Thermal Conversion of Ethanol into Carbon Nanotube Coatings with Adjusted Packing Density

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ABSTRACT: The ability to control the growth of carbon nanotube (CNT) coatings with adjusted packing density is essential for the design of functional devices with an emphasized interaction with the surrounding medium. This challenge is addressed in the present study using an innovative single-pot chemical vapor deposition (CVD) process based on the thermal conversion of ethanol to CNTs. Benefitting from the relatively safe and easily bio-derived carbon source is enabled using a cobalt catalyst and a magnesium oxide promoter. The resulting innovative direct-liquid injection CVD opens up new opportunities for low-temperature CNT deposition. The simultaneous formation of a cobalt catalyst along the process results in a sustainable CNT growth that is substantially emphasized with the deposition time. Furthermore, the formation of these catalyst nanoparticles in the porous structure nucleates new CNTs and results in a substantial film densification. Relative to densely packed CNTs that feature a density exceeding 1000 mg/cm³, the investigated process enables an adjusted density from 0.1 to 20 mg/cm³ with no significant impact on the quality of the obtained multiwalled CNTs. This unprecedented control over the packing density of the CNT film paves the way toward the development of high-performance functional nanocomposite coatings.

1. INTRODUCTION

Carbon nanotubes (CNTs) have attracted great attention in various applications such as chemical and biological sensing, thermal management, and polymer nanocomposites and as black coatings for space applications owing to their high aspect ratio, chemical stability, and electronic and optical properties.

The synthesis of CNTs was reported using different methods such as arc discharge, laser ablation, and chemical vapor deposition (CVD). Thermal CVD has typically retained a considerable attention as an inexpensive mass production method. Not surprising that a massive effort is spent to understand the underlying growth mechanisms on various surfaces and using a variety of catalysts and promoters. Although most of the reported low-temperature CVD growth processes for CNTs demonstrate the plasma activation as an efficient approach, the thermal CVD remains the method of choice.

The low-temperature CVD synthesis usually involves the highly reactive carbon source: acetylene. Although less reactive, alcohols are considered as a promising alternative as high-quality CNTs can be obtained. This advantage results from the simultaneous hydroxyl radical etching of the formed amorphous carbon, which extends the lifetime of the catalyst and yields CNTs with a better quality. The hydroxyl radicals are either issued from the thermolysis of the alcohol or from the implementation of water vapor as an additive. The surface state in the thin-film technology plays a pivotal role in determining the properties of the synthesized coatings. This is particularly true for the growth of CNTs as their formation is a result of a subtle interplay between the catalyst nature and size, surface functional groups, and the carbon source.

An enhancement of the CNT growth was reported with the basicity of the growth surface, which was associated with the preferential conversion of hydrocarbons to fragments susceptible to undergo aromatization. Acid surfaces, however, were shown to favor the formation of nonsuitable complex unsaturated hydrocarbons. This effect was exploited in our previous study, and a single step CNT growth was obtained starting at 330 °C.

Controlling the density of the grown CNTs is an important asset to adapt their suitability for different applications. High-density CNTs are, for instance, suitable for supercapacitors and heat dissipation devices. Whereas sparsely grown CNTs are suitable for functionalization, heterogeneous catalysis, and reinforced composite materials. In the last applications, CNTs are mostly detached from the substrate and suspended in liquids before their processing to achieve the desired density. Other reported approaches are based on the adjustment of the density of the catalyst nanoparticles on the substrate prior the CNT growth.

In the present work, we report on a mechanistic study for an innovative low-temperature growth process where the basic promoter and the catalyst nanoparticles are simultaneously deposited along the conversion of ethanol into CNTs. A focus is given to the possibility to adjust the density of the obtained CNT layer. Understanding the interplay between the
processing parameters and the growth characteristics is of prior importance for any upscaling or further developments.

2. RESULTS AND DISCUSSION

In this study, we do focus on the systematic investigation of the CNT film density as a function of the deposition parameters, an aspect that is usually marginalized despite its importance. This shortcoming is presumably related to the quick deactivation of the catalytic nanoparticle. A deactivation of Co and Fe nanoparticle catalysts was reported after a duration that might be as short as 1 min during the growth of CNTs. The presence of the catalyst in the form of metal carbide is essential to maintain the diffusion of carbon and precipitation of CNTs. To secure a continuous growth of CNTs, the deactivated catalytic nanoparticles need to be substituted without interrupting the process.

The deposition of CNTs was carried out using the ethanol mixed solution of Co(acac)₂ and Mg(acac)₂. Depending on the deposition temperature, ethanol acts as a reducing agent for Co(acac)₂ to produce the catalytic nanoparticle which is in the form of metallic or carbide of cobalt, whereas Mg(acac)₂ yields MgO under the same conditions. Therefore, the process with ethanol mixed solution of Co(acac)₂ and Mg(acac)₂ is expected to form Co–MgO or CoCₓ–MgO depending on the growth temperature. Here, the CNT growth catalyst is identified as being Co or CoCₓ, whereas MgO is identified as the basic growth promoter. The obtained CNT films were characterized using Raman scattering and secondary-ion mass spectrometry (SIMS) methods, and the results are displayed in Figure 1. The depth profile analysis with the SIMS technique shows a regular intensity of carbon across the film. This signal decays abruptly at the interface, where the intensity of elements from the substrate is detected (Si).

The signals attributed to magnesium and cobalt are present all across the film but the intensities in both cases show spikes at the interface. These spikes might be associated with the backward displacement of the Co and MgO nanoparticles during the Cs⁺ bombardment. Such a displacement is certainly favored by the low density of the CNT film. The overall profile, however, indicates clearly that carbon, Co, and Mg are present all across the deposited films.

The quantitative determination of the catalyst “Co” and promoter “Mg” content was assessed by the energy-dispersive X-ray spectroscopy analysis. This analysis reveals representative atomic ratios of

\[
\begin{align*}
\text{Co/(C + Co + Mg)} &= 0.044 \pm 0.004 \\
\text{and Mg/(C + Co + Mg)} &= 0.091 \pm 0.006
\end{align*}
\]

The thermogravimetric analysis, not shown, was performed in air at a ramp of 10 K/min using the as-grown film. The profile reveals a single weight loss step starting at ~290 °C and ending with a plateau at 380 °C. The low-temperature oxidation of the CNT is attributed to the catalytic action of Co₃O₄ formed during the heating step or upon exposure to air. The oxidized cobalt catalyst in addition to MgO results in 9% of the initial mass.

Figure 1. SIMS depth profile (left panel) and Raman surface analysis (right panel) of the as-grown CNT films using a precursor ethanol solution of Mg(acac)₂ and Co(acac)₂. The films are obtained at 485 °C and under a pressure of 7 mbar.

Figure 2. Thickness of the CNTs as a function of deposition time (upper panels) and surface SE-micrographs after 5, 10, and 15 min.
The Raman scattering evidences the two characteristic signals corresponding to the in-plane, G: 1615/cm, and defect-related (D: 1360/cm) vibrations in the CNTs. No features related to radial breading modes are detected, which is an indication of the multiwall structure of the obtained CNTs.36

The continuous supply of the precursor solution (ethanol—Co(acac)2—Mg(acac)2) was investigated at the deposition temperature of 485 °C and the pressure of 7 mbar, while increasing the deposition time from 5 to 180 min. The geometric thickness of the obtained CNT film, displayed in Figure 2, features a trend that diverges significantly from the conventional linear increase of the thickness with the deposition time in CVD processes. In fact, the growth of the CNT is reasonably expected to take place at a constant rate on every single-catalyst nanoparticle: \( v_{CNT} = N_{catalyst} \cdot k_1 \cdot t \), whereas the number of the catalyst nanoparticles increases linearly with time as well; \( N_{catalyst} = k_2 \cdot t \). This situation corresponds to two consecutive reactions with constant rates. On the basis of this assumption, the deposition of the CNT film on the surface is expected to evolve as a function of the square of the time, which is confirmed by the linear trend observed in Figure 2. The linear fit features a coefficient of determination of: \( nR^2 = 0.993 \). The surface scanning electron microscopy (SEM) observation of the grown films after 5, 10, and 15 min shows similar morphology consisting of randomly oriented CNT. This observation confirms the absence of an incubation time, which is in line with the observed kinetics. A high-magnification SEM surface morphology, displayed in Figure 3, shows CNTs diameter around 10 nm. The cross-sectional SEM observation evidences the random nature of the grown CNTs on silicon substrates, while maintaining a uniform overall thickness.

The effect of the temperature from 390 to 630 °C, Figure 4, reveals a window, 450–580 °C, where the grown thickness after 2 h of deposition is maximal. It is worth mentioning that the geometric thickness of the film does not correspond to the length of the individual CNT as they present a random orientation. Therefore, although the temperature effect results in a trend that appears as the conventional three deposition regimes: kinetic, diffusion limited, and thermodynamic; care should be taken for the interpretation of this experimental result.

It is worth reminding that no CNTs grew in the absence of MgO below 500 °C. Therefore, the growth of CNTs can be impacted by any parameter that disturb the synergetic coformation or distribution of the catalyst and the promoter.

The effect of the total pressure on the growth rate was investigated by restricting the pumping capacity, while maintaining a constant inlet flow rate and composition. At a substrate temperature of 485 °C, the pressure was adjusted up to 10 mbar. As displayed in Figure 4, the attained thickness after 2 h of deposition rises linearly with the pressure. While increasing the total pressure, the partial pressures of ethanol, Mg(acac)2, and Co(acac)2 all increase linearly. The obtained trend evidences that the limiting step is a first order in respect to the partial pressure of one of the reactants. This conclusion is further confirmed by the observed linear increase of the grown thickness with the increase of the flow rate (injection time) at a constant pressure.

The mechanistic study reveals an appealing CNT growth temperature window with relatively high and stable growth rate. The deposition rate within this window can be further adjusted by controlling the total pressure in the reactor and the feeding rate of the reactants.

The various investigated parameters have, as seen in Figures 2 and 4, a clear impact of the growth rate assessed by measuring the geometrical thickness of the CNT film. The monitored data, however, do not inform about the packing density of CNTs within the obtained films. Combining the weight gain and the geometrical thickness enabled assessing the film density as a function of all investigated parameters. The assessed data highlight various trends with the processing parameters. One illustrative example, effect of the deposition time, is provided in Figure 5. This example shows a substantial

Figure 3. SEM cross-sectional micrographs of CNTs after different deposition times and a high-magnification representative surface morphology.

Figure 4. Effect of the deposition temperature, pressure, and injection time (from left to right) on the deposited thickness of CNT after 2 h of deposition.

Figure 5. Density (\( \rho \)) of CNT films as a function of their thickness (\( d \)) for different deposition durations (\( t \)), pressures, temperatures, and injection opening times. The error bars correspond to the calculated uncertainty based on the precision at determining the mass and thickness of the film.
increase of the film density with the increase of the deposition time, an increase that could be fitted with a power law. The analysis of the various trends, however, reveals that the key parameter influencing the density of the film is their thickness. Figure 5 displays the log–log plot of the density of the obtained films as a function of their thickness regardless of the investigated processing parameter. A single trend could be identified with a power law with the exponent: $1.9 \pm 0.2$. It is worth noticing that the individual CNTs nucleate on the catalytic nanoparticle that are continuously deposited along the process on the substrate and also as a decoration of the formed CNTs. Therefore, the growth of CNTs contributes to the rise of the geometrical thickness and also to the densification of the film via infiltration.

The overall study shows that the density of the CNT films is very low relative to the densely packed vertically aligned CNTs. The last lies typically around 30 mg/cm$^3$ using various chemistries, a density that was raised to 570 mg/cm$^3$ using liquid-mediated zipping.$^{37}$ Efforts were reported on the densification of the as-grown CNTs via the catalyst layer engineering using a CVD process based on the catalytic decomposition of $\text{C}_2\text{H}_2$. These results are highlighted in Figure 6. A density of 300 mg/cm$^3$ was reported for the grown CNT at 600 °C using a TiSiN buffer layer to limit the bulk diffusion of the catalyst and an upper discontinuous aluminum layer to limit its lateral diffusion.$^{38}$ With a growth at 700 °C, a CNT density of 250–350 mg/cm$^3$ was obtained using a sputtered catalyst stack: $\text{Al}/\text{Fe}/\text{Al}$. At a higher deposition temperature, 750 °C, and using a consecutive catalyst deposition approach, a film density of ∼1000 mg/cm$^3$ was attained.$^{40}$ Probably, the highest reported CNT film density is 1600 mg/cm$^3$, which was reached at 450 °C using a stack of $\text{SiO}_2$, $\text{Cu}$, $\text{Ti}$, $\text{Mo}$, and $\text{Co}$ layers as a catalyst prior thermal treatment.$^{41}$

It is worth noting that the present study enables attaining a substantially contrasting density range. The possibility to adjust this parameter is in line with the controlled infiltration and densification upon the rise of the thickness. A 2 orders of magnitude change of the density is observed with the variation of the thickness, which is a considerable asset for the adaptation of the film properties to various applications.

This flexible approach contrasts greatly with those based primarily on the control of the density of the initial catalyst nanoparticles prior the CNT formation.$^{24,40,42}$ The last is limited by the commonly observed deactivation of the catalyst.$^{30}$ The density tuning as observed in Figure 5 is, however, limited by the coupled thickness-density dependency, and it is challenging to perceive thick films with a very low density. This drawback can be overcome for applications where a matrix or core/shell structure is needed. In this case, the sequential deposition of the CNTs and of the matrix enables decoupling the thickness-density dependency.

Raman spectroscopy was used to evaluate the effect of the processing parameters on the quality of the as-deposited CNTs. High values of the ratio of the signals, $I_d/I_g$, inform about the high crystallinity in the obtained CNTs. The integrated peaks from Raman spectra, Figure 6, are displayed for all deposited CNTs while varying the temperature, pressure, deposition time, and the precursor injection time. The deposition parameters are represented between the 0 and 1 to delimit the explored range. For this purpose, the injection opening times (4, 5, 6, 7, and 10 ms) were divided by 10 ms and the deposition pressures (3, 4, 5, 7, 9, and 10 mbar) were divided by 10 mbar. Similarly deposition temperatures (390, 420, 450, 485, 530, and 580 °C) were divided by 580 °C and deposition durations (30, 40, 60, 90, 120, 150, and 180 min) by 180 min.

As shown in Figure 6, the ratio $I_d/I_g$ features values between 1.2 and 1.8 irrespective of the deposition parameters. This observation confirms that the quality of the outer layers of the CNTs is not sensitive to the deposition parameters within the investigated ranges. The reported transmission electron microscopy observations show indeed that the MgO-promoted CNT growth yields CNTs with the defect-rich outer surface.$^{6}$

3. CONCLUSIONS

A mechanistic study was performed for the growth of randomly oriented CNTs from the thermal conversion of ethanol on the cobalt catalyst and using MgO as a promoter. The process enables a wide temperature window where the growth rate is significantly high. The grown thickness is shown to follow a power law kinetics, which was associated with the rise of the number of catalyst particles with the deposition time. The formation of these nanoparticles within the bulk of the porous film enables a densification that correlates essentially with the film thickness. The control of the film density within 2 orders of magnitude is unprecedented for the CVD growth of CNTs. This densification is insensitive to the processing parameters and does not influence the quality of the obtained CNTs.

4. EXPERIMENTAL SECTION

Films of CNTs were grown on 4″ silicon wafers by direct liquid injection CVD in a custom-built cold wall, vertical stagnation point flow reactor. Ethanol solution containing 0.6 × 10$^{-3}$ mol L$^{-1}$ cobalt acetylacetonate ($\text{Co}(\text{acac})_2$) and 0.6 × 10$^{-3}$ mol L$^{-1}$ magnesium acetylacetonate ($\text{Mg}(\text{acac})_2$) was used as the precursor. The injection of the single mixed precursors’ feedstock was performed as a pulsed spray using a frequency of 4 Hz and opening times adjusted between 4 and 10 ms. The injection was performed in an evaporation tube maintained at 220 °C. The substrates were maintained at a constant temperature between 380 and 630 °C during deposition. Nitrogen was used as the buffer gas at a flow rate of 550 sccm, whereas the chamber pressure was adjusted in the range of 3–10 mbar. The standard time of deposition was set at 2 h except when investigating the growth kinetics at 485 °C, where the deposition time was varied from 5 to 180 min.

The thickness of the obtained films was measured using an Alpha Step D-500 profilometer from KLA-Tencor. Cross-
sectional microscopic investigations of as-grown CNTs were carried out on a Hitachi SU-70 FE-SEM, whereas the surface morphology was inspected by SEM (FEI Helios NanoLab 650) at a working distance of 4 mm and an accelerating voltage of 5 kV. Raman spectroscopy was performed using an inVia Raman spectrometer from Renishaw with a 532 nm laser at a power of 0.44 mW to avoid noncontrolled surface heating. The SIMS was performed, on an area of 60 μm in diameter, using SC-Ultra with a primary Cs+ beam at an incidence of 63.2°. The current and energy of the beam were fixed at 25 nA and 5.5 keV, respectively, during the depth profile analysis. The detected positive ions are MCs with $x = 1$ or 2.

The density of the grown film was assessed from the combined geometric thickness obtained by cross-sectional microscopy ($t_{\text{CNT}}$) and the specific mass gain due to deposition.

$$\text{Density of CNTs} (\rho) = \frac{m_2 - m_1}{A \times d}, \text{mg/cm}^3$$

where $m_1$ and $m_2$ are the masses of the substrate before and after coating, respectively, whereas $A$ is the coated surface and $d$ is the thickness of coated film.

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**Notes**

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