



Short Communication

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



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ABSTRACT

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 ($\text{CuSO}_4/\text{SiO}_2$) 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., $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$ or $\text{Cu}(\text{CH}_3\text{COO})_2/\text{SiO}_2$, 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 byproducts (e.g., amorphous carbon (a-C) and metal nanoparticles (NPs)) are three main 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 $\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$ exhibited high CNT growth activity (2.3 g CNT/g Cu·h) at 750–850 °C through a synergistic interaction between Cu NPs, SO_4^{2-} and Al_2O_3 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 $\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$ catalysts.

Here, we aimed to achieve high-yield CNT growth without the production of a-C through two simple adjustments: (1) by replacing the $\gamma\text{-Al}_2\text{O}_3$ support with amorphous SiO_2 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 ($\gamma\text{-Al}_2\text{O}_3$ (132 m²/g), Degussa Co. and SiO_2 (254 m²/g), Cabot Co.) with the required amounts of the following aqueous solutions:

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$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99.9%, Aldrich), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.9%, Aldrich) or $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (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-SCIEX ELAB 6100 DRC) to be 10.2 wt.% for $\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$, 9.9 wt.% for $\text{CuSO}_4/\text{SiO}_2$ and 10.1 wt.% for $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$. 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 $\text{C}_2\text{H}_4/\text{He}$ mixture (flow rate = 100 mL/min, $\text{C}_2\text{H}_4/\text{He}$ 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. Fig. 1a, for the $\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst, shows as-grown multi-walled CNTs (MWCNTs) clustered with numerous a-C. In a blank test, we did not observe any forms of carbon species deposited on pure $\gamma\text{-Al}_2\text{O}_3$ at elevated temperatures under the same CVD conditions. It was noted that a stronger metal-support interaction (MSI) between sulphated-Cu NPs and $\gamma\text{-Al}_2\text{O}_3$ 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 $\gamma\text{-Al}_2\text{O}_3$ support with amorphous SiO_2 , the growth of unwanted a-C was effectively terminated, as shown in Fig. 1b. 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 $\text{CuSO}_4/\text{SiO}_2$ catalysts. However, when $\text{Cu}(\text{NO}_3)_2$ or $\text{Cu}(\text{CH}_3\text{COO})_2$ were used as the catalyst precursors, regardless of whether the support was SiO_2 or $\gamma\text{-Al}_2\text{O}_3$, 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., $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$ and $\text{Cu}(\text{CH}_3\text{COO})_2/\text{SiO}_2$, 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 $\text{Cu}(\text{NO}_3)_2$, $\text{Cu}(\text{CH}_3\text{COO})_2$ or $\text{Cu}(\text{thd})_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate), on amorphous SiO_2 , Al_2O_3 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., $\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$, sulphate-activated $\text{Cu}(\text{NO}_3)_2/\gamma\text{-Al}_2\text{O}_3$ or atomic layer epitaxy-Cu/ SiO_2 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 properly 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., $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$ or $\text{Cu}(\text{CH}_3\text{COO})_2/\text{SiO}_2$. The clear re-activation of CNT growth over the inert copper catalyst $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$ 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 $\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$ 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 $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$ and $\text{CuSO}_4/\text{SiO}_2$ 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 $\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst, interestingly, the hydrogen-activated $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$ and $\text{CuSO}_4/\text{SiO}_2$ catalysts could only generate CNTs without the formation of a-C, demonstrating only single peaks in Fig. 1g–II, 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 $\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$ and $\text{CuSO}_4/\text{SiO}_2$ catalysts are presented in Fig. 1h. The $I_{\text{G}}/I_{\text{D}}$ ratio of the as-grown CNTs over the $\text{CuSO}_4/\text{SiO}_2$ catalyst is 1.09 (the same as those grown over the hydrogen-activated $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$ catalyst). However, the $I_{\text{G}}/I_{\text{D}}$ ratio of the CNTs grown over the $\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst is lower, 0.86. This demonstrates that as-grown CNTs fabricated over $\text{CuSO}_4/\text{SiO}_2$ or hydrogen-activated $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$ catalysts exhibit better graphitic features, which is consistent with the results of the TEM and TGA measurements.

A typical TEM image of the as-grown CNTs fabricated using the $\text{CuSO}_4/\text{SiO}_2$ catalyst is shown in Fig. 2a. Branched (multi-branched, T-type and Y-type) and simple bamboo-like MWCNTs are the main products shown in Fig. 2b–e. Various branched MWCNTs were generated by moving or splitting of the Cu NPs under the CNT growth conditions. In this study, we consider the CNT growth mechanism for copper catalysts to be similar to that described by the vapour–solid–solid (VSS) model [19], owing to the low carbon solubility of the copper catalysts. Moreover, magnified images of a bamboo-like CNT before and after the transport of Cu NPs are shown in Fig. 2f and g, respectively. These indicate that the graphitic layers of the CNTs are parallel to the tube growth axis, which should obey the VSS model.

Table 1
Variable process parameters for the study of CNT growth over various copper catalysts.

Cu catalysts	Carbon feedstock ^a	Growth temperature (°C)	Growth yield ^b	
			a-C (g a-C/g Cu·h)	CNTs (g CNT/g Cu·h)
$\text{Cu}(\text{CH}_3\text{COO})_2/\text{SiO}_2$	$\text{C}_2\text{H}_4/\text{He} = 1/9$	800	2.41	ND ^c
$\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$	$\text{C}_2\text{H}_4/\text{He} = 1/9$	800	3.25	ND
	$\text{H}_2/\text{C}_2\text{H}_4/\text{He} = 1/1/9$	800	ND	3.16
$\text{CuSO}_4/\text{SiO}_2$	$\text{C}_2\text{H}_4/\text{He} = 1/9$	700	ND	0.49
	$\text{C}_2\text{H}_4/\text{He} = 1/9$	750	ND	0.69
	$\text{C}_2\text{H}_4/\text{He} = 1/9$	800	ND	1.23
	$\text{C}_2\text{H}_4/\text{He} = 1/9$	900	ND	6.10
$\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$	$\text{C}_2\text{H}_4/\text{He} = 1/9$	800	1.69	3.96
	$\text{C}_2\text{H}_4/\text{He} = 1/9$	900	4.94	4.05

^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.

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