

SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBES FROM LIQUEFIED PETROLEUM GAS

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Hydrocarbons such as methane, ethylene, and CO with high purity (> 99.9%) have been widely used to synthesize single-walled carbon nanotubes (SWCNTs). Here, liquefied petroleum gas (LPG) was used to synthesize SWCNTs by catalytic chemical vapor deposition. The LPG converted into CNTs and other stable hydrocarbons. The BET specific surface area of SWCNT was about 583 m²/g. The as-grown SWCNT showed good graphitization. The graphitization can be further modulated by the growth temperature. Certain amount of sulfur in LPG was a promoter for SWCNT growth. Compared SWCNTs obtained from methane, more semiconductive SWCNTs were synthesized from LPG as carbon source. The LPG is in low price, thus, a methodology to lower the production cost of SWCNTs with hydrocarbon mixtures is realized.

Keywords: Single-walled carbon nanotubes; liquefied petroleum gas; fuel; production.

1. Introduction

Carbon nanotube (CNT) is an attractive material owing to its unique properties such as the small size, cylindrical structure, and high aspect ratio of length to diameter. Various potential applications of CNTs, including conductive and high-strength composites, sensors, field emission displays, hydrogen storage media, and nanometer-sized semiconductor devices, were put forward.¹ Compared with multi-walled CNTs (MWCNTs), the single-walled CNTs (SWCNTs) are of perfect structure, such as smaller diameter, larger aspect ratio, and lower defect density.¹ Consequently, the SWCNTs show an outstanding performance in many aspects, including reinforced composite materials,² transparent

conductive films,^{3,4} field emission displays,^{5,6} sensors, transistors,^{7,8} etc. They are potential to be the next generation of electronics.^{9,10} To realize those applications, the need for large amount of cheap SWCNTs was proposed. In the past decade, great endeavors have been made in the large scale synthesis of high purity SWCNTs at low cost. Various processes, such as HiPCO process,¹¹ CoMo catalysis process,^{12,13} alcohol chemical vapor deposition,^{14,15} floating catalyst process,^{16–18} arc discharge,^{19,20} and nano-agglomerate fluidized bed^{21–23} had been developed, but the as-grown SWCNTs were still expensive. Further purifications were needed to obtain high purity SWCNTs.^{11–23} Until now, it is

still difficult to produce SWCNTs at large scale with a low cost. For further researches on SWCNTs and the ultimate commercialization of SWCNTs, a cheap catalyst, a simple synthesis method, and a cheap carbon source are necessary.

Chemical vapor deposition (CVD) shows more advantages in controllable synthesis of SWCNTs and carbon sources are needed for this process. Carbon sources including hydrocarbons such as methane, ethylene, and CO with high purity (higher than 99.9%) have been widely adopted to synthesize SWCNTs in previous studies. But these pure carbon sources are expensive and are limited in supply, compared to cheap fuels such as liquefied petroleum gas, coal, and natural gas. Since these fuels contained sulfur of several to several hundred ppm, which would seriously poison the catalyst, few reports were concentrating on using LPG, coal, natural gas, camphor or eucalyptus oil directly.^{24–34} Our group reported high purity agglomerated CNTs can be achieved from the decomposition of the LPG containing 13 ppm sulfur by Fe/Mo/Al₂O₃ catalyst.²⁴ MWCNT arrays can also be obtained with LPG as carbon source by floating catalyst process.^{32,33} As far as we have concerned, no reports concerned SWCNTs from LPG. However, it is an effective way to satisfy the urgent need of controllable production of SWCNTs from LPG at a low cost.

In this article, LPG, which is a cheap and achievable fuel, was used as carbon source for direct synthesis of SWCNTs from powder catalyst. High quality SWCNTs can be obtained from LPG. A concept to reduce the SWCNT cost by using cheap commercial fuel as carbon source was illustrated.

2. Experimental

2.1. Catalyst preparation

The Fe/MgO catalyst was prepared and used to synthesize the SWCNTs. The procedure for the Fe/MgO catalyst preparation and the production of the SWCNTs have been reported elsewhere.³⁵ In brief, magnesium oxide powder (BET surface area 25.9 m²/g) was suspended in distilled water to form a uniform suspension by strong stirring at 80°C. Subsequently, a solution of iron nitrate (Fe(NO₃)₃·9H₂O) was added dropwise slowly into the suspension with stirring. The molar ratio of the salt in the solution to the magnesium oxide was 1:99. After drying the suspension at room temperature or at 60°C and grinding the solid, the

catalyst of Fe(1%)/MgO for SWCNT production was obtained.

2.2. CNT synthesis

To synthesize the SWCNTs, approximately 100 mg of the catalyst was sprayed uniformly into a quartz boat, which was then inserted into the center of a quartz tube (id: 25 mm, length: 1200 mm). The quartz tube, mounted in an electrical tube furnace, was heated to 600°C in an air atmosphere. Subsequently, argon was fed at a flow rate of 600 ml/min. Then the reactor was heated to the temperature of 750–900°C. A mixture of LPG (80 ml/min) and carrier gas was introduced into the quartz tube and maintained at the reaction temperature for 15 min before the furnace was cooled to room temperature under Ar protection.

2.3. Characterization

The compositions of LPG and exhaust gas were analyzed by an online gas chromatograph (Shimadzu 14B) with a 50 m PLOT Al₂O₃ capillary column and a flame ionization detector. The morphology of the CNTs was characterized by scanning electron microscopy (SEM, JSM 7401F at 3.0 kV). The sample for transmission electron microscopy (TEM) was prepared by sonication of about 3 mg of as-grown products in ethanol and several drops were put onto a TEM grid. The quality of the sample was characterized by TEM (JEM 2010 at 120.0 kV). Raman experiments have been performed with a Raman spectrophotometer Renishaw, RM2000 in ambient condition. The spectra were recorded using a He–Ne laser excitation line of 633 nm. The BET surface area of the products were analyzed by single point BET measurement,³⁵ and the carbon content was obtained by TGA (Q500, heated at 20°C/min).

3. Results and Discussion

Compared to most SWCNT precursor, the LPG had a complex composition — even contained some sulfur. The typical compositions of the LPG and the exhaust from CVD process at the growth temperature of 850°C were shown in Table 1. It can be seen that the main components of LPG were C₃ and C₄ alkanes and alkenes. For the existence of about 20 ppm H₂S, the mixture expresses an unpleasant smell. After the CVD process, the weight percentages of C₃ and C₄ have decreased greatly, while those of CH₄ and C₂H₄ increased consumedly and

Table 1. Typical weight percentage composition of the hydrocarbon in the feed LPG and the exhaust from the CVD process at a growth temperature of 850°C.

	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	C ₄ H ₁₀	C ₄ H ₈	C ₅ +
LPG	0.60	2.63	0.28	17.67	6.53	32.59	36.47	3.23
Exhaust	42.69	2.23	42.98	1.70	4.10	2.16	1.75	2.39

even became the major part of the exhaust. This indicated the fact that during the CNT growth process, the LPG converted into the solid carbon product and gaseous hydrocarbons, such as CH₄, C₂H₄, and aromatic hydrocarbons. Obviously, it is an effective carbon source for SWCNT synthesis, although the hydrocarbon cracking mechanism is complex in this process.³⁶

Typical SEM images of the products cling on the conductive tape were shown in Fig. 1. Abundant fibrous products grew densely at the growth temperature of 900°C over Fe/MgO catalysts with a Fe content of 1% in molar ratio. Due to the confined space, high flexibility of SWCNT and the presence of Van der Waals attraction, SWCNTs are always in the form of bundles. The diameters of

SWCNT bundles grown on the catalysts were less than 20 nm. After careful observation, we found that SWCNTs preferred to grow out from mesopores and nanopores of the catalysts (Figs. 1(a) and 1(b)). Furthermore, the SWCNTs were easily tangled and tended to form large bundles. They showed distinctly different morphologies from the MWCNT agglomerates grown from powder catalysts.³⁷ With a multi-wall graphite layer structure, MWCNTs were strong enough to break up the catalyst particle agglomerates, and a multi-stage agglomerate structure was formed during the CVD process.³⁷ However, the SWCNT bundles were too flexible to break the catalyst agglomerate. They showed a confined growth in the porous powder catalysts with little effect on breaking the catalyst agglomerate. Thus, the good fluidized properties were maintained. SWCNTs can be easily produced in nano-agglomerated fluidized bed in large scale.³⁸

The carbon content of the product grown at 900°C from LPG was about 16.3%, indicating that the SWCNT yield was about 19.5% for per gram catalyst. The BET specific surface area of the product was 117.4 m²/g,³⁵ thus, it was about 583 m²/g for pure CNT product, which was much higher than that of MWCNTs.^{39,40} The formation of SWCNTs was further confirmed by the observation with TEM. The SWCNTs formed into CNT bundles with diameters of about 3–20 nm (Fig. 1(c)). LPG is mainly composed of C₃ and C₄ alkanes and alkenes, which are easier to be pyrolyzed into amorphous carbon than other carbon sources such as methane, ethylene, and CO.^{22,37,38,41–43} However, there was a little amorphous carbon cling on the CNT wall (Figs. 1(c) and 1(d)). The main impurities were particle-like catalysts, which were mainly consisted of MgO that can be easily removed by acid solution.

Furthermore, the formation of high quality SWCNTs was macroscopically demonstrated by the presence of radial breath modes (RBM) in the low wavenumber region (100–300 cm⁻¹) of Raman spectra (Fig. 2). When the growth temperature was higher than 750°C, the as-grown products from the LPG showed obvious RBM peaks which confirmed

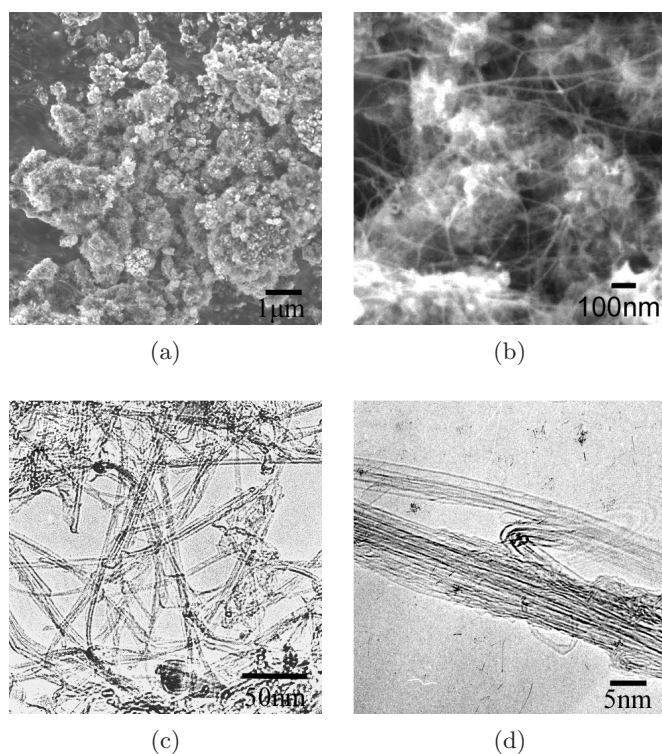


Fig. 1. The as-grown SWCNTs from LPG with Fe(1%)/MgO catalyst at 900°C. (a) SEM image of the agglomerated structure of SWCNTs, (b) HRSEM image of the interwoven SWCNTs on catalyst, (c) TEM image of tangled SWCNT bundles, and (d) HRTEM image of the SWCNT bundles.

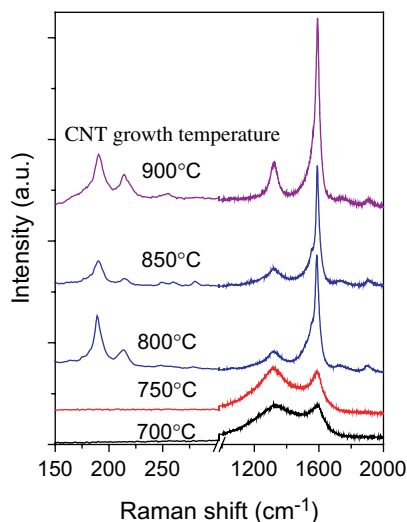


Fig. 2. Raman spectra of as-grown products grown on Fe/MgO from LPG at different reaction temperatures.

the existence of SWCNTs. But when the temperature was lower than 750°C, no RBM peaks appeared in the Raman spectra. From the SEM images from Figs. 3(a) and 3(b), thin tubular structure can hardly be found, while MWCNTs of large diameter were obtained. When the growth temperature was 800–900°C, a lot of small SWCNT bundles were

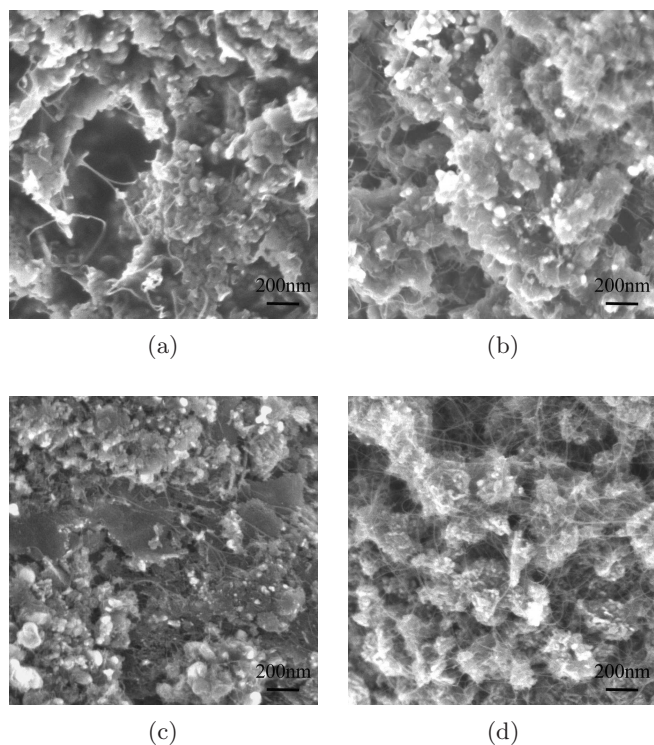


Fig. 3. SEM images of as-grown products grown on Fe/MgO from LPG at different reaction temperatures (a) 700°C, (b) 750°C, (c) 800°C, and (d) 850°C.

synthesized as shown in Figs. 3(c) and 3(d). Then there was a growth temperature turning point, which was about 800°C, for SWCNT growth from Fe/MgO catalyst.

The turning point of SWCNT growth temperature was also confirmed by RBM peaks and I_G/I_D ratio of the Raman spectra. A high value of I_G/I_D ratio was obtained if SWCNTs were grown on the catalysts. When the growth temperature was 700 or 750°C, the I_G/I_D ratio was about 1, which was a normal value for MWCNTs. When the growth temperature was above 750°C, the I_G/I_D ratio was more than 8, indicating good graphitization of SWCNTs grown out of the catalyst site. The value of I_G/I_D increased with higher temperature (Fig. 4). This indicated that SWCNT products with better graphitization were obtained at higher growth temperature. Thereby, the graphitization of SWCNTs can be modulated by growth temperature and LPG is a good carbon source for SWCNT synthesis.

Not only the growth temperature, but also the growth atmosphere can obviously affect the graphitization of SWCNT product. Here, LPG which mainly consisted of C₃, C₄ hydrocarbon with 20 ppm S, was used as carbon source. It was commonly believed that the long chain hydrocarbons were much easier to be pyrolyzed at high temperature due to thermal stability,⁴⁴ and amorphous carbon would be formed on the surface of as-grown products. However, the 20 ppm sulfur, which

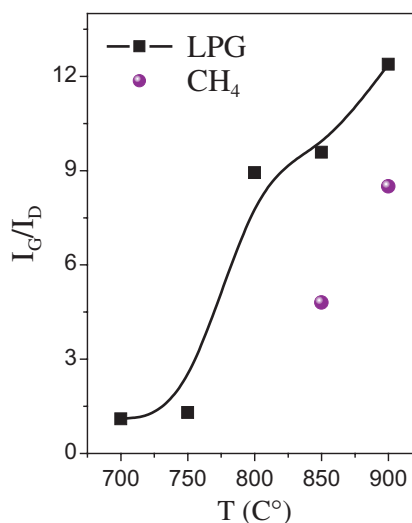


Fig. 4. The graphitization (I_G/I_D ratio) of SWCNT via growth temperature with various temperatures and carbon sources. The graphitization of SWCNT from methane can also be found in Ref. 22.

was always a promoter for SWCNT formation and growth in the floating catalyst process,^{12,13,44,45} was also an inhibitor for amorphous carbon formation. The S element can accumulate on the Fe nanoparticles, which brings the division of the large particles into small Fe catalyst particles, and then, as a result, high quality SWCNTs were formed.^{16,17,44,45} The SWCNTs synthesized from the LPG showed better graphitization than those from methane (Fig. 4),²² which indicated that the sulfur in LPG maintained the catalyst with small size so as to promote high quality SWCNTs growth.

The differences in the distribution of tube diameters in different samples with LPG and methane²² can be confirmed by the Raman spectra. For example, the SWCNT from methane always showed 4–6 RBM peaks, while for the SWCNT products from LPG, just 2 RBM peaks were found. Even for the G band of the LPG sample is much wider than that in the methane sample, shown in Fig. 5. The G bands for SWCNTs contain two main contributions: the highest frequency band is referred to as ω^+ , and is best fitted to a Lorentzian function; the other contribution (ω^-) is actually two bands that depend on the electronic properties of the individual SWCNTs from which they arise. The ω^- band for semiconducting tubes, which appears $\sim 50 \text{ cm}^{-1}$ below ω^+ , is also usually best fitted by a Lorentzian function. The ω^- for metallic tubes, which is $\sim 80 \text{ cm}^{-1}$ below ω^+ , can be described by a Breit–Wigner–Fano function. Fitting the appropriate lineshapes to the G bands shows that the sample from LPG has a much larger contribution from semiconducting tubes: see

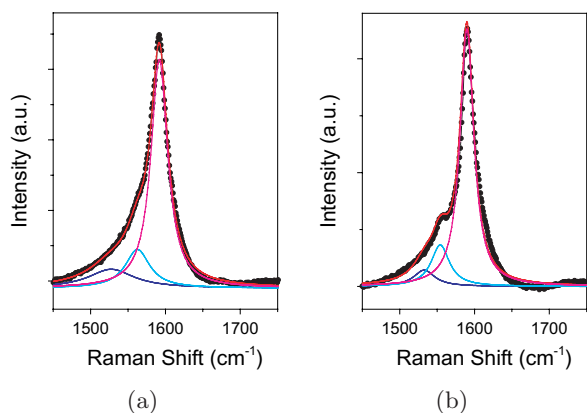


Fig. 5. Raman spectra of samples from (a) methane and (b) LPG, showing fits of two Lorentzian and one Breit–Wigner–Fano curves to G band region. The larger area of the semiconducting ω_{smei}^- peak in the LPG spectra ($\sim 1560 \text{ cm}^{-1}$) indicates the presence of more semiconducting tubes than the methane sample (see also Table 2).

Table 2. Integrated intensities of ω_{met}^- and ω_{smei}^- for SWCNT products grown from methane and LPG.

Precursor	$T/^\circ\text{C}$	Area of peaks (normalized to area of ω^+)		
		ω_{met}^-	ω_{smei}^-	$\omega_{\text{met}}^-/\omega_{\text{smei}}^-$
Methane	900	0.24	0.19	1.23
LPG	900	0.061	0.21	0.29

Table 2 and Fig. 5. The ratio of metallic SWCNT to semiconducting SWCNT is modulated by the carbon source obviously, which consisted with the reports of Andrews *et al.*³⁰

Finally, it can be noted that the synthesis of high-quality SWCNTs can be achieved from cheap and abundant resources of LPG, although it is a mixture of hydrocarbons. Meanwhile, the fact that mixed carbon source did not affect SWCNT growth obviously suggested other cheap carbon sources, including natural gas (mainly CH_4), water gas (H_2 , CO), dry gas in FCC process (H_2 , CH_4 , C_2H_4 , CO , etc.), coal gas (H_2 , CH_4 , CO , CO_2 , etc.), gasoline (C_4 – C_{10} hydrocarbon mixtures), diesel oil (C_{10} + hydrocarbon mixtures), are also effective carbon sources for SWCNT growth in future.

4. Conclusions

SWCNTs were synthesized in the catalytic CVD from LPG, which is an effective carbon source and the appropriate amount of sulfur can promote the growth of CNTs. The SWCNTs grown from Fe(1%)/MgO at 900°C have a yield of 16.3%. The BET specific surface area of pure CNT product was $583 \text{ m}^2/\text{g}$. The graphitization of SWCNTs can also be modulated by the growth temperature and carbon source. Certain amount of sulfur was a promoter for SWCNT growth. More semiconducting SWCNTs were obtained by LPG as carbon source. Due to the low prices of LPG and extensive reserves, high quality of SWCNT can be obtained at a low cost, providing a methodology to lower the production cost of SWCNTs from fuel or hydrocarbon mixtures in future.

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