Cobalt Catalyzed Carbon Nanotube Growth on Graphitic Paper Supports

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Abstract: The catalytic growth of multi-wall carbon nanotubes on carbon paper is reported. The study employed three cobalt carbonyl clusters as catalyst precursors. These were deposited on graphitic paper prior to chemical vapour deposition (CVD) of methane or ethylene. The clusters show differentiated growth behaviour in accordance with precursor size, and with Co₂(CO)₈ displaying additional activity in the growth of helical nanotube structures. We therefore report an approach for the decoration of graphitic papers with carbon nanotubes with a view to the production of high area supports.

Keywords: Molecular catalyst precursors, cluster seed size, nanotube growth.

1. INTRODUCTION

Since their identification by Iijima in 1991 [1], carbon nanotubes (CNTs) have been the subject of intensive research owing to their unique electronic and mechanical properties [2]. While various synthetic strategies for their production have been devised, chemical vapor deposition (CVD) has been established as one of the more commonly used techniques by virtue of its versatility in terms of the effect of experimental parameters (such as flow speed and composition of the gaseous carbon precursors, deposition temperature and time) on the type of CNTs produced. Nevertheless, the development of procedures that are able to achieve sufficient morphological and structural product control remains an ongoing challenge. This is, on the one hand, due to there being an as yet incomplete understanding of the tube formation mechanism and, on the other hand, groups reporting a lack of control over catalyst morphology. The result of these issues is that irregular tube structures are generally obtained. In the case of morphological control, both experimental and computational studies have demonstrated the importance of catalyst particle size in influencing the resulting tube diameters [3]. More fundamentally, particle diameters in the nanometer regime are known to affect the metal melting point through the Gibbs-Thomson effect. In addition, the temperature at which liquefaction of nanoparticulate species occurs (and which can be assumed to influence the agglomeration behaviour), has been shown to depend on saturation of the metal species with carbon [4]. These issues pose intrinsic problems in that it is not trivial to maintain narrow particle size distributions for commonly employed nanoparticulate catalysts derived from either physical vapour deposition or wet chemical methods (such as sputtering and metal salt reduction). In seeking to overcome these limitations, researchers have more recently focused on the employment of molecular clusters as catalyst precursors, and on the deposition of these on various supports. Most notably, use of the high pressure carbon monoxide (HiPco) process to produce single-walled carbon nanotubes (SWCNTs) using iron pentacarbonyl has offered control over nanotube yield and morphology by means of controlling the deposition parameters [5].

In recent years, considerable effort has been directed towards addressing both the issue of seed size control and the development of a wider range of suitable supports with which to provide CNT-based high surface area systems. In this context, some of the present authors have previously reported CNT syntheses using both nickel formate precursors and colloidal cobalt nanoparticles on supports ranging from silicon wafers to stainless steel [6]. Furthermore, we have recently sought to control both seed dispersity and the resulting tube morphology via the use of dendrimer-capped Co₃₂ nano-clusters [7]. This work demonstrated the matching of cluster seed size to tube diameters for the growth of SWCNTs.

To the best of our knowledge, Keller et al. report the only application of molecular cobalt carbonyl clusters as precursors to carbon nanotube growth thus far [8]. Our studies systematically investigate three molecular cobalt carbonyl clusters as catalyst precursors: namely dicobalt octacarbonyl (Co₂(CO)₈, 1) [9], chloromethylidyne tricobalt nonacarbonyl (Co₃(CO)₉(C₂H₇), 2) [10] and tetracobalt dodecacarbonyl (Co₄(CO)₁₂, 3) [11]. We have investigated each of the three precursors under differing conditions using graphitic paper (“Toray® paper”) as the support system. By these means, we have been able to demonstrate that tube morphologies and yields can be controlled as a function of cluster size. Simultaneously, we present CNT decorated graphitic paper as a novel and, as yet, little explored high surface area support that offers potential advantages in both catalytic and fuel-cell applications. The increase in specific surface area in combination with the well-known advantages of graphitic papers (such as their high mechanical strength and permeability) may prove advantageous where membrane properties offer a lead over conventional heterogeneous systems [12]. By way of an example, such enhanced graphitic materials may find application in fuel-cell technology, where carbon paper based membrane systems are currently in use [13]. The possibility of decorating such membranes with carbon nanotubes (with defined areal densities and morphologies) suggests a convenient route by which to fine-tune their permeable properties.

2. MATERIALS AND METHODS

An overview of the experimental details is presented in Table 1. In all experiments, commercially available graphitic paper (Toray paper 060, Toray Industries) was used. While 1 was purchased commercially, 2 and 3 were synthesized [10, 11]. For catalyst deposition, amounts of clusters corresponding to 1 weight-% of the metal relative to carbon support were dissolved in 5 ml of freshly distilled solvent prior to stirring in an inert atmosphere for either 1 or 24 h.

The cluster-decorated carbon support was dried in vacuo and heated in a tubular furnace for 10 min at flow speeds of 0.2 l·min⁻¹ (precursor gas) and 0.7 l·min⁻¹ (argon). Samples were measured by HRSEM and, for the purpose of investigating the tube growth mechanism, by HRSTEM. In both cases, analysis was performed using a Hitachi S-5500 cold field emission scanning electron microscope with an integrated BSE and BF/DF DUO-STEM detector and an Oxford Instruments EDS (Energy Dispersive X-ray Emission Spectroscopy) system.
Spectroscopy) system. Measurements were made at accelerating voltages of between 2 and 10 kV and with a lateral resolution of around 1.5 nm. Images were taken in secondary electron, bright field and dark field modes. While STEM is similar to SEM, it allows extra surface information to be obtained by monitoring secondary electrons, with cross-sectional information being gathered in bright field mode, and high-angle dark field images allowing selective monitoring of the catalyst particles relative to the carbon background. Elemental compositions were analyzed in tandem with all EM methods by EDS and EDS mapping. HRTEM samples were prepared by sonicating the CNT coated carbon paper samples in abs. ethanol (Sigma-Aldrich) for 5 min and then droplet coating Cu TEM-grids (Agar-Scientific, 300 mesh, carbon holey film) with the resulting nanotube suspension. The measurements were done on a JEOL JEM-3011 high-resolution transmission electron microscope at nominal magnifications in the range 300,000-800,000. The exact magnification was previously characterized using images of lattice fringes in large (> 10 nm) particles of colloidal gold. The electron optical parameters were $C_0 = 0.6$ mm, $C_C = 1.2$ mm, electron energy spread = 1.5 eV and beam divergence semi-angle = 1 mrad. Elemental composition was elucidated by EDS (nominal beam width = 4 nm) using a PGT prism Si/Li detector and an Avalon 2000 analytical system. Raman measurements were performed using a Ramascope-1000 with a spectral resolution of 0.1 cm$^{-1}$ and a spatial resolution of 1 μm. The system was operated in conjunction with a microscope and a video camera. Laser radiation ($λ=633 nm$) was used as the excitation source employing a holographic notch-filter with a cut-off at ~100 cm$^{-1}$. To allow direct comparison, the spectra displayed in the figures were subjected to neither normalization nor background subtraction. Thermogravimetric and differential calorimetric measurements were performed on a TGA/SDTA851e and a DSC27HP spectrometer, respectively. In both cases, spectra were measured under an argon atmosphere at atmospheric pressure using heating rates of 1 °C min$^{-1}$ and 10 °C min$^{-1}$.

### 3. RESULTS

Prior to CVD treatment, all as-prepared samples were investigated by HRSEM (Fig. 1). All samples displayed agglomeration of individual molecular clusters, while deposition from dichloromethane solution led to decreasing agglomerate sizes that correlated with the molecular precursor from 570±44 nm for 1 to 197±13 nm and 146±11 nm for 2 and 3, respectively. An initial SEM analysis of the CNT samples grown at 750 °C (Fig. 2) reflects this trend in terms of the resulting tube morphology showing a decrease in both average CNT length and diameter from precursors 1 to 3. Interestingly, for the dichloromethane deposited samples, SEM reveals an evenly nanotube-coated support for catalyst 2 with ethylene as a carbon feedstock (d). With the same carbon precursor, 3 develops a notably lower tube density (f), whereas methane remains inactive as a carbon source for growth experiments involving either 2 or 3. For the C$_2$-cluster 1, isolated patches of tubes predominate for the ethylene feedstock (b), with similar growth activity noted for methane (a). Additionally, 1 shows limited activity in the growth of helical tubes (Fig. 3), which remain a minority product, as the low-magnification image (Fig. 3b) shows. To further investigate the growth process and, specifically, the role of the catalyst, selected experiments were repeated at a lower CVD deposition temperature of 650 °C, with THF employed as an alternative solvent for cluster deposition, in order to attempt to enhance control over cluster agglomeration. Among the samples grown at 650 °C, the highest growth activities were found in cases where ethylene was used as the carbon source. Those samples in which catalyst precursors 2 and 3 were deposited on the support from dichloromethane (experiments 8 and 13) were found to produce notable tube yields, however, under comparable conditions, the use of 1 lead to the observation of only sparse CNT coatings. Under these experimental conditions, generally smaller mean seed sizes were observed.

### Table 1. Summary of the Experimental Data

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Co Source</th>
<th>Solvent$^a$</th>
<th>CVD Temp. (°C)$^b$</th>
<th>Precursor Gas</th>
<th>CNT Length (μm)</th>
<th>CNT Diameter (nm)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>CH$_2$Cl$_2$</td>
<td>750</td>
<td>CH$_4$</td>
<td>2.9±0.4</td>
<td>44±7.4</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>CH$_2$Cl$_2$</td>
<td>750</td>
<td>C$_2$H$_4$</td>
<td>6.1±1.0</td>
<td>34±4.4</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>CH$_2$Cl$_2$</td>
<td>650</td>
<td>C$_2$H$_4$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>THF</td>
<td>750</td>
<td>CH$_4$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>THF</td>
<td>750</td>
<td>C$_2$H$_4$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>CH$_2$Cl$_2$</td>
<td>750</td>
<td>CH$_4$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>CH$_2$Cl$_2$</td>
<td>750</td>
<td>C$_2$H$_4$</td>
<td>2.3±0.5</td>
<td>35±8.4</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>CH$_2$Cl$_2$</td>
<td>650</td>
<td>C$_2$H$_4$</td>
<td>2.2±0.5</td>
<td>21±2.6</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>THF</td>
<td>650</td>
<td>C$_2$H$_4$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>THF</td>
<td>750</td>
<td>C$_2$H$_4$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>CH$_2$Cl$_2$</td>
<td>750</td>
<td>CH$_4$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>CH$_2$Cl$_2$</td>
<td>750</td>
<td>C$_2$H$_4$</td>
<td>0.8±0.1</td>
<td>18±1.9</td>
</tr>
<tr>
<td>13</td>
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<td>CH$_2$Cl$_2$</td>
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<td>C$_2$H$_4$</td>
<td>0.7±0.1</td>
<td>21±1.1</td>
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<tr>
<td>14</td>
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<td>650</td>
<td>C$_2$H$_4$</td>
<td>0.54±0.03</td>
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<td>15</td>
<td>3</td>
<td>THF</td>
<td>750</td>
<td>C$_2$H$_4$</td>
<td>0.58±0.2</td>
<td>22±1.3</td>
</tr>
</tbody>
</table>

$^a$metal/support weight ratio = 0.01.
$^b$CVD deposition time: 10 min.
Catalyst deposition time = 24h.
although only few and isolated areas of CNT growth resulted. Despite this general trend, experiment 13 (3 deposited from CH₂Cl₂, CVD temperature 650 °C), showed the highest CNT yields obtained in this series of experiments. It is noteworthy that at the higher deposition temperature of 750 °C, an increased density of tubes was also observed for precursor 3.

Representative samples that showed CNT growth activity were investigated by HRTEM and laser Raman spectroscopy in order to qualitatively analyze the graphite lattice for defects. In order to investigate the decomposition of cobalt clusters and their transition into the metallic state, 1-3 were investigated by thermogravimetric analysis in conjunction with differential scanning calorimetry. Laser Raman spectroscopy (Fig. 4) showed small peaks at 469 cm⁻¹, 673 cm⁻¹ and 505 cm⁻¹ (not displayed) next to the characteristic D, G and D' bands of graphitic materials. These are attributable to traces of Co₃O₄, which result from catalyst oxidation subsequent to CVD treatment [13]. D-band and G-band peaks at 1329 cm⁻¹ and 1579 cm⁻¹ were found for the products using precursors 1 and 2, whereas the corresponding values for cobalt cluster 3 were 1330 cm⁻¹ and 1584 cm⁻¹, respectively. Thermal analyses (Fig. 5) revealed endothermic peaks at 52.7 °C and 149.0 °C (DSC) for precursor 1. By comparison with the corresponding Thermogravimetric (TGA) spectra, these signals may be ascribed to cluster decomposition. The gradual ligand loss most likely proceeds initially via dissociation of the bridging and only subsequently via the loss of the terminal carbonyl ligands. The corresponding temperatures found for precursors 2 and 3 are 139.1 °C and 165.1 °C, respectively. Although under the given TGA measurement conditions, a distinction between individual ligand dissociation steps cannot be made for 2 and 3, additional processes take place at 86.1 °C, 162.8 °C and 182.9 °C for 2 and 80.3 and 105.2 °C for 3. As TGA analysis suggests the latter processes not to be linked to any mass losses of the clusters, they may correspond to crystallographic reformation processes.

4. DISCUSSION

The growth of CNTs is dependent on a number of complex interactions. Not insignificant are the choice of carbon feedstock and the temperature at which deposition occurs. In addition, significant dependencies also arise from the electronic influence of the supporting medium on both the nature of the catalytic species and nanoparticle seed sizes. Not surprisingly, a correlation is noted between seed size and the diameters/lengths of the resulting nanotubes.

Data here are in clear agreement with previous reports, which demonstrate such relationships for similar experimental conditions, e.g. the use of colloidal cobalt particles in conjunction with PECVD 4 [6e, 14]. To propose a mechanism by which nanotube growth occurs we must consider the interaction between the graphitic support, the molecular precursor and subsequently the metallic particles that result from the deposition process. In this regard, in most cases TEM (Fig. 2, insets) and STEM (Fig. 6) indicate a tip-growth mechanism for the three clusters [15], substantiating a weak metal-support interaction under the experimental conditions reported here. The observation of catalytic agglomerates up to several hundred nm wide both before and after CVD treatment (see Fig. 3) further supports this growth mechanism. Hence, for a strong metal-support interaction (i.e., bond formation between the metal precursor and the support surface) the resulting seed sizes would be expected to display both lower mean values and better dispersities, since seed separation would occur at the stage of initial contact between the precursor and the support upon deposition [2a]. In the present case, the tubes were generally found to be capped with the catalyst metal, embedded into several layers of graphene. The kinetics of catalyst deactivation by means of carbon deposition on the seed particles should thus determine the lengths of the resulting tubes. Conspicuously, especially in cases where seeds showed a significant tendency to sinter, tubes show considerable variation in tip seed sizes (Fig. 6b, d, f), suggesting that agglomerates consist of smaller precursor particles of varying morphology and crystallographic composition. Therefore, seeds of different sizes may become available for tube growth depending on the choice of molecular precursor and the initial deposition conditions [16].

Fig. (7) shows the variations in Raman D/G band intensity ratios I_D/I_G for the growth experiments from dichloromethane at 750 °C ranging from 0.93 (experiment 2) using precursor 1, to 0.52 (experiment 7) using precursor 2 and 0.71 for precursor 3 (experiment...
Fig. (2). HRSEM and selected HRTEM (inset; scale bar: 5nm) images of the samples deposited from CH₂Cl₂ and grown at either 750 °C (a-f) or 650 °C (g-h); see Table 1, precursor and carbon feedstock in brackets.) Experiment: (a) 1 (1, CH₄), (b) 2 (1, C₂H₄), (c) 6 (2, CH₄), (d) 7 (2, C₂H₄), (e) 11 (3, CH₄), (f) 12 (3, C₂H₄) and (g-h) 13 (3, C₂H₄, (g shown at higher magnification than h)).
In agreement with the results obtained from the electron microscopic analysis, this data confirms a maximum of graphitized carbon relative to amorphous and disordered carbon depositions for precursor 2 [17]. In comparison, the corresponding value for experiment 13 was found to be 1.21, suggesting that CVD temperatures higher than 650 °C are necessary to energetically favour C-atom diffusion towards the growing tube relative to its amorphous deposition on the seeds. Comparing DSC with the results of the thermogravimetric measurements, it becomes obvious that the relevant stages in the formation of the metallic seeds (the naked cluster in the metallic state) from their molecular precursors involve loss of the ligand sphere, and that this may take place in several steps. While the temperatures at which ligand loss occurs can be clearly identified from TGA results, which show stoichiometric agreement with the corresponding ligand sphere (the first endothermic peaks), we assume that subsequent peaks correspond to crystallographic rearrangements that are eventually followed by a melting process at higher temperatures. Unfortunately, this last step could not be measured owing to instrument limitations.

As the initial seed sizes (Fig. 1) show, when taken in conjunction

**Fig. (3).** HRSEM images of helical multi-wall carbon nanotubes from experiment 2 (precursor 1 in CH₂Cl₂, CVD temp. 750 °C, carbon feedstock C₂H₄), accelerating voltage: 3.0 kV. (a) magnification 18,000, (b) magnification 70,000.

**Fig. (4).** Laser Raman spectra for experiments (a) 2, (b) 7, (c) 12 and (d) 13. Peak assignment (cf. Fig. 4a): D (1329-1330 cm⁻¹), G (1579-1584 cm⁻¹) and D' (2661 cm⁻¹).

**Fig. (5).** DSC (—) and TGA (---) spectra of (a) 1, (b) 2 and (c) 3.
with the observed tube dimensions (Table 1), the particle sintering process occurs predominantly at the stage of cluster deposition. However, the final CNT growth kinetics will be co-determined by the melting points of the naked clusters. The melting of transition metal nanoparticles is known to depend, most importantly, on the size of the agglomerate itself [18]. This is described by the Gibbs-Thompson equation:

\[ T_m(r) = T_m^{\text{bulk}} \left[ 1 - \frac{2\gamma K(r)}{\Delta H} \right] \]

in which \( T_m^{\text{bulk}} \) is the bulk melting temperature, \( \Delta H \) the latent heat per unit volume, \( \gamma \) the metal/support interfacial tension and \( K \) is reciprocally dependent on \( r \), the particle radius. Consequently, a

Fig. (6). HRSTEM images of two examples of nanotubes (experiment 9, left and right column; magnifications 220,000 and 350,000, respectively). Secondary electron (a-b), high-angle dark field (c-d) and bright field images (e-f).
melting point depression can be expected for decreasing particle sizes. Furthermore, carbon-saturated binary cobalt phases are known to show an additional decrease in melting point relative to bulk cobalt [19]. However, although both the initial seed sizes and resulting tube dimensions show a steady trend, we believe that a decreased degree of seed crystallinity might be responsible for the maximum in tube yield observed for precursor 2 (at a CVD temperature of 750 °C, experiment 7). Similar effects are proposed to play a role for 3 at the lower deposition temperature of 650 °C. In this context, Helveg et al. have previously noted metallic step edges to be energetically favorable for CNT growth [20], whilst interaction between graphene and Co(0 0 1)nop crystallographic planes have been reported to be favored by Shibuta et al. [21]. In consequence, we believe that, over and above particle agglomeration and the melting process exhibited by the metallic core, the crystallinity of the agglomerate is also a function of catalyst precursor and CVD temperature. The upshot of this is that polycrystalline areas are likely to predominate in cases such as experiment 7 (precursor 2 at a CVD temperature of 750 °C) and experiment 13 (precursor 3 at 650 °C), while further coalescence takes place with precursors 1/3 at 750 °C and 1/2 at 650 °C. Furthermore, the generation of small quantities of coiled carbon nanotubes for catalyst precursor 1 at 750 °C raises questions as to whether similar crystallographic disorder might be responsible for these byproducts. In this vein, such structures are presently known to require anisotropic carbon extrusion leading to the insertion of C5–C7 pairs into hexagonal carbon rings [22].

5. CONCLUSION

In summary, we have shown that molecular cobalt carbonyls can be used as precursors to carbon nanotube growth catalysts. By varying the nuclearities of the cobalt carbonyl complex substrates, we have been able to demonstrate the possibility of controlling both the morphology and yield of multi-wall carbon nanotubes. Simultaneously, we have shown the potential of graphitic Toray paper as a support system for surface area enhancement.

We are currently pursuing further enhancements of the systems described, focusing on the improvement of seed size control by means of support functionalization. In order to better understand the CNT growth mechanism, we are initiating the computational modelling by semi-empirical and density functional methods of both the molecular cluster decomposition process and the influence of metal-support interaction on tube morphologies. Investigations will ultimately focus on the development of precisely fabricated systems for deployment in membrane applications relevant to fuel cell technology and industrial scale heterogeneous catalysis.

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