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FABRICATION OF CARBON NANOTUBES FROM LIQUEFIED PETROLEUM GAS BY CHEMICAL VAPOUR DEPOSITION

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Abstract: This paper presents the fabrication of carbon nanotubes from liquefied petroleum gas (LPG) by chemical vapour deposition with Fe/SiO_2 as a catalyst. The morphology and tube diameter of the carbon nanotubes are dependent on the flow rates of H_2 and LPG, and the crystal growth temperature. The obtained CNTs were characterized using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), scanning electron microscope (SEM), scanning transmission electron microscope (STEM), and Brunauer-Emmett-Teller surface area analyses. The results indicate that the suitable conditions for forming the nano-sized tubes are 700 °C for 2 hours with the H_2 and LPG flow rate of 140 $mL \cdot min^{-1}$ and 80 $mL \cdot min^{-1}$, respectively. The multi-walled structures with long, less defective tubes and identical external diameter of 52 nm and BET surface area of 93 $m^2 \cdot g^{-1}$ are obtained.

Keywords: carbon nanotubes, chemical vapour deposition, catalyst, Fe/SiO_2, external diameter, liquefied petroleum gas

1 Introduction

Carbon nanotubes (CNTs) are an attractive material that draws attentions of many scientists, industrialists and civilians. A great number of studies on the fabrication, characterization and application of CNTs have been performed extensively and intensively in the past decades [2]. Since the first discovery of CNTs in 1991 [11], the researchers have been deployed and found out a variety of singular physical properties of this material such as mechanical durability, electrical and thermal conductivity, and its widespread technological applications. There are three main ways for the fabrication of CNTs, namely, arc discharge, laser vaporization and chemical vapour deposition (CVD). Despite the high quality of nanotubes, the first two methods require high temperatures and complicated equipment, which restricts their feasibility. On the contrary, CVD is one of the most promising methods for fabricating CNTs because of low temperature, high yield and excellent purity [9]. Besides, the catalyst substrate used for the fabrication of CNTs in this method is usually harmless and suitable for a large-scale production such as $CaCO_3$, SiO_2, zeolite or Al_2O_3 [1]. Among them, Al_2O_3 and SiO_2 are the most popular substrates due to their high stability at the growth temperatures of CNTs and good connection to catalyst nanoparticles that give high efficiency. The catalysts used for the fabrication of CNTs are usually

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d-group metals such as Co, Fe, and Ni. The advantage of these metals is that their diffusion temperature in SiO_2 or Al_2O_3 is in the range of the growth temperature [4]. Many investigations focus on the fabrication of CNTs from expensive pure carbon sources such as CH_4, C_2H_2, C_2H_4, C_3H_8. With the aim of reducing cost, cheap natural carbon sources such as natural gas or liquefied petroleum gas (LPG) are used for the fabrication of CNTs [13]. There are some important factors affecting the growth and purity of CNTs such as catalyst particle size, initial gas flow rate, growth temperature, etc. It has been recognized that LPG as a carbon source is used, and the conditions for fabricating CNTs such as the flow rate of the reactants, growth temperature need to be investigated.

In the present work, the influence of H_2, LPG flow rate, and growth temperature on the fabrication of CNTs by chemical vapour deposition on SiO_2-support Fe catalyst is under investigation.

2 Materials and methods

2.1 Preparation of silica

In this study, silica (SiO_2) employed as the substrate for the catalyst for the fabrication of CNTs was prepared from rice husk ash collected from the waste of Thua Thien Hue Prime Joint Stock company (Hue city, Vietnam). Coarse impurities in the rice husk ash were removed. A mixture consisting of rice husk ash and 2.5 M NaOH (Merck) solution was prepared with $NaOH/SiO_2$ molar ratio of 0.6. In order to completely extract SiO_2 from rice husk ash, the mixture was heated to 100 °C with stirring and kept at this temperature for 1.5 hours. Subsequently, a liquid glass solution was obtained after filtering. The SiO_2 gel was formed after adding HCl 12 % (Merck) solution into the above solution and heating at 200 °C for 3 hours. Finally, the precipitate was washed with deionized water and then furnaced at 900 °C for 1 hours to obtain the SiO_2 powder.

2.2 Preparation of Fe_2O_3/SiO_2 pre-catalyst

The pre-catalyst (Fe_2O_3/SiO_2) was prepared from $Fe(NO_3)_3{\cdot}9H_2O$ (Merck) and SiO_2 produced from the rice husk ash. In detail, a thin layer of SiO_2 substrate was covered by $Fe(NO_3)_3$ solution in such a way that the percent of Fe_2O_3/SiO_2 is 35 % (w/w) and dried at 100 °C until a constant mass was obtained. The solid mixture was then furnaced at 500 °C for 3 hours in order to completely pyrolyse $Fe(NO_3)_3$ to form Fe_2O_3/SiO_2 pre-catalyst.

2.3 Growth of carbon nanotubes

Carbon nanotubes were fabricated from liquefied petroleum gas (Dung Quat oil refinery) with the Fe/SiO_2 catalyst using the chemical vapour deposition method. The Fe/SiO_2 catalyst was prepared in a refractory brick tube before the growth of CNTs. A small ceramic boat containing the pre-catalyst was placed in this tube. The tube was made noble with N_2 at a flow rate of 100 $mL{\cdot}min^{-1}$ for 1 hour before heating to 400 °C. At this temperature, an H_2 gas flow of 100 mL·min^{-1} was blown into the tube for 2 hours to reduce Fe_2O_3 to Fe. After that, a mixture of H_2 and LPG was blown into the tube and the growth of CNTs took place.

2.4 Characterization of carbon nanotubes

The crystal phase of the obtained CNTs was determined using X-ray diffraction (XRD). The element composition of CNTs was calculated from energy-dispersive X-ray spectrum (EDS); the morphology and the diameter the CNTs were observed using scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM). The BET surface area of CNTs was analysed using N_2 adsorption and desorption.

3 Results and discussion

3.1 CNTs fabrication condition

Effect of H_2 flow rate

Jeong et al. [12] suggested that H_2 added to the reacting gas mixture for the CNTs' growth contributes to cleaning the active sites of the catalysts from being covered with amorphous carbon. Without the presence of H_2 during LPG thermal decomposition, aligned carbon nanotubes mix with spherical carbon particles formed on the substrate [9]. Therefore, in order to study the effect of H_2 on the diameter of CNTs, 7 flow rates at 60, 80, 100, 120, 140, 160 and 180 mL·min^{-1} were tested, and they were denoted as H1, H2, H3, H4, H5, H6 and H7. Other parameters were held constant (Table 1). The external diameters of CNTs were determined based on the SEM images shown in Fig. 1 using the Perfect Screen Ruler software (n = 15). The measurement is illustrated in Fig. 2.

Table 1. External diameter of the tubes of CNTs samples synthesized with different H_2 flow rates

Notation	H1	H2	H3	H4	H5	H6	H7
H_2 flow rate (mL·min^{-1})	60	80	100	120	140	160	180
External diameter of tubes (nm) (n = 15)	–	63 ± 5	65 ± 8	68 ± 7	**52 ± 5**	72 ± 19	70 ± 12

Note: LPG flow rate is 80 mL·min^{-1}; growth temperature is 700 °C; and growth time is 2 hours.

As can be seen from Table 1, CNTs did not form when the H_2 flow rate was low at 60 mL·min^{-1} (H1). The average external diameter of the tubes first increases from 63 to 68 nm, then drops to 52 nm, after that it rises again to around 70 nm. The average external diameter of the tubes at H5 is the smallest (52 ± 5 nm) at the flow rate of 80 mL·min^{-1}. Besides, a high uniformity of the tubes is observed in samples H2 to H5. Two last samples have a great number of tubes with very large external diameter, therefore the average tube size unexpectedly increases to around 70 nm. It was found that a much higher H_2 flow rate was used for chemical vapour deposition of methane in other studies using different catalysts: 240 mL·min^{-1} on Fe–Mo/Al_2O_3 [1], 350 mL·min^{-1} on ferrocene [10], 400 mL·min^{-1} on Fe/Si [6], or even 900 mL·min^{-1} for the decomposition of CO gas on Fe [7]. Hence, the H_2 flow rate of 140 mL·min^{-1} in the present work not only is an advantage on synthesizing CNTs but also limits the redundant amount of H_2 released.

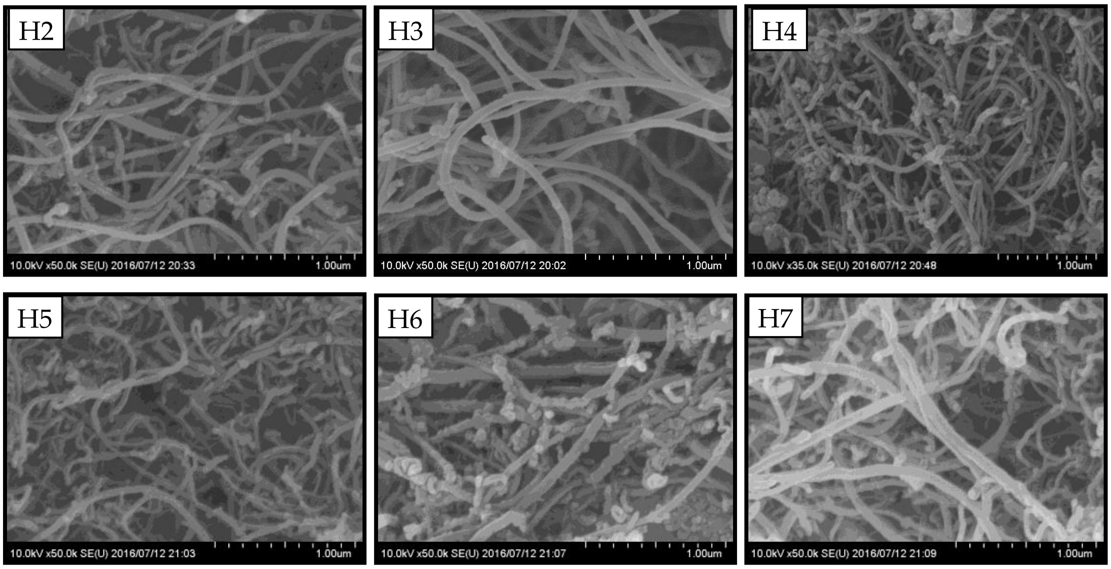


Fig. 1. SEM images of CNTs samples synthesized with different H_2 flow rates

1000 nm	253
Diameter = 500*18/253 = 71.2 nm	18

Distance X: Y:

Points X: 1060 Y: 444

Cursor X: 714 Y: 49

X	Y	Leng...
10	15	18
253	3	253

Fig. 2. Illustration of measuring external diameters of tubes

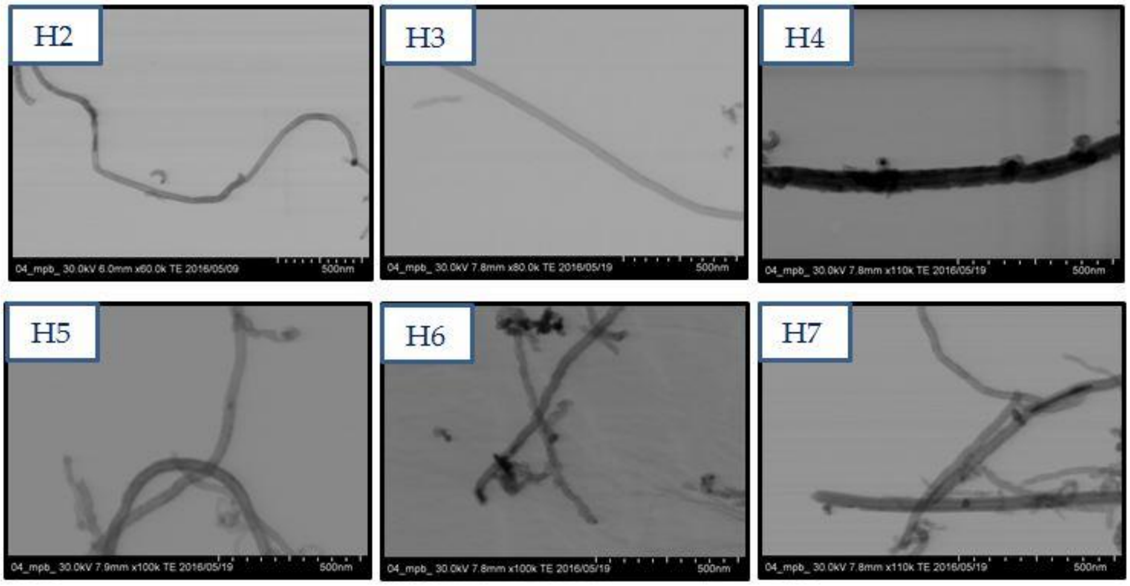


Fig. 3. STEM images of CNTs samples synthesized with different H_2 flow rates

The STEM images of all the samples are presented in Fig. 3. They show that the tubes of the samples have clear walls. The tube walls of sample H2, H3 and H5 are less defective than those of sample H4, H6 and H7. This confirms that the obtained material is carbon nanotubes. Therefore, 140 mL·min^{-1} was chosen as the H_2 flow rate for further experiments.

Effect of LPG flow rate

LPG is the initial material for CNTs fabrication, therefore the effect of LPG flow rate on the growth of CNTs needs to be studied. The investigation was carried out on 7 samples of CNTs denoted as L1 to L7 corresponding to LPG flow rate varying in the range of 60–180 mL·min^{-1} (Table 2).

Table 2. External diameter of the tubes of CNTs samples synthesized with different LPG flow rates

Notation	L1	L2	L3	L4	L5	L6	L7
LPG flow rate (mL·min^{-1})	60	80	100	120	140	160	180
External diameter of tubes (nm) (n = 15)	–	**52 ± 5**	60 ± 7	63 ± 7	69 ± 9	57 ± 7	71 ± 13

Note: Fixed conditions: H_2 flow rate is 140 mL·min^{-1}, growth temperature is 700 °C, and growth time is 2 hours.

The results indicate that CNTs did not form when the LPG flow rate is 60 mL·min^{-1}. In other words, low LPG flow rate does not support the growth of CNTs. At other flow rates, CNTs formed with average tube external diameters increasing from 52 nm to 71 nm as the flow rate increases. The standard deviation of the diameters also rises with the flow rate, indicating that the tubes become less uniform. The flow rate of 80 mL·min^{-1} provides the tubes with the smallest diameter and highest uniformity (52 ± 5 nm). This is a relatively low flow rate compared with that of other reports such as 120 mL·min^{-1} [3], 300 mL·min^{-1} [13], and 600 mL·min^{-1} [8]. Large-scale CNTs production should be carried out with low LPG flow rate to reduce cost.

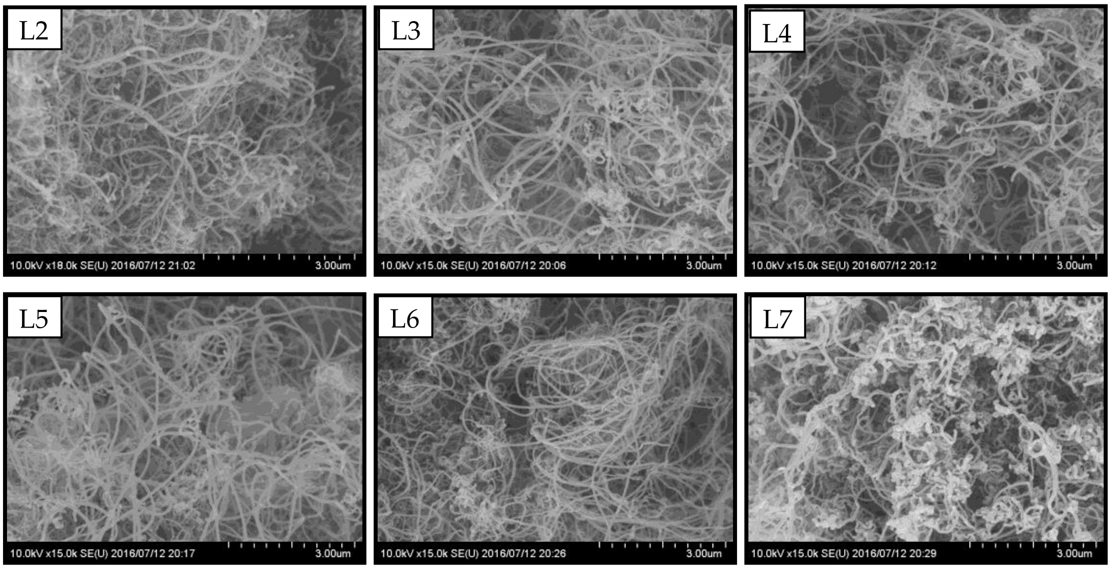


Fig. 4. SEM images of CNTs samples synthesized with different LPG flow rates

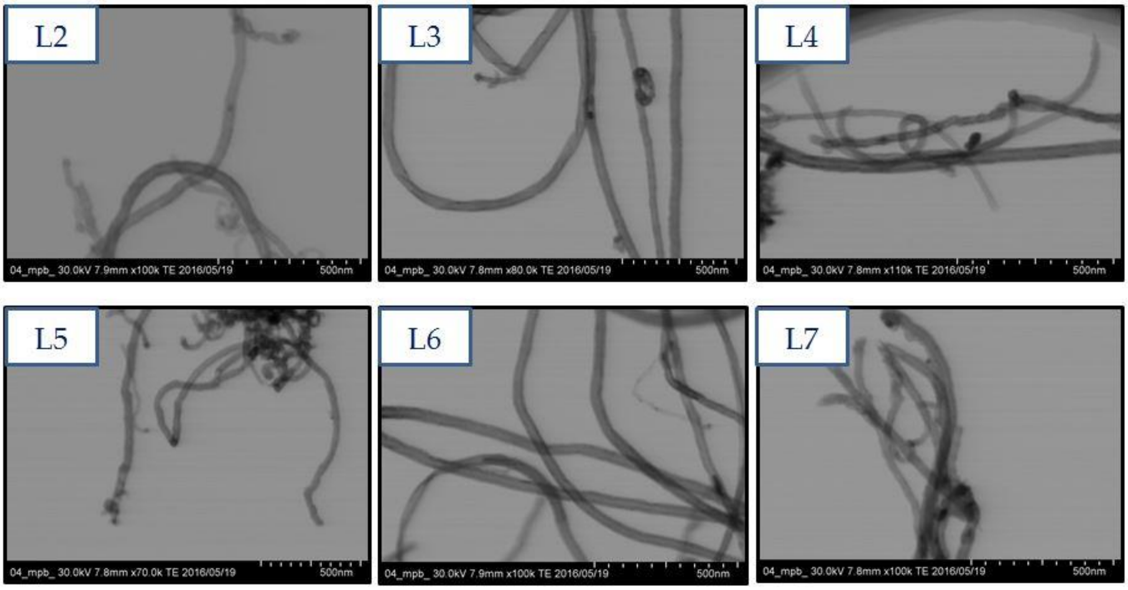


Fig. 5. STEM images of CNTs samples synthesized with different LPG flow rates

The SEM images shown in Fig. 4 reveal that the morphorlogy of the tubes do not differ much when increasing LPG flow rates from 80 mL·min^{-1} to 180 mL·min^{-1}. The tubes are long with small defects. This is also confirmed again by the STEM images (Fig. 5). However, some by-products appear in the sample with the LPG flow rate of 180 mL·min^{-1}. Therefore, 80 mL·min^{-1} was chosen as the LPG flow rate for further experiments.

Effect of growth temperature

The growth temperature affects the crystallinity of CNTs. Furthermore, the diffusion of carbon to the catalyst is a thermally activated process, and hence, higher temperatures lead to higher growth rates that may be desirable for mass-production processes. However, very high temperatures lead to the formation of pyrolytic amorphous carbon [15]. The main components of LPG are hydrocarbons C_3 (propane and propene) and C_4 (butene and butane). Therefore, the suitable synthesized temperature for CNTs must be higher than the Fe_2O_3 reduction temperature (more than 400 °C) and the C_3 and C_4 hydrocarbon decomposition temperatures (more than 600 °C) [4, 14]. Besides, the interaction between the catalyst particles and the substrate can also be influenced by temperature. Therefore, in order to determine a suitable growth temperature for the preparation of CNTs, 6 samples of CNTs denoted from T1 to T6 were fabricated at different temperatures from 550 °C to 800 °C (Table 3). The external diameters of the tubes were recorded.

Table 3. External diameters of tubes of CNTs samples synthesized at different temperatures

Notation	T1	T2	T3	T4	T5	T6
Growth temperature (°C)	550	600	650	700	750	800
External diameter of tubes (nm) (n = 15)	–	–	65 ± 5	**52 ± 5**	79 ± 7	75 ± 12

Note: Fixed conditions: H_2 flow rate is 140 mL·min^{-1}; LPG flow rate is 80 mL·min^{-1}; growth time is 2 hours.

The results show that CNTs did not form when the growth temperature was lower than 650 °C. This is because, belove this temperature, LPG does not decompose. From 650 °C to 800 °C, the tubes formed with a diameter fluctuating from 52 to 79 nm. As can be seen in Fig. 6 and Fig. 7, at 650 °C and 700 °C, CNTs exhibit smaller and more uniform tubes than those fabricated at 750 °C and 800 °C. The uniformity is also confirmed by the values of standard deviation of the tube diameters (Table 3). The SEM images (Fig. 6) and STEM images (Fig. 7) reveal that the T5 and T6 samples synthesized at higher temperatures have broken tubes, and a small amount of amorphous carbon appears. Sample T4 synthesized at 700 °C has the smallest and most uniform tubes, therefore this temperature is the best for the fabrication of the CNTs.

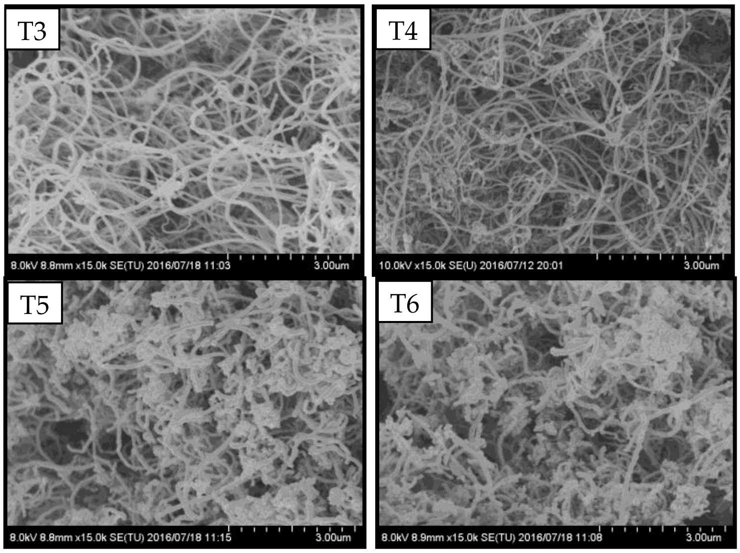


Fig. 6. SEM images of CNTs samples prepared at different growth temperatures

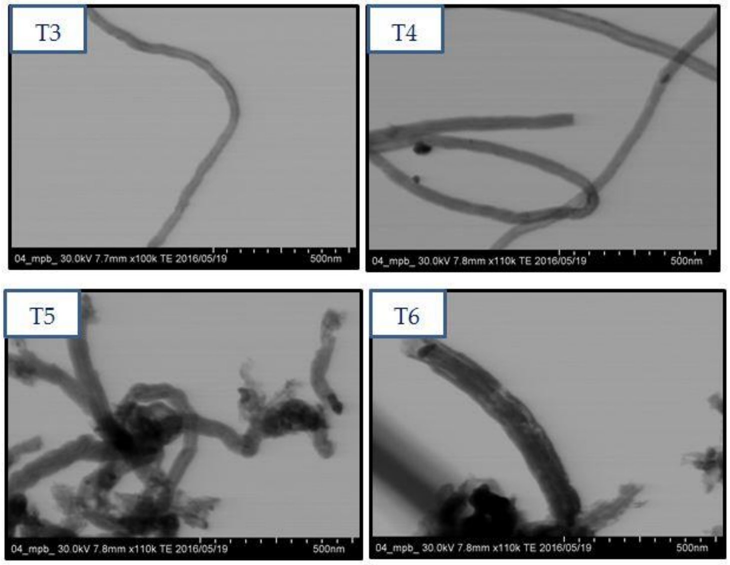
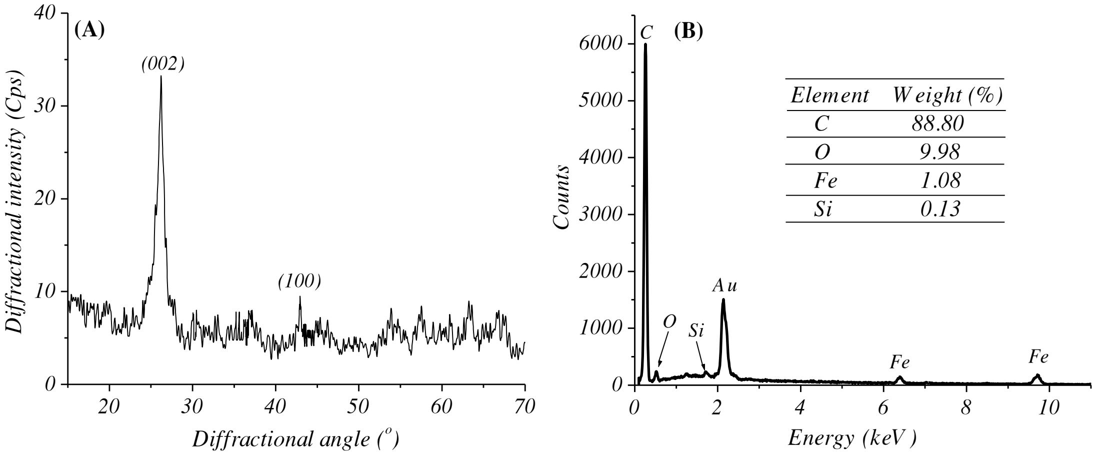


Fig. 7. STEM images of CNTs synthesized at different growth temperatures

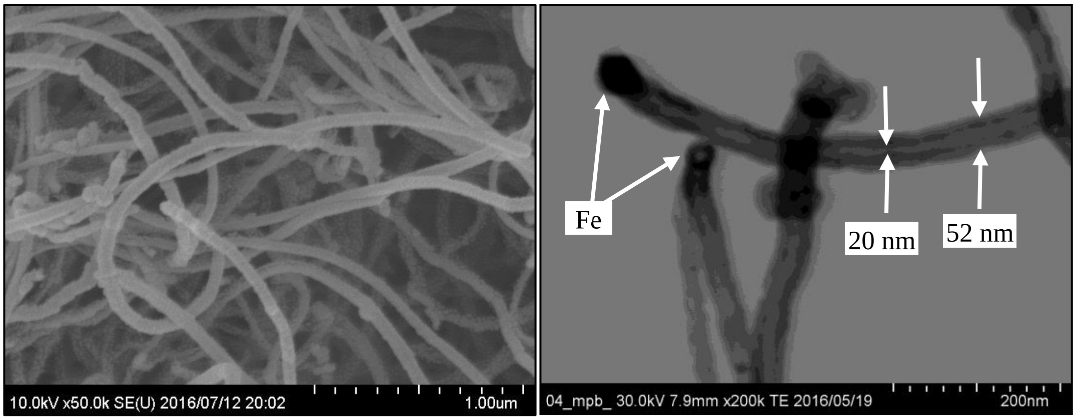
3.2 Characterization of CNTs

The phase and purity of the obtained CNTs were studied using the XRD (Fig. 8a). Cao et al. [5] reported that the (002) and (100) peaks represent the carbon crystal phase. As can be seen on the XRD pattern of the sample (Fig. 8A), two peaks at 26.22° and 42.92°, indexed as (002) and (100) diffraction planes of hexagonal graphite appear, confirming the carbon crystal phase (JCPDS card files, no 41–1487) [16]. Also, EDX study (Fig. 8B) proves that the main composition of the product is carbon (88.80 %) with low-intensity peaks of O, Fe, Si representing a small portion of these elements.



Element	Weight (%)
C	88.80
O	9.98
Fe	1.08
Si	0.13

Fig. 8. XRD pattern (A) and EDX spectrum (B) of CNTs sample



(A) (B)

Fig. 9. SEM (A) and STEM (B) images of CNTs sample

In the fabrication process of NCTs, long, less defective tubes with high uniformity formed (Fig. 9A). A small number of particles appear on the tubes might be the residues of the Fe/SiO_2 catalyst. The tube structure is clearly seen from the STEM images (Fig. 9B). The tubes have the internal and external tube diameter of around 20 and 52 nm, respectively. This indicates that the material might be multiwalled CNTs with the wall thickness of about 30 nm. The surface area of the samples was calculated from the nitrogen adsorption and desorption isotherm (Fig. 10), and it has the value of about 93 $m^2 \cdot g^{-1}$.

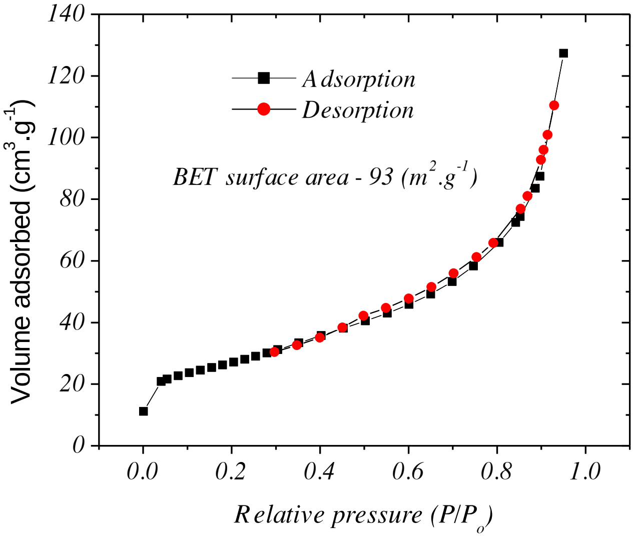


Fig. 10. Nitrogen adsorption and desorption isotherm of CNTs

4 Conclusions

The CNTs were successfully fabricated from LPG using the CVD method. The influence of H_2 and LPG flow rate, and growth temperature on the diameter, uniformity, and purity of CNTs was investigated. The suitable conditions for the fabrication of CNTs with high quality and purity are as follows: H_2 and LPG flow rates are 140 mL·min^{-1} and 80 mL·min^{-1}, and the growth temperature is 700 °C. Long, less defective tubes with the internal and external diameter of around 20 and 52 nm formed in the process. The BET surface area of the material is 93 m^2·g^{-1}.

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