Short Communication

Purity-controllable growth of bamboo-like multi-walled carbon nanotubes over copper-based catalysts

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A R T I C L E   I N F O

Article history:
Received 3 December 2012
Received in revised form 11 January 2013
Accepted 16 January 2013
Available online 1 February 2013

Keywords:
Purity-controllable
Bamboo-like
Carbon nanotubes
Copper catalysts

A B S T R A C T

The growth of bamboo-like multi-walled carbon nanotubes (CNTs) without the formation of amorphous carbons was performed using copper-based catalysts by catalytic chemical vapour deposition (CVD) with diluted ethylene at 700–900 °C. The as-grown CNT soot was characterised by transmission electron microscopy, thermogravimetric analysis and Raman spectroscopy. The weak metal–support interaction of a sulphate-assisted copper catalyst (CuSO4/γ-Al2O3) can provide high-purity growth with remarkable yields of CNTs (2.24–6.10 CNT/g Cu·h) at 850–900 °C. Additionally, hydrogen-assisted CVD can activate inert copper catalysts, e.g., Cu(NO3)2/γ-Al2O3 or Cu(CH3COO)2/γ-Al2O3, for the growth of CNTs.

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1. Introduction

The growth of carbon nanotubes (CNTs) has been intensively studied for more than 20 years. Nevertheless, the formation mechanism of CNTs is not yet fully understood despite recent advances in the growth of CNTs [1–3]. Structure-uncontrollable processes, low synthetic efficiency and undesired by-products (e.g., amorphous carbon (a-C) and metal nanoparticles (NPs)) are three major challenges that limit the development of CNTs and further applications. Catalytic chemical vapour deposition (CCVD) is a promising route to solve the above-mentioned problems that has presented many new concepts [1–5]. Conventionally, CCVD using iron-group metal catalysts has greatly improved most of the aforementioned problems, namely structural control (e.g., chirality of single-walled CNTs (SWCNTs) [4]) and the growth efficiency of CNTs [5]. Although the preparation of high-purity CNTs is not currently a problem, most studies have discussed the optimum conditions for removing metal NPs instead of a-C, which will remain an uncertainty in further applications, especially in electronic devices.

Recently, new progress in CNT growth using copper-group (Cu, Ag and Au) metal elements has been reported regarding the synthesis of SWCNTs in the temperature range of 750–950 °C [6–9]. The main factors affecting the growth of CNTs using copper-group metals are the size of metal clusters and possibly the solubility of carbon on the nano-scale and the chemical composition of the metal catalysts [6,7]. Additionally, previous studies have noted that copper catalysts are sensitive to carbon sources in growing CNTs [8,10]. In fact, copper-based metal catalysts are sensitive to carbon sources and to the structural composition of growing CNTs, which is why diverse results have been obtained even for copper catalysts prepared using a similar procedure with the same catalysts precursors or under similar CNT growth conditions [6–13].

In our previous study, we found that the sulphated-assisted copper catalyst CuSO4/γ-Al2O3 exhibited high CNT growth activity (2.3 g CNT/g Cu·h) at 750–850 °C through a synergistic interaction between Cu NPs, SO4 2− and Al2O3 during CVD [8]. This finding suggests that if copper NPs can be fixed in typical thermally stable structures, it will effectively lead to a high activity for CNT growth. Nevertheless, one major weakness of this study is the high ratio of a-C/CNTs (20–55%) observed in the as-grown CNT soot over CuSO4/γ-Al2O3 catalysts.

Here, we aimed to achieve high-yield CNT growth without the production of a-C through two simple adjustments: (1) by replacing the γ-Al2O3 support with amorphous SiO2 and (2) by adding hydrogen to the carbon feedstock. These two adjustments produced bamboo-like CNTs of extra-high purity (approximately 100%) with a remarkable growth yield of 6.10 g CNT/g Cu·h. These findings provide new insights into CNT growth using non-magnetic metal nanoparticles. In addition, the synthesis of CNTs on Cu NPs without a-C represents a new in-situ technology for developing electronic devices, e.g., field emitters [14] or lithium-ion battery [15], without the electromagnetic interference associated with conventional iron-group catalysts.

2. Experimental

Copper catalysts were prepared by impregnating metal oxide supports (γ-Al2O3 (132 m2/g), Degussa Co. and SiO2 (254 m2/g), Cabot Co.) with the required amounts of the following aqueous solutions:
CuSO4·5H2O (99.9%, Aldrich), Cu(NO3)2·3H2O (99.9%, Aldrich) or Cu(CH3COO)2·H2O (99.9%, Aldrich). The initial ratio of copper in the catalysts was fixed at approximately 10 wt.% for each sample and further quantified by inductively coupled plasma mass spectrometry (PE-SCIX ELAB 6100 DRC) to be 10.2 wt.% for CuSO4/γ-Al2O3, 9.9 wt.% for CuO/SiO2 and 10.1 wt.% for Cu(NO3)2/SiO2. Prior to CNT growth via the CVD process, the prepared samples were dried in oven at 120 °C for 16 h without any oxidation or reduction treatments.

The CNTs were synthesised in a fixed-bed quartz tube reactor (1 cm in outer diameter and 20 cm in length). Typically, a catalyst sample (approximately 100 mg) was placed in the reactor and heated to the required temperatures (500–900 °C) under helium flow (40 mL/min). Once the synthesis temperature was reached, the reaction was initiated by introducing a flowing C2H4/He mixture (flow rate = 100 mL/min, C2H4/He ratio at 1:9) over the required time periods.

The CNT yield and the amount of amorphous carbon were characterised by thermogravimetric analysis (TGA, TA Q500) according to previous studies [8,16]. A parametric study for the CNT growth over various copper catalysts is shown in Table 1. A transmission electron microscope (TEM, JEOL-JEM 2100) was used to investigate the structural morphologies of the as-grown CNTs. Raman scattering spectroscopy (JOBIN-YVON T64000) with a laser excitation wavelength of 532 nm was used.

3. Results and discussion

TEM micrographs of the as-grown CNTs or a-C produced using various copper-based catalysts are shown in Fig. 1a–c. In a blank test, we did not observe any forms of carbon species deposited on pure γ-Al2O3 at elevated temperatures under the same CVD conditions. It was noted that a stronger metal-support interaction (MSI) between sulphated-Cu NPs and γ-Al2O3 could improve the decomposition rate of the hydrocarbons and the diffusion rate of the deposited carbon species simultaneously [16]. Therefore, a weak MSI effect for the copper catalysts should improve the problem of a-C formation. Interestingly, when we replaced the γ-Al2O3 support with amorphous SiO2, the growth of unwanted a-C was effectively terminated, as shown in Fig. 1h. Bamboo-like MWCNTs are the main products, with the outer diameters of the tubes ranging from 20 to 80 nm for those grown over the CuSO4/SiO2 catalysts. However, when Cu(NO3)2 or Cu(CH3COO)2 were used as the catalyst precursors, regardless of whether the support was SiO2 or γ-Al2O3, only a-C-covered Cu NPs were observed after CVD with diluted ethylene. Typical and magnified TEM images are shown in Fig. 1c–d. The images show that free-standing Cu NPs in non-structure-stabilised copper catalysts, e.g., Cu(NO3)2/SiO2 and Cu(CH3COO)2/SiO2, could easily deactivate during the CVD process. In our previous studies [8,16,17], we found that copper catalysts prepared by impregnating various copper precursors, such as Cu(NO3)2·Cu(CH3COO)2 or Cu(thd)2 (thd = 2,2,6,6-tetramethyl-3,5-heptanediionate), on amorphous SiO2, Al2O3 or silicon wafer will form copper catalysts with free-standing Cu NPs, which only generated a-C after ethylene CVD process at 750–900 °C. However, structure-stabilised copper catalysts, e.g., CuSO4/γ-Al2O3, sulphate-activated Cu(NO3)2/γ-Al2O3 or atomic layer epitaxy-Cu/SiO2 catalyst with MSI, can generate MWCNTs with the same CVD conditions. It was noted that free-standing Cu NPs can yield the growth of CNTs, especially SWCNTs [6,19] or aligned SWCNTs [18], via CVD with alcohol-based feedstock. These findings depict that a crucial step for CNT growth over copper catalysts would be the decomposition route of carbon feedstock instead of the factor of catalysts precursors. Additionally, a method for positively controlling the decomposition routes of carbon-bearing molecules over copper catalysts could regulate the formation of CNTs or a-C. Hydrogen is ordinarily used to suppress the decomposition rate of carbon sources and to maintain the catalytic activity of metal NPs because it strips away unsaturated carbon species into gaseous hydrocarbons. Therefore, the addition of hydrogen to the carbon feedstock should activate the inert copper catalysts, e.g., Cu(NO3)2/SiO2 or Cu(CH3COO)2/SiO2. The clear re-activation of CNT growth over the inert copper catalyst Cu(NO3)2/SiO2 is presented in Fig. 1e. The growth yields of a-C (lower combustion temperature at 471 °C) and CNTs (higher combustion temperature at 546 °C) were characterised using oxidation TGA profiles and first-derivative curves as shown in Fig. 1f–g. The a-C and CNT peaks were assigned according to the results of previous studies [8,16]. In Fig. 1f–i, the yield of the as-grown carbon soot for CuSO4/γ-Al2O3 is approximately 28.24 wt. % (5.65 g soot/g Cu-h); however, the first-derivative curve (Fig. 1g-i) indicates a mixture of a-C (30%) and CNTs (70%). Therefore, the growth yield of the CNTs is approximately 3.96 g CNT/g Cu-h. Accordingly, the CNT growth yields over the hydrogen-activated Cu(NO3)2/SiO2 and CuSO4/SiO2 catalysts are approximately 3.16 and 1.23 g CNT/g Cu-h, respectively. Although the CNT growth yields are lower than the yield over the CuSO4/γ-Al2O3 catalyst, interestingly, the hydrogen-activated Cu(NO3)2/SiO2 and CuSO4/SiO2 catalysts could only generate CNTs without the formation of a-C, demonstrating only single peaks in Fig. 1g–i.

III. This finding indicates that free-standing Cu NPs are easily deactivated by the encapsulation of a-C via the decomposition of hydrocarbons, which can be avoided by the addition of hydrogen to the carbon feedstock, leading to remarkably high-yield and high-purity CNTs. Sulphate-assisted copper NPs that do not interact strongly with the support lead to lower CNT yields; however, the purity of the CNTs is significantly improved. The Raman spectra of the as-grown CNTs synthesised over the CuSO4/γ-Al2O3 and CuSO4/SiO2 catalysts are presented in Fig. 1h. The Ic/Ia ratio of the as-grown CNTs over the CuSO4/SiO2 catalyst is 1.09 (the same as those grown over the hydrogen-activated Cu(NO3)2/SiO2 catalyst). However, the Ic/Ia ratio of the CNTs grown over the CuSO4/γ-Al2O3 catalyst is lower, 0.86. This demonstrates that as-grown CNTs fabricated over CuSO4/SiO2 or hydrogen-activated Cu(NO3)2/SiO2 catalysts exhibit better graphitic features, which is consistent with the results of the TEM and TGA measurements.

Table 1

<table>
<thead>
<tr>
<th>Cu catalysts</th>
<th>Carbon feedstocka</th>
<th>Growth temperature (°C)</th>
<th>Growth yieldb</th>
<th>a-C CNTs g CNT/(g Cu·h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(CH3COO)2/SiO2</td>
<td>C2H4/He = 1/9</td>
<td>800</td>
<td>3.24</td>
<td>ND</td>
</tr>
<tr>
<td>Cu(NO3)2/SiO2</td>
<td>C2H4/He = 1/9</td>
<td>800</td>
<td>3.25</td>
<td>ND</td>
</tr>
<tr>
<td>CuSO4/SiO2</td>
<td>H2/CH3COOH/He = 1/1/9</td>
<td>800</td>
<td>ND</td>
<td>3.16</td>
</tr>
<tr>
<td>CuSO4/γ-Al2O3</td>
<td>C2H4/He = 1/9</td>
<td>700</td>
<td>ND</td>
<td>0.49</td>
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<tr>
<td>CuSO4/γ-Al2O3</td>
<td>C2H4/He = 1/9</td>
<td>750</td>
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<td>0.69</td>
</tr>
<tr>
<td>CuSO4/γ-Al2O3</td>
<td>C2H4/He = 1/9</td>
<td>800</td>
<td>ND</td>
<td>1.23</td>
</tr>
<tr>
<td>CuSO4/γ-Al2O3</td>
<td>C2H4/He = 1/9</td>
<td>900</td>
<td>ND</td>
<td>6.10</td>
</tr>
<tr>
<td>CuSO4/γ-Al2O3</td>
<td>C2H4/He = 1/9</td>
<td>800</td>
<td>1.69</td>
<td>3.96</td>
</tr>
<tr>
<td>CuSO4/γ-Al2O3</td>
<td>C2H4/He = 1/9</td>
<td>900</td>
<td>4.94</td>
<td>4.05</td>
</tr>
</tbody>
</table>

a Total flow rate is 100 mL/min.
b The growth yields of a-C (amorphous carbon) and CNTs were determined by thermo-oxidative decomposition TGA profiles for all samples.
c ND stands for non-detects.
Although the growth yield of the CNTs synthesised at 800 °C over the CuSO4/SiO2 catalyst is only a quarter of that of the CNTs grown over the CuSO4/γ-Al2O3 catalyst, the selectivity towards CNTs is approximately 100%. An extremely high selectivity for CNT growth over the CuSO4/SiO2 catalyst suggests a potentially low-cost process that requires no further post-treatments. Nevertheless, the wide range of growth temperatures for the formation of CNTs over the CuSO4/SiO2 catalyst should be discussed. Therefore, we grew CNTs using the CuSO4/SiO2 catalyst at various temperatures (500–900 °C). The growth yields were characterised by TGA measurements and are shown in Fig. 3 and Table 1. Surprisingly, although the combustion peaks of the samples shift to higher temperature and widen with increasing growth temperature, only CNTs were generated, without the formation of a-C, as shown in the right panel of Fig. 3. As shown, the CNT growth yields significantly increase at temperatures of 850–900 °C. The CNT growth yield over the CuSO4/SiO2 catalyst at 900 °C displaying in Table 1 is approximately 6.1 g CNT/g Cu·h, which is nearly 1.5 times that observed for the CNTs grown over the CuSO4/γ-Al2O3 catalyst. More importantly, the as-grown CNTs were fabricated with extra-high purity without the formation of a-C. Although the detailed mechanism needs more studies, a plausible reason is that the CuSO4/γ-Al2O3 catalyst should have higher activity for the decomposition of carbon source-ethylene through a stronger MSI between sulphated-Cu NPs and Al2O3 comparing to that of the CuSO4/SiO2 catalyst. Therefore, at 800 °C, CuSO4/γ-Al2O3 catalyst could give higher CNT growth yield (3.96 g CNT/g Cu·h) compared with that of CuSO4/SiO2 catalyst (1.23 g CNT/g Cu·h). At higher temperature—900 °C, although the soot (CNTs+a-C) formation yield of CuSO4/γ-Al2O3 catalyst is quite higher than that of CuSO4/SiO2 catalyst, however the ratio of a-C was estimated to approximately 55%, therefore the CNT growth yield is only 4.05 g CNT/g Cu·h, which is similar to that generated at 800 °C (3.96 g CNT/g Cu·h). In other words, the formation of a-C on CuSO4/γ-Al2O3 catalyst at 900 °C is the main pathway. For CuSO4/SiO2 catalyst, higher temperatures could generally give higher decomposition rate of carbon source-ethylene to promote the growth of CNTs instead of a-C owing to a
weak MSI. Similar results have been reported in a review article [20]. Nevertheless, a kinetic study for the decomposition of hydrocarbons and the formation of CNTs on various copper catalysts is under studying, and will be discussed later. In this study, our observations provide new insights into the CNT growth process using non-magnetic metal catalysts and into further integrated applications using Cu NPs and CNTs.

4. Conclusions

We have developed a simple way of synthesising MWCNTs without the formation of a-C using copper-based catalysts through CVD at 700–900 °C. The carbon source used is known to be a key factor for CNT growth using copper-based catalysts. With ethylene, hydrogen-assisted CVD can be used to synthesise CNTs over copper catalysts with free-standing Cu NPs. In this study, the growth yields of CNTs were dependent on the temperature, the addition of hydrogen to the carbon source and the metal–support interaction.

Acknowledgements

J. H. Lin expresses his sincere appreciation to the National Science Council of the Republic of China for financially supporting this study (NSC-101-2113-M-024-002).

References


Fig. 3. Left panel: oxidation TGA profiles of the as-grown CNTs using 9.9 wt.% CuSO4/SiO2 catalyst at various temperatures (500–900 °C) with diluted ethylene (C2H4/He = 1/9 = 100 mL/min) for 30 min. Right panel: first-derivative curves of TGA profiles displayed in the left panel.