



# Highly selective synthesis of single-walled carbon nanotubes from methane in a coupled Downer-turbulent fluidized-bed reactor

Song Yun, Weizhong Qian\*, Chaojie Cui, Yuntao Yu, Chao Zheng, Yi Liu, Qiang Zhang, Fei Wei

*Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China*

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## Abstract

For the synthesis of single-walled carbon nanotubes (SWCNTs) from  $\text{CH}_4$  over a Fe/MgO catalyst, we proposed a coupled Downer-turbulent fluidized-bed (TFB) reactor to enhance the selectivity and yield (or production rate) of SWCNTs. By controlling a very short catalyst residence time (1–3 s) in the Downer, only part of Fe oxides can be reduced to form Fe nano particles (NPs) available for the growth of SWCNTs. The percentage of unreduced Fe oxides increased and the yield of SWCNTs decreased accordingly with the increase of catalyst feeding rate in Downer. SWCNTs were preferentially grown on the catalyst surface and inhibited the sintering of the Fe crystallites which would be formed thereafter in the downstream TFB, evidenced by TEM, Raman and TGA. The coupled Downer-turbulent fluidized-bed reactor technology allowed higher selectivity and higher production rate of SWCNTs as compared to TFB alone.

## Key words

carbon nanotube; chemical vapor deposition; methane; fluidized-bed; catalyst

## 1. Introduction

Single-walled carbon nanotubes (SWCNTs) possess excellent mechanical and electrical properties, as well as huge aspect ratio and high surface area, and have potential applications in electrochemical energy storage, catalysis, composite and nanodevice, etc. [1]. Production of SWCNTs with high selectivity and high purity is crucial to their application. Since the diameter of CNT depends on metal crystallize size of the catalyst, controlling the state of catalyst in the chemical vapor deposition process is crucial to prepare SWCNTs with narrow size distribution [2–18]. However, the sintering of metal on the catalyst, once reduced by hydrogen or carbon source, is very quick and multiwalled CNTs (MWCNTs) will be produced when the metal crystallize size is larger than 5 nm [3–14]. Actually, tuning the interaction of metal and catalyst support and the dispersion state of metal was crucial to increase the stability of metal crystallite under high temperature [2,5–7,9,17]. Moreover, the reactor also plays an important role in influencing the size of metal crystallites of catalyst. Previous work suggested that, whether in a fixed-bed or a fluidized-bed reactor, simultaneous reduction on catalyst,

if in large amounts, would result in rapid aggregation of metal crystallites formed on the catalyst surface [14].

In the present work, we proposed a concept to increase the selectivity of SWCNTs in a coupled Downer-turbulent fluidized-bed (TFB) reactor. Firstly, the residence time of catalyst was controlled to be less than 2 s in the Downer reactor. If the contact time of catalyst with carbon source was too short, it would result in insufficient reduction of Fe oxides on the catalyst, and simultaneously, growing some SWCNTs on the catalyst surface. The preferentially grown SWCNTs would occupy some part of the surface of MgO support, and were effective to inhibit the aggregation of Fe nanoparticles (NPs) formed in the downstream TFB reactor and consequently, allowed the growth of SWCNTs with high selectivity. Effect of catalyst feeding rate on the size distribution of SWCNTs was studied by Raman, TGA and TEM. Using the coupled Downer-TFB reactor technology, the production rate of SWCNTs was increased to 50 folds than the previously reported value [5], as well as maintaining a high selectivity to SWCNTs. The present method paved the way for the large-scale production of SWCNTs with controlled diameter and high selectivity.

\* Corresponding author. Tel: +86-10-62794133; Fax: +86-10-62772051; E-mail: [qianwz@tsinghua.edu.cn](mailto:qianwz@tsinghua.edu.cn)

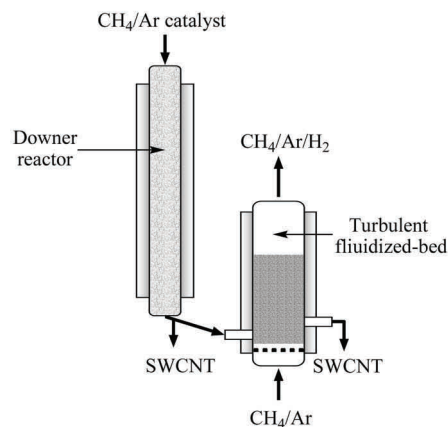
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## 2. Experimental

The model catalyst used here was a Fe/MgO catalyst with Fe loading of 1% (weight ratio) [11]. The carbon source was CH<sub>4</sub> (99.99% purity) and the carried gas was Ar (99.999% purity). The quartz-made experimental setup consisted of a Downer (1.5 m in length, 20 or 30 mm in diameter) and a TFB (50 mm in diameter and 1 m in length) (Figure 1). Then the catalyst powders carried by the gases (pure CH<sub>4</sub> or the mixed gases of CH<sub>4</sub> and Ar) were fed into the Downer from its top. Catalysts were in situ heated and reduced (by CH<sub>4</sub>) for CNT growth in Downer at 900 °C. The catalyst residence time in the reactor was 1.2–2.4 s at gas velocities of 0.6–1.3 m/s. Then, catalysts, SWCNTs and gases flowing out of the Downer from its bottom entered the TFB reactor operated at temperature of 900 °C as well. Another gas flow (pure CH<sub>4</sub> or mixture of CH<sub>4</sub> and Ar) was fed into the bottom of TFB to maintain a gross gas velocity of 0.3 m/s. The catalyst residence time in TFB was 3–6 min for the sufficient growth of SWCNTs. Finally, SWCNT products in TFB were cooled in Ar atmosphere to ambient temperature.

Gas samples at the exit of TFB or Downer were analyzed by a gas-chromatography (HP4890D, thermal conductive detector (TCD) and carbon sieve column). SWCNT samples took from the Downer or TFB reactor alone, and from the coupled reactor were characterized by transmission electron microscopy (TEM, JEM 2010, 120 kV), scanning electron microscopy (SEM, JSM 7401F, 10–30 kV), and Raman spectrometer (RM2000, Renishaw, excited at 633 nm

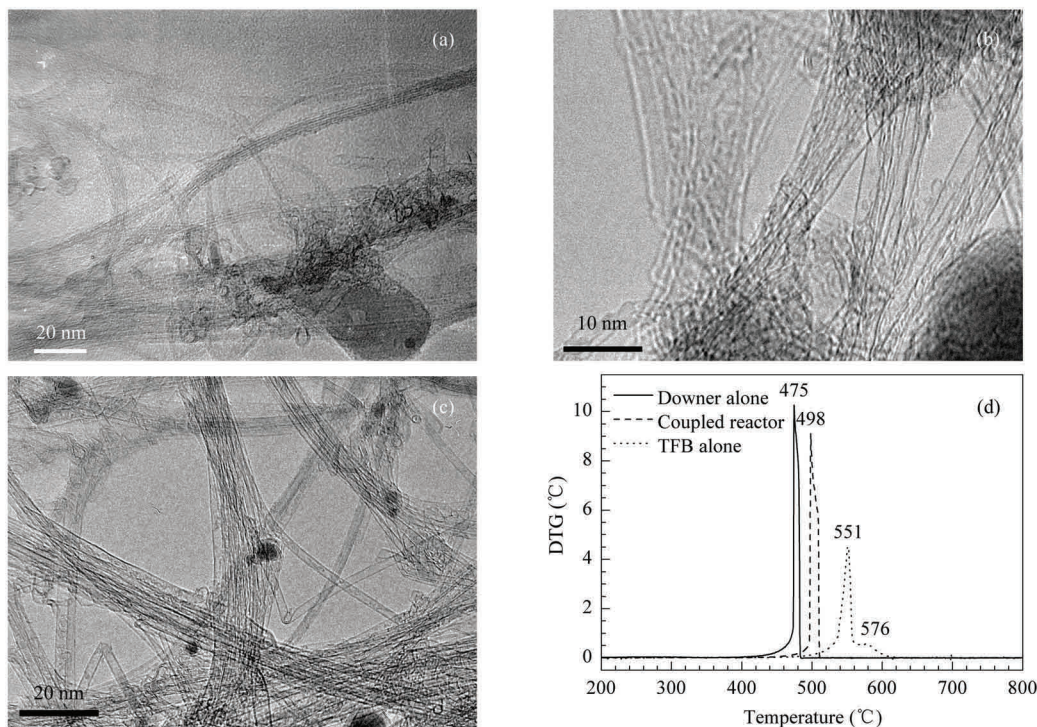
and 514.5 nm). The thermal oxidative property of SWCNTs prepared in different reactors was characterized by thermogravimetric analyzer (TGA, TA2050). To remove the catalyst components from the SWCNTs product, it was treated in HCl at 30 °C for 24 h. All MgO support and most Fe were removed effectively. The purity of SWCNTs product after the purification was about 96.4%–98%.



**Figure 1.** Schematic of the coupled Downer-TFB reactor system for SWCNT synthesis

## 3. Results and discussion

Figure 2 presents the SWCNTs grown on the same catalyst (1%Fe/MgO) in different reactors. Predominant product

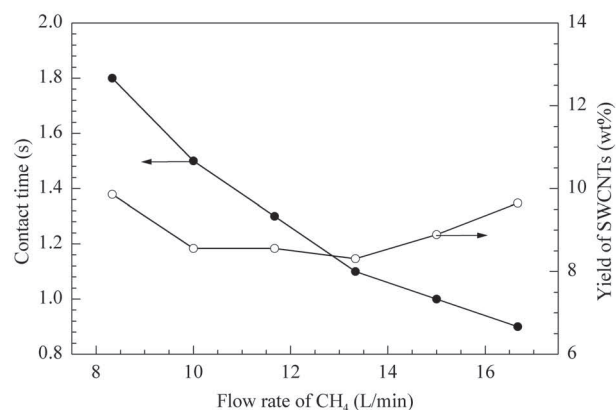


**Figure 2.** TEM images of SWCNTs in different reactors. (a) SWCNTs in TFB alone, (b) SWCNTs in Downer (30 mm ID) alone, (c) SWCNTs in coupled Downer-TFB, (d) TGA of SWCNTs in Downer alone. Reaction conditions: Partial pressure and flow rate of CH<sub>4</sub> were 100% and 8.3 L/min, respectively; coupled reactor, and in TFB alone

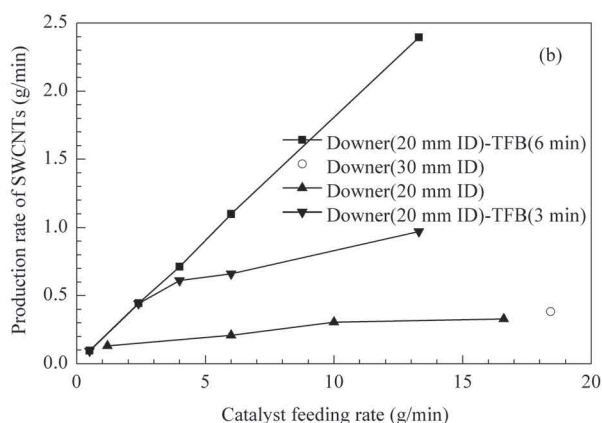
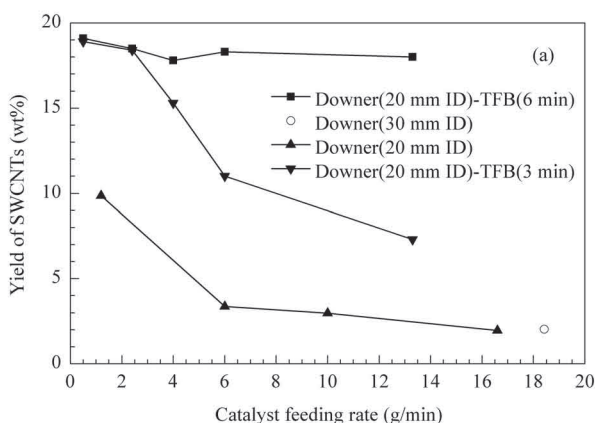
in TFB alone was SWCNT bundle (Figure 2a), but there were still some MWCNTs with the diameter of 3–6 nm. Similarly, predominant double-walled CNTs (DWCNTs) with some MWCNTs were prepared over a 3%Fe/MgO catalyst in TFB alone according to Ref. [14]. In contrast, SWCNTs produced in Downer alone were free of MWCNT impurities (Figure 2b). These SWCNTs formed a kind of bundles consisting of 5–10 individual tubes with diameter of 1–2 nm. Moreover, when the SWCNTs grown about 1–2 s in Downer were fed into TFB for the continued growth for 3–6 min, their morphology remained nearly the same (Figure 2c). TGA results of different samples after the purification are shown in Figure 2(d). SWCNTs from Downer alone had a peak at 475 °C, while samples from the coupled reactor had a peak at 498 °C. Both were characteristic peaks of SWCNTs [2,5–7,11]. Lower burning temperature was assigned to the smaller diameter tubes, since large diameter tubes were relatively insensitive to oxygen etching [16]. In contrast, the samples from TFB alone had two peaks at 551 °C and 579 °C. These indicated that the SWCNTs product may contain some DWCNTs or MWCNTs, in agreement with TEM characterization (Figure 2a).

To understand the reactor effect on the selectivity of SWCNT product, the growth processes of SWCNTs in Downer alone and the coupled reactor were thoroughly analyzed. TGA analysis indicated that the yield of SWCNTs, based on the total weight of catalyst, ranges from 8.5% to 10% when the catalyst feeding rate was about 1–2 g/min in Downer alone (Figure 3). The value was similar to that reported in Ref. [8] and was nearly independent of the flow rate of methane. Since the catalyst residence time in Downer was only 1–3 s, the high yield of SWCNTs suggests the high activity of the catalyst and high growth rate of SWCNTs. However, when the catalyst feeding rate was increased to 10–20 g/min in a Downer reactor with inner diameter of 20 mm or 30 mm, the yield of SWCNTs gradually decreases to 2% (Figure 4a). Considering that the life time of most catalysts for growing S/DWCNTs was 3–10 min [1,5,6,9,11,14], the low yield of SWCNTs here was not due to the deactivation of catalysts.

In order to understand this, we calculated the convective heat transfer in Downer (Figure 5). When catalyst and carbon source at ambient temperature were fed into a Downer with 1.5 m in length, they were elevated to 650–700 °C in 0.6 s when the catalyst feeding rate was 1.2 g/min. At this temperature, the nucleation and reduction of catalyst began to grow CNTs [2–14]. In this case, catalyst passed already 0.5 m from the entrance and there was only 1.2 s left for the growth of SWCNTs at 800–900 °C in Downer. When the catalyst feeding rate was further increased to 12 g/min, with the gas velocity unchanged, longer time (about 0.7 s) was needed to heat catalyst to the temperature necessary for the reduction and nucleation. As a result, the growth time of SWCNTs in Downer was further shortened. In our previous work, we used temperature-programmed reduction method to prove that there were two types of Fe oxide species on the catalyst [5]. Apparently, such short residence time of catalyst in the Downer reactor only allowed the reduction of some Fe oxides which were much easily reduced in relatively low temperature. Apparently, the insufficient reduction of the catalyst resulted in the insufficient growth time of SWCNTs in Downer under high catalyst feeding rate. Thus, the absolute production rate of SWCNTs was difficult to increase further and remained at 0.15–0.3 g/min (Figure 4b).



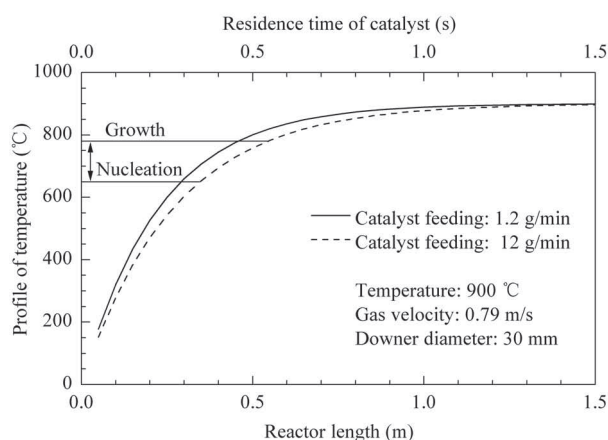
**Figure 3.** Dependences of SWCNT yield on the catalyst contact time with carbon source and the flow rate of CH<sub>4</sub>



**Figure 4.** Yield and production rate of SWCNTs in the Downer and Downer-TFB reactor. (a) Yield of SWCNTs at different catalyst feeding rates, (b) Production rate of SWCNTs at different feeding rates



On the other hand, when the growth process of SWCNTs was conducted in a coupled Downer-TFB reactor, the insufficiently reduced catalyst in Downer can be further reduced in TFB for the continued growth of SWCNTs. Actually, the yield of SWCNTs can be increased from 2% in Downer alone to 8% for 3 min and 18% for 6 min in TFB, respectively, when the catalyst feeding rate was 15 g/min. Since the maximal yield of SWCNTs was 18% over this catalyst [5,9,11,14], it was able to calculate the percentage of catalyst reduced in Downer alone based on the yield of SWCNTs under different catalyst feeding rates. When the catalyst feeding rate was 2–3 g/min, 50% catalyst can be reduced in Downer (Figure 4a). However, only 25% of catalyst was reduced in Downer when the catalyst feeding rate was higher than 10 g/min. Similarly, under high catalyst feeding rate, about total 50% catalyst was reduced in TFB for 3 min and the total reduction of all catalysts needs 6 min residence in TFB. From the calculation in Figure 5 and the data in Figure 4, it was clear that the controlling of residence time of catalyst in different reactors directly influenced the reduction ratio of metal on the catalyst and was favorable for the enhanced growth of SWCNTs.



**Figure 5.** Axial direction temperature profile of the catalyst in Downer under different catalyst feeding rates

Raman characterization was used to understand the effect of the coupled reactor on the diameter control of CNT product. Raman method is more advantageous over the TEM method in the detection of sample in large amounts and the detailed diameter information of SWCNT bundle (Figure 6, Tables 1 and 2). The radial breathing mode (RBM) at 100–400  $\text{cm}^{-1}$  reflects the diameter and density distributions of SWCNTs/DWCNTs [1,9,11,14,19,22]. Using the equation proposed in Ref. [22], the diameter of SWCNTs was calculated and labeled on Figure 6(b) and 6(d). RBM peaks at 190 and 180–134  $\text{cm}^{-1}$  were assigned to the tube diameter of 1.26 nm and 1.6–2.4 nm, respectively. RBM peaks at 214, 248.7, and 277  $\text{cm}^{-1}$  were assigned to DWCNTs with inner diameter of 1.11, 0.95, and 0.84 nm, respectively, since our catalyst was unable to grow SWCNTs with diameter of 0.84–1.11 nm in large amounts [9,11,14]. CNT samples in different reactors exhibited different intensities or the content

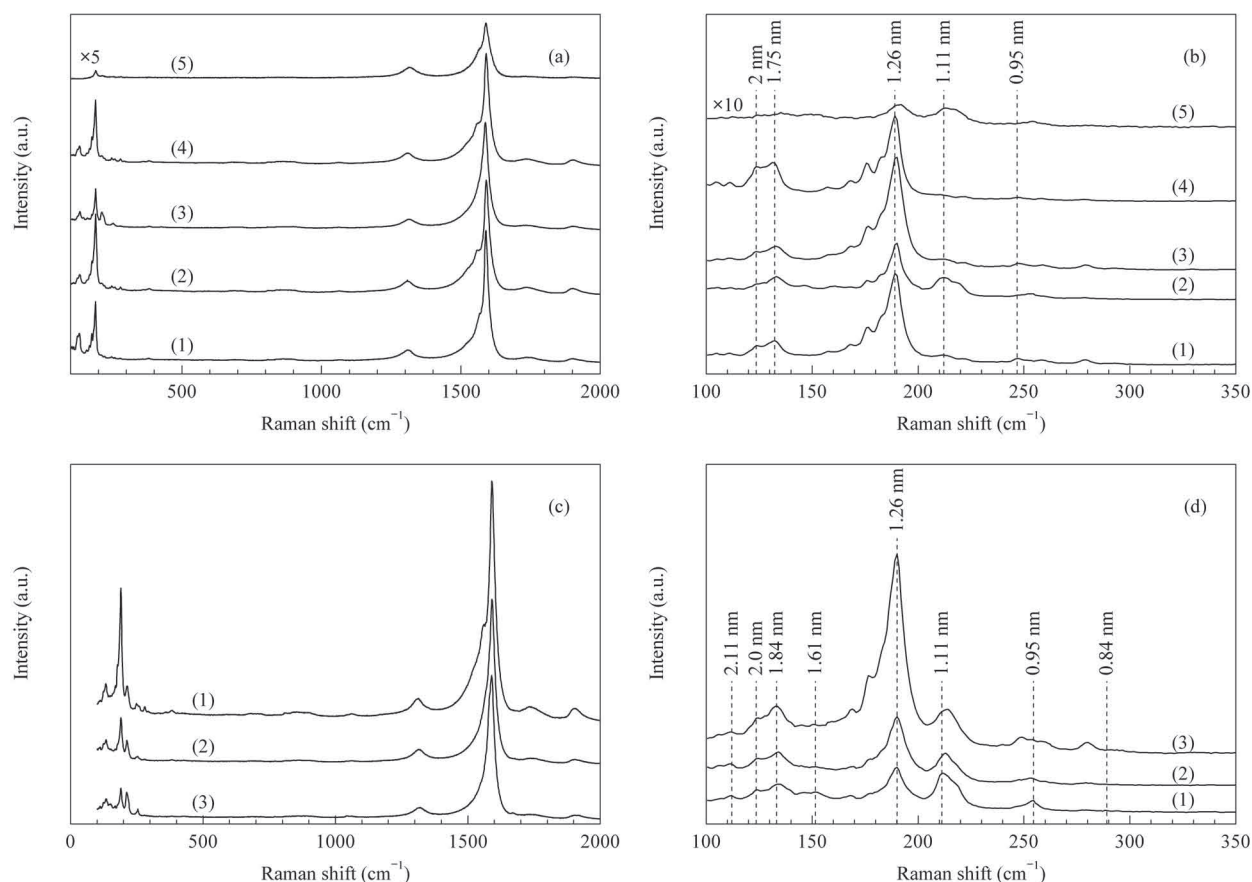
of tubes with certain diameter (i.e. 1.26 and 1.75 nm) (Figure 6). In detail, the intensity of 1.26 nm SWCNTs was the highest in Downer alone (Figure 6a), but it becomes gradually weak in the coupled reactor with increasing catalyst feeding rate (Figure 6b), and in TFB alone (Figure 6a). Note that, even using the same catalysts, the diameter distribution of tubes was wider in TFB alone and the product was a mixture of DWCNTs and SWCNTs with weight ratio of 1 : 1. It suggested that the operation state of Downer alone and the coupled reactor was much more favorable to the production of SWCNTs with high selectivity, compared to that of TFB alone. The intensity ratio of D band (1340  $\text{cm}^{-1}$ ) to G band (1590  $\text{cm}^{-1}$ ) ( $I_D/I_G$  ratio) was used to reflect the purity of SWCNTs (Tables 1 and 2). The  $I_D/I_G$  ratio was 0.109–0.132 for SWCNTs in Downer alone or the coupled reactor, and was nearly independent of the flow rates of  $\text{CH}_4$  (3.6–9.6 L/min) and Ar (0–6.2 L/min) and the catalyst feeding rate (Figure 6b). These  $I_D/I_G$  values were much smaller than that (0.216, Table 1) grown in TFB alone for 6 min. The smaller  $I_D/I_G$  ratio means few defects and higher purity of carbon products prepared in Downer alone and in the coupled reactor [23]. In addition, considering that only part of SWCNTs was sensitive to the Raman laser with the wavelength of 633 nm [22,24], we also made Raman characterization using 514.5 nm laser (Figure 7). The diameter distribution and peak intensity of tubes having response at 514.5 nm were both similar in Downer alone and in the coupled reactor when the catalyst feeding rate was 0.5 g/min. When further increasing the catalyst feeding rate from 4 to 13 g/min, the intensity of the peak at 130–200  $\text{cm}^{-1}$  became very weak, due to the insufficient growth of SWCNTs. Similar to the characterization at 633 nm, the values of  $I_D/I_G$  ratio of SWCNTs in the coupled reactor and in Downer alone were both smaller than 0.125. Since the characterization by using Raman laser at 514.5 and 633 nm covered most tubes with diameter of 1.2–2 nm prepared in the present work [24], these results confirmed that SWCNTs with high selectivity were prepared in the coupled reactor.

**Table 1.** Parameters for preparing SWCNTs in Figure 6(a) and  $I_D/I_G$  value of SWCNTs of Figure 6(a)

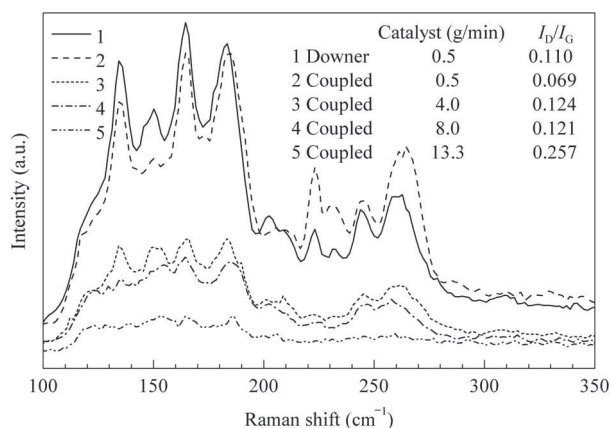
No.	Temperature (°C)	$\text{CH}_4/\text{Ar}$	Contact time (s)	Catalyst feeding rate (g/min)	$I_D/I_G$
1	900	6.0/6.2	1.3	2.0	0.109
2	900	3.6/6.2	1.6	1.4	0.132
3	900	9.6/0	1.7	2.1	0.112
4	900	6.0/0	2.7	1.2	0.121
5	900	2.0/1.0	180	–	0.216

**Table 2.** Parameters for preparing SWCNTs in Figure 6(c) and  $I_D/I_G$  value of SWCNTs of Figure 6(c)

No.	Catalyst feeding rate (g/min)	Space velocity of $\text{CH}_4$ (L/(g <sub>cat</sub> ·min))		Yield of SWNTs (%)	$I_D/I_G$	Conversion of $\text{CH}_4$ (%)
		Downer	TFB			
1	0.5	562	3	18.9	0.108	4.5
2	2.4	117	0.63	18.4	0.097	21.0
3	4.0	70	0.38	15.3	0.088	28.1



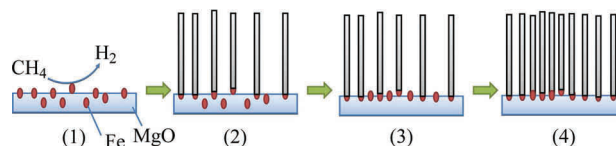
**Figure 6.** Raman spectra of SWCNT product in different reactors using 633 nm laser. (a) Raman spectra of SWCNTs in TFB alone and Downer alone; (b) Detailed RBM information of SWCNTs, which was part of (a); (c) Raman spectra of SWCNTs in coupled reactor; (d) Detailed RBM information of SWCNTs, which was part of (c). (1)–(4) Downer, (5) TFB



**Figure 7.** Raman spectra of SWCNT product in different reactors using 514.5 nm laser

Based on the results above, we propose here a growth mode of SWCNTs in the coupled reactor (Figure 8). Originally, the Fe oxides, before reduction, were dispersed uniformly in the bulk phase of MgO support [9,11]. When entering Downer, some Fe oxides near the surface of MgO support were preferentially reduced to metallic Fe NPs suitable for the quick growth of SWCNTs. Due to the short residence time of catalyst and carbon source in Downer, part of Fe oxides on

the catalyst was not reduced and its reduction will be further carried out in the downstream TFB. The pre-grown SWCNTs on the catalyst occupied some surface space of the catalyst and consequently, inhibited the sintering of metal NPs on the catalyst due to the space confinement effect. As a result, SWCNTs with high selectivity and free of MWCNTs were produced. Apparently, the confined effect of pre-grown SWCNTs on the sintering of the metal NPs depended on the temperature and catalyst feeding rate as discussed above. The selectivity control of SWCNTs was mainly carried out in Downer reactor. But the sufficient growth of SWCNTs to the maximal yield was done in the downstream TFB. From this point of view,



**Figure 8.** Continued growth model of SWCNTs in the coupled Downer-TFB reactor. (1) Methane adsorption and decomposition on the Fe NPs to release hydrogen; (2) SWCNT growth on the preferentially reduced Fe NPs in Downer; (3) Continued reduction of Fe NPs (embedded deeply in the bulk phase of MgO support) in TFB. (4) Growth of SWCNTs/DWCNTs from the confined Fe NPs (by the pre-grown SWCNTs on the catalyst support) in TFB (some Fe NPs grew bigger to grow to DWCNTs)

the production rate of SWCNTs in the coupled reactor was determined by the catalyst feeding rate in Downer and the final yield of SWCNTs in TFB. Actually, the production rate of 2.2–2.3 g/min (Figure 5) implied the super-large scale production of SWCNTs. Note that reactors used here (Downer or the TFB) were relatively mature in other industrial-scale processes [20,21]. It was feasible to use the coupled reactor system for the large-scale production of SWCNT in high selectivity and at low cost.

#### 4. Conclusions

We reported a coupled Downer-TFB reactor method to control the reduction of Fe/MgO catalyst and therefore, the selectivity and production rate of SWCNTs could be enhanced. TEM and Raman characterizations of the catalyst suggest that the catalyst was insufficiently reduced in the Downer reactor under large feeding rate and the pre-grown SWCNTs on the catalyst in Downer inhibited metal sintering in the downstream TFB reactor. A growth mode of SWCNTs was proposed to explain the phenomenon. The coupled Downer-TFB reactor technology was favorable for the scalable synthesis of SWCNTs with high yield and high selectivity.

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