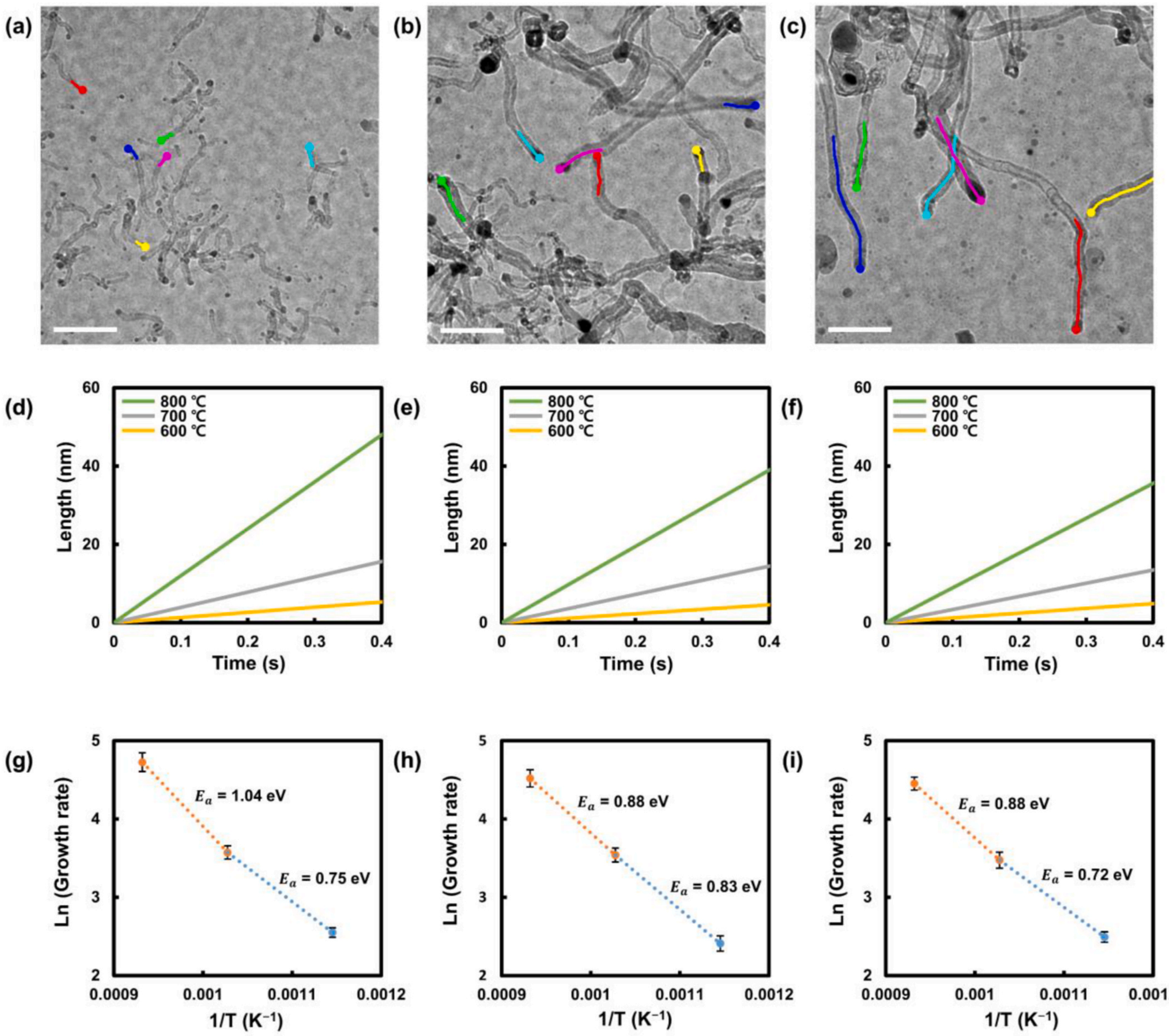

Fig. 4. CNF and CNT growth kinetics from *in situ* TEM experiments. Representative images showing the growth trajectories at (a) 600 °C, (b) 700 °C, and (c) 800 °C. Averaged growth lengths as a function of time for particle sizes in the range of (d) 18–20 nm (e) 21–23 nm, and (f) 24–26 nm. Arrhenius plots for the CNF and CNT growth rates with particle sizes in the ranges (g) 18–20 nm, (h) 21–23 nm, and (i) 24–26 nm. The blue and orange dotted lines correspond to the 600–700 °C and the 700–800 °C temperature ranges. Scale bars are 100 nm. (A colour version of this figure can be viewed online.)

temperature on the degree of graphitization was verified by determining the sp^2 fraction or the sp^2/sp^3 ratio change, and EELS analysis confirmed that there was no significant difference in temperature effect between *in situ* and post-analysis results.

Jacobson et al. reported that thermal healing of disorders and defects in graphene on a Ni surface requires temperatures greater than 700 °C [80] and Fan et al. reported that the defect density in a graphitic wall growing on a catalyst particle surface is directly related to the adhesion force between them [29]. Consequently, a change in the sp^2 fraction (or defect density) with temperature could induce a change of structure.

3.4. *Temperature-dependent growth kinetics*

To study the temperature-dependent growth kinetics, the trajectories of CNF and CNT were monitored, and their growth rates were measured by dynamically observing their growth (Fig. 4a–c). We focused on CNFs and CNTs growing by tip-growth mode and a statistical analysis was performed on 70 cases at 600 °C, 101 cases at 700 °C, and 68 cases at 800 °C. Results show that growth rates are affected by both particle size and temperature (Fig. S10) [12,81–84]. The growth rate was faster as the catalyst particle size decreased and also increased with temperature. Therefore, we distributed the particles into three groups of similar sizes (18–20 nm, 21–23 nm, and 24–26 nm), to eliminate the effect of particle size when studying temperature dependence. Fig. 4d–f shows the average values of the selected results, and the whole data with individual growth rates measurements are in given in Figs. S11 and S12 and Videos S4–6.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.carbon.2024.118843

Estimating the activation energies (E_a) from the growth rates of CNF and CNT gives important clues to understanding the carbon diffusion pathway during growth. Hence, we calculated the activation energies of CNF and CNT growth using the Arrhenius equation. So far, studies on activation energies for CNF and CNT formation are usually derived based on the CVD-grown end product. These calculated values could be erroneous since they include the nucleation and termination steps in addition to the actual growth step. Therefore, the direct observation of CNF and CNT during the growth stage gives us a better picture of the actual growth process and allows to calculate the corresponding activation energies.

As shown in Fig. 4g–i, in the temperature range 600–700 °C, there was no significant difference in activation energies for the three size groups. However, in the 700−800 °C temperature range, the E_a values obtained for the 18–20 nm group were slightly higher than for the other two size groups. We attribute this difference to the hampered growth rate for low particle sizes at high temperature, caused by the relatively large amount of dissolved carbon. Nevertheless, it is seen that the overall trends with temperature are similar for the three size groups. At temperature ranges of 600–700 °C and 700–800 °C, the average activation energies for CNFs and CNTs were 0.76 eV and 0.93 eV for the three different groups. The increase in activation energy from CNF to CNT indicates either a change in the state of the catalyst or that the diffusion of carbon was affected by the increased amount of interstitially dissolved carbon, as explained in Fig. 2, S5 and Table S4.

The free carbon atoms generated from a decomposed carbon source on the surface of the catalyst can diffuse in several ways to form graphitic walls, including surface diffusion (diffusion along the surface), bulk diffusion (diffusion through the particle), subsurface diffusion (diffusion from the surface to the subsurface), and subsurface bulk diffusion (diffusion along the layer just below the surface). The theoretical values of activation energies derived from DFT calculations for surface diffusion, bulk diffusion, subsurface diffusion, and subsurface bulk diffusion are 0.19–0.29 eV ($\theta = 0.0625$–0.11 ML), 1.62–1.83 eV, 0.55–0.76 eV ($\theta = 0.0625$–0.11 ML), and 0.86–1.16 eV ($\theta = 0.0625$–0.11 ML) [18,85], where a monolayer (ML) is defined by the atomic density on the Ni(111) surface, and θ is the surface coverage of carbon in the ML. Furthermore, after the formation of graphitic walls, we need to consider an additional diffusion pathway, which is the diffusion at the interface between the grown graphitic wall and the catalyst surface. The activation energies for this interface diffusion can be differentiated depending on whether the grown structure is a CNF or CNT. In the case of a CNF, the interface diffusion is energetically less favorable compared to bulk diffusion [29]. In contrast, for a CNT, the activation energy of interface diffusion is close to that of surface diffusion when the grown walls have zig-zag edges (when they have armchair edges, the activation energy for interface diffusion becomes higher than that of surface diffusion) [28]. Comparing our derived activation energies with the theoretical values from DFT calculations, we infer that subsurface bulk diffusion would be the rate-determining step for CNF and CNT growth in the temperature range of 600–800 °C.

Based on the above findings, looking at each growing structure in more detail, F-CNF at 600 °C could be formed by the simultaneous precipitation of carbon atoms at the rear surface of the catalyst by surface diffusion as well as by subsurface bulk diffusion. Because the surface diffusion would be energetically favorable, the subsurface bulk diffusion would be the rate-determining step during CNF formation. A similar approach could be applied to T-CNF grown at 700 °C. However, at higher temperatures, due to the increased amount of dissolved carbon, the subsurface bulk diffusion to the backside of the particle (side opposite to the growth direction) would be relatively difficult [16], while the interface diffusion would be energetically unfavorable. Hence, a transition from F-CNF to T-CNF is likely to occur. B-CNT growth at 800 °C would be the result of different degrees of contribution from each of the diffusion pathways, which are surface-, interface-, and subsurface bulk diffusion. The main diffusion pathways for the growth of graphitic walls during CNT formation would be the energetically favorable surface diffusion and interface diffusion, and the overall growth would be determined by the subsurface bulk diffusion.

3.5. *Tip-to base-growth mode change during the CNT growth*

At the temperature of 800 °C, in addition to B-CNT growing by tip-growth mode (Fig. 5a), a CNT growing by base-growth mode was also observed (Fig. 5b and Video S7). This growing CNT formed a M-CNT in the shape of a hollow cylinder without having internal closures (knots) which are seen in the general bamboo-type structure. It is generally known that a transition to a base-growth can occur depending either on the particle size or on the catalyst-substrate interaction. However, in our experiment, this transition was seen in particles with sizes ~30 nm. Therefore, under our experimental conditions, we think that this transition could be due to increase in interaction energy with the substrate, since at these temperatures, the catalyst could be in a more molten-like state and the amount of dissolved carbon could be higher [86].

Supplementary video related to this article can be found at https://doi.org/10.1016/j.carbon.2024.118843

4. Conclusion

One of the significances of *in situ* TEM lies in its unique capability to capture novel structural changes at atomic and nano scale. However, what distinguishes our *in situ* TEM experiment is its ability to provide empirical evidence through direct observation of precise changes occurring within the actual growth environment. This offers an understanding of phenomena that have not been adequately comprehended with conventional analytical methods. Typically, such methods depend on theoretical models and simulation outcomes to provide explanations. Our *in situ* TEM experiment offers new understanding on the temperature-dependency of CNF and CNT growth from Ni catalysts, shedding light on aspects that were previously unclear. We developed a new system for introducing ethanol vapor into a MEMS-based closed cell for comprehensive statistical analysis of the growth dynamics of CNFs/CNTs with improved yield for the first time. Direct atomic- and

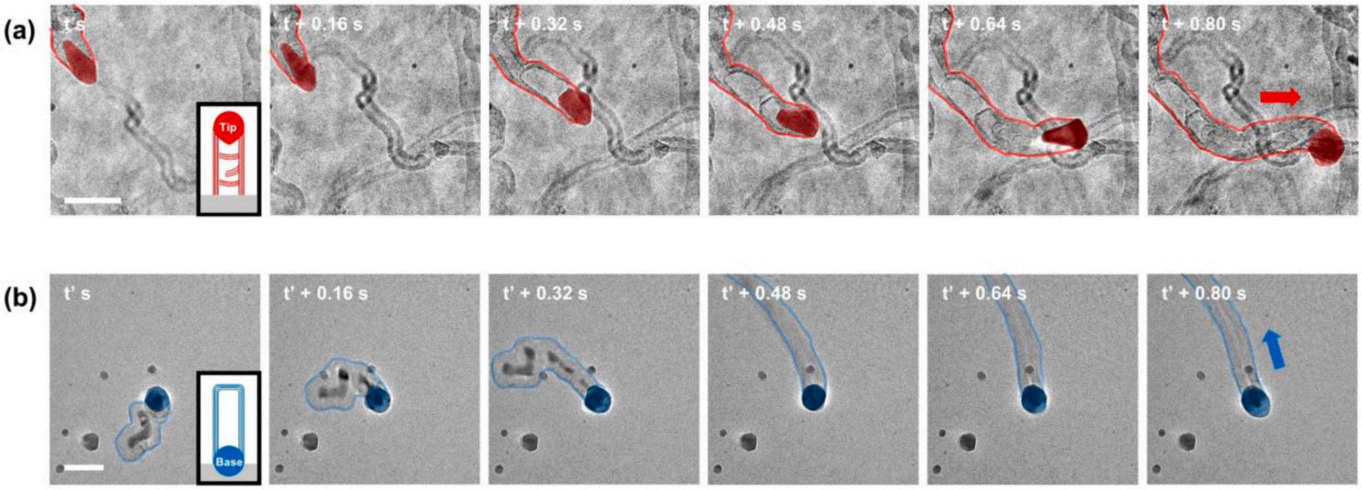

Fig. 5. *In situ* TEM observation of the CNT tip-to base-growth mode change at 800 °C. Sequential TEM images showing (a) a B-CNT growing by tip-growth mode and (b) M-CNT growth through base-growth mode. Scale bars are 50 nm. (A colour version of this figure can be viewed online.)

nanoscale imaging in combination with the complementary spectroscopic analyses revealed temperature-dependence of CNFs/CNTs growth (600–800 °C) at near atmospheric pressure; CNFs and CNTs were formed in the low and high temperature ranges, respectively. Statistical analysis of SAED patterns, using rotationally averaged intensity profiles, demonstrated that the Ni catalyst's active state while the reaction took place was nickel carbide. This finding contradicts earlier assumptions that the catalyst was pure nickel, as reported in other *in situ* TEM studies. The Ni lattice expanded, likely due to increased amount of dissolved carbon during the growth, which could reduce the adhesion force between the graphitic walls and the catalyst. We analyzed the carbon bonding state with respect to temperature by combining *in situ* EELS, post-mortem EELS, XPS, and Raman spectroscopy in a relatively quantitative manner. Combined spectroscopy revealed that the degree of graphitization increased with temperature, which would also contribute to lowering the adhesion force between graphitic wall and the catalyst. These temperature effects may be the reason for the observed structural change from CNF to CNT with increase in temperature. Furthermore, we determined activation energies by analyzing experimental data on the growth rates of CNFs/CNTs with respect to temperature and particle size. Our analysis revealed that subsurface bulk diffusion is the rate-determining step for CNF and CNT growth, which would be affected by the increased carbon concentration depending on the growth temperature. Our findings thus contribute to improving our understanding on the growth mechanisms of CNF and CNT formation under diverse environments, going beyond the limitations of previous studies. A greater understanding of the growth mechanism is expected to enable better structure control and help in setting guidelines to obtain the most ideal structure for a specific application.

CRediT authorship contribution statement

Myeonggi Choe: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization. **Handolsam Chung:** Methodology, Formal analysis, Investigation, Writing – original draft, Visualization. **Wonjun Kim:** Investigation. **Younggeun Jang:** Resources. **Zhaoying Wang:** Formal analysis. **Zonghoon Lee:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2024.118843.

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