Research Article

Synthesis of Nitrogen-Doped Carbon Nanotubes Using Injection-Vertical Chemical Vapor Deposition: Effects of Synthesis Parameters on the Nitrogen Content

Abdoulilil Hachimi,¹ Belabbes Merzougui,^{2,3} Abbas Hakeem,¹ Tahar Laoui,⁴ Greg M. Swain,⁵ Qiaowan Chang,⁶ Minhua Shao,⁶ and Muataz Ali Atieh^{2,3}

¹Center of Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

²Qatar Environment & Energy Research Institute (QEERI), Qatar Foundation, Doha, Qatar

³College of Science and Engineering, Hamad Bin Khalifa University (HBKU), Qatar Foundation, Doha, Qatar

⁴Department of Mechanical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

⁵Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA

⁶Department of Chemical and Biomolecular Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong

Correspondence should be addressed to Belabbes Merzougui; bmerzougui@qf.org.qa, Tahar Laoui; laoui@kfupm.edu.sa, and Muataz Ali Atieh; mhussien@qf.org.qa

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Nitrogen-doped CNTs (N-CNTs) were synthesized using an injection-vertical chemical vapor deposition (IV-CVD) reactor. This type of reactor is quite useful for the continuous mass production of CNTs. In this work, the optimum deposition conditions for maximizing the incorporation of nitrogen were identified. Ferrocene served as the source of the Fe catalyst and was dissolved in acetonitrile, which served as both the hydrocarbon and nitrogen sources. Different concentrations of ferrocene in acetonitrile were introduced into the top of a vertically aligned reactor at a constant flow rate with hydrogen serving as the carrier. The effects of hydrogen flow rate, growth temperature, and catalyst loading (Fe from the ferrocene) on the microstructure, elemental composition, and yield of N-CNTs were investigated. The N-CNTs possessed a bamboo-like microstructure with a nitrogen doping level as high as 14 at.% when using 2.5 to 5 mg/mL of the ferrocene/acetonitrile mixture at 800°C under a 1000 sccm flow of hydrogen. A production rate of 100 mg/h was achieved under the optimized synthesis conditions.

1. Introduction

CNTs and nitrogen-doped CNTs as emerging materials for many applications can be synthesized by many methods, such as arc-discharge, laser ablation, spray pyrolysis, and chemical vapor deposition (CVD). CVD method can be categorized into thermal-assisted [1–3] and plasma-assisted [4] processes. Due to the strong electric fields in plasma sheaths, the growth of carbon materials by plasma CVD tends to have an individually and vertically free-standing shape [4, 5]. For many years, horizontally aligned CVD reactors have been used to produce carbon materials in variety of forms including

aligned or entangled, straight or coiled, and even a desired architecture of nanotubes at predefined sites on a patterned substrate with high purity but with low yield (few grams) [6, 7]. Vertically aligned CVD reactors with different synthesis mechanisms have been used to produce large quantities in the order of kg/h [8–13]. Recently, great attentions have been devoted to the study of nitrogen-doped carbon nanotubes (N-CNTs) because of their excellent properties, especially the electrical conductivity and electrocatalytic activity for oxygen reduction reaction [1, 2, 14–22].

Boncel et al. [23] pointed out that the synthesis of N-CNTs using an injection CVD technique has been typically

carried out using a horizontal reactor. Many factors including reaction temperatures, types of carrier gas and reactors, flow rates, carbon and nitrogen sources, and catalysts affect the shape, nitrogen content, and properties of N-CNTs. The reaction temperature plays a key role in determining the binding configuration of nitrogen atoms to the surrounding carbon atoms. For instance, Lee et al. [2] and Koós et al. [24] found that nitrogen insertion into the CNT microstructure depended inversely on the growth temperature. Yadav et al. [25], however, revealed that N-doped CNTs grown at low temperatures acquired a higher degree of microstructural disorder associated with the higher nitrogen doping. The effect of the carrier gas, commonly hydrogen, has been widely studied. The hydrogen was found to decrease the amount of nitrogen incorporated onto the N-CNTs owing to the equilibrium in the reactor between nitrogen and hydrogen radicals leading to the formation of stable gases such as HCN and NH_3 [26, 27]. In other words, the added hydrogen can lead to gas phase reactions that decrease the levels of reactive nitrogen species, such as $\text{CN}^\bullet$. N-CNTs have been produced using different sources of carbon and nitrogen such as pyridine [28], melamine [29], and acetonitrile [30, 31] and catalyst sources such as ferrocene [32, 33] and nickelocene [34, 35].

The incorporation of nitrogen changes the overall microstructure of CNTs and subsequently alters their physical, chemical, and electrical properties. In other words, the physiochemical properties of nitrogen-doped CNTs strongly depend on the nitrogen doping level, crystallinity, and nanotube dimensions such as diameter and wall thickness [14]. Several bonding configurations that result from nitrogen insertion into the lattice structure have been reported, namely, N-pyridinic, N-pyrrolic, N-quaternary, and N-oxides [14, 36, 37].

In the present study, an injection-vertical CVD (IV-CVD) reactor was constructed and used to synthesize N-CNTs. To the best of our knowledge, this is the first study using an IV-CVD reactor to produce N-CNTs. Our motivation of using such a reactor design is its capability of mass production of N-CNTs in a continuous process, which is highly desirable for industrial applications. The overall goal of this work is to identify the optimum deposition parameters for producing nitrogen-doped CNTs with the highest nitrogen content. The effects of the synthesis parameters, specifically the hydrogen flow rate, growth temperature, and catalyst loading, were investigated to determine their correlations with the levels of nitrogen doping.

2. Experiments

2.1. Synthesis of N-CNTs. An injection-vertical chemical vapor deposition (IV-CVD) system was used for growing the N-CNTs. Figure 1 shows a schematic diagram of the reactor that consists of a vertically aligned quartz tube (10 cm diameter, 100 cm height) heated by a tube furnace. The reactive gases were introduced at the top of the reactor.

For synthesis of the N-CNTs, Ar gas was used for flushing the reactor. The deposition temperature (700 to

1000°C), hydrogen (H_2) flow rate (750 to 2000 mL/min), and ferrocene (FcH)/acetonitrile (ACN) concentration (2.5–20 mg/mL) were systematically varied to obtain the highest nitrogen doping. The FcH/ACN solution was passed into the top of the vertical reactor for 1 h at a constant flow rate of 30 mL/h. The deposition time was typically 1 h. After growth, the reactor was allowed to cool to room temperature under an Ar gas flow. The N-CNTs were recovered from the inner wall as well as from the collector at the bottom of the reactor and subsequently weighted and characterized. In order to better understand the role of incorporated nitrogen in the morphology and microstructure, nitrogen-free CNT samples were also synthesized in the same IV-CVD reactor using FcH/para-xylene at 5 mg/mL under an H_2 flow rate of 1000 mL/min and a deposition temperature of 800°C.

2.2. Characterizations of N-CNTs. A field emission scanning electron microscope (FE-SEM), equipped with energy-dispersive X-ray spectroscopy (EDS) (Tescan Lyra-3), was used to analyze the morphology and elemental composition of N-CNTs. To quantify the nitrogen content, boron nitride (BN) and graphite were used for calibration of the EDS measurements. X-ray diffraction patterns were collected with a Rigaku Miniflex II instrument using a $\text{CuK}\alpha 1$ (1.5406 Å) source line at 30 kV and 15 mA. The XRD patterns were recorded in the static scanning mode from $2\theta = 5$ to 60° at a detector angular speed of $0.5^\circ/\text{min}$ and a step size of 0.02° . Matching crystal lattice parameters and space group analysis were determined with Philips X'Pert-plus (V. 2) software using diffraction patterns file (PDF-2) from ICDD (2011). XPS studies were carried out using a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al $\text{K}\alpha$ X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multichannel plate, and delay line detector; all operated at a base pressure less than 1.0×10^{-9} Torr. Survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. HR-TEM analysis was performed with Titan ST (FEI Co.) operated at 300 kV with a point resolution of 2 Å.

3. Results and Discussion

Several factors affect the incorporation (doping) of nitrogen into the CNT microstructure including the hydrogen flow rate, growth temperature, and catalyst loading. During injection of the FcH/ACN solution at the selected temperature and H_2 flow rate, the solvent evaporates and decomposes to produce reactive carbon and nitrogen species, presumably $\text{CH}_3^\bullet$ and $\text{CN}^\bullet$. The catalyst is produced from the decomposition of FcH into Fe atoms, which form metallic particles on the inner wall of quartz tube [35]. Cracking or decomposition of the ACN and FcH leads to the formation of free radicals, which are transported to the Fe catalyst sites where they adsorb and react to grow N-CNTs [26].

3.1. Morphological and Microstructural Analysis of N-CNTs. The morphological and microstructural characterizations of the N-CNTs were performed using SEM and TEM. Figure 2 displays SEM images of an N-CNT sample deposited

FIGURE 1: Schematic diagram of the IV-CVD reactor used for producing N-CNTs.

FIGURE 2: SEM micrographs of an N-CNT sample deposited using 5 mg/mL of FcH/ACN at an H_2 flow rate of 1000 mL/min and a deposition temperature of 800°C for 1 h.

using a 5 mg/mL FcH/ACN solution at an H_2 flow rate of 1000 mL/min and a deposition temperature of 800°C. These conditions were selected as a starting point for the optimization based on prior work with this reactor design. It can be seen that the CNTs have a tubular structure with a wide range of diameters from 50 to 300 nm. They were grown as closed-end tubes. HR-TEM images shown in Figure 3 reveal the tubes possess a bamboo-like structure with various

numbers of carbon layers (Figure 3(a)). Some tubes are thick consisting of about eight carbon layers (Figure 3(b)). EDS analysis revealed that the N-CNTs primarily consist of carbon and nitrogen with traces of oxygen, silicon (coming from the quartz reactor), and iron (catalyst).

The resulting N-CNTs have a similar size and microstructure as those reported by Lim et al. [27], who used similar deposition conditions but a different catalyst (NiFeMgO)

FIGURE 3: TEM micrographs at (a) low and (b) high magnification of an N-CNT sample deposited using 5 mg/mL of FcH/ACN at an H_2 flow rate of 1000 mL/min, a deposition temperature of 800°C, and a deposition time of 1 h. Dark spots are the Fe catalyst particles.

and temperature (400–600°C). The Fe catalyst particles were randomly distributed throughout the N-CNT network with a size in the range of 8–20 nm (Figure 3(a)).

3.2. Effect of Hydrogen Flow Rate on the Nitrogen Content in N-CNTs. Figure 4 shows the atomic percentage of nitrogen (measured by EDS) in the N-CNTs as a function of H_2 flow rate between 750 and 2000 mL/min. For these studies, a 5 mg/mL solution of FcH/ACN was used at a deposition temperature of 800°C. The maximum nitrogen content was obtained at an H_2 flow rate of 1000 mL/min. This result could be linked to the role that H_2 plays in the kinetic formation of N-CNTs, specially maintaining the Fe catalyst in the fully reduced form and affecting the availability of the reactive nitrogen and carbon species, $CN^\bullet$ and $CH_3^\bullet$.

Hao et al. [26] carried out a similar study using a MgO-supported Fe catalyst and ACN with and without H_2 . The authors found that the H_2 significantly reduced the amount of nitrogen in the CNTs. A reason for this is the formation of HCN during the pyrolysis of ACN due to the reaction between H_2 and free radicals of CN. The formation of stable HCN reduces the level of reactive nitrogen species in the gas phase for incorporation. In addition, Lim et al. [27] found that the addition of H_2 increased the growth rate of carbon nanofibers (CNFs) when using both acetonitrile and acrylonitrile as the source of carbon. The yield of CNFs with H_2 in the reactant gas was 4–8 times higher than that without H_2 . The presence of H_2 makes catalyst surface more active by keeping the Fe in the fully reduced form. Under their deposition conditions, no more than 5 at.% of nitrogen was achieved when H_2 was introduced, while in the absence of H_2 the nitrogen content increased to 10 at.%. In our experiments, the maximum nitrogen content obtained was 14 at.% at 800°C, 1000 mL/min of H_2 and 5 mg/mL of FcH/ACN. This doping level is significantly higher than that reported by Lim et al. [27], who used the similar growth conditions but with a horizontal fixed-bed reactor.

The mass of N-CNTs (Figure 4) collected as a function of the H_2 flow rate. The results reveal an increasing mass

FIGURE 4: Effect of H_2 flow rate on the nitrogen content and mass N-CNTs deposited with 5 mg/mL of FcH/ACN at 800°C for 1 h.

with increasing H_2 flow rate. From the data, a production rate of around 100 mg/h is calculated at 1000 mL/min. The production rate in this vertical reactor was measured by the amount of N-CNTs collected from the wall of the reactor and the collector placed at the bottom of the reactor for a fixed reaction time. This trend is in agreement with the work of van Dommele et al. [38] and Wasel et al. [39] for undoped CNTs. The increasing flow rate of H_2 leading to a higher production rate may be due to (i) reduced soot formation on the catalyst that would inactivate it and (ii) maintaining Fe catalyst in its fully reduced and most active form.

3.3. Effect of Temperature on the Nitrogen Content. The growth temperature is another key parameter in the production of N-CNTs [31, 40]. It plays a critical role in the decomposition of FcH above 500°C [3, 41] leading to the formation of Fe nanoparticles that grow in size by particle collisions [42]. Ayala et al. [41] suggested that when the growth temperature is increased, Fe particles sinter together

FIGURE 5: Effect of growth temperature on the nitrogen content in N-CNTs at 1000 mL/min of H_2 and 5 mg/mL of FcH/ACN and deposition time of 1 h.

producing larger nanoparticles, leading to the formation of larger diameter nanotubes. The growth temperature also affects the availability of reactive carbon species from the decomposition of ACN. Figure 5 shows the atomic percentage of nitrogen in the N-CNTs as a function of growth temperature. It can be concluded that the temperature of maximum nitrogen incorporation is near 800°C. The effect of deposition temperature on the nitrogen doping of CNTs is somewhat inconsistent with the literature. For example, Lee et al. [2] showed that the incorporation of nitrogen varies inversely with the growth temperature particularly at high temperatures. They observed that the percentage of nitrogen decreased by 30% when the deposition temperature was increased from 800 to 1000°C. In the other work, Koós et al. [24] reported the nitrogen content decreased by nearly 50% when increasing the temperature from 800 to 900°C. In our work, we only saw a few percent reduction when the deposition temperature was increased from 800 to 1000°C.

3.4. Effect of Catalyst Concentration on the Nitrogen Content in N-CNTs. These studies were performed with various FcH concentrations in ACN from 2 to 15 mg/mL while maintaining a constant growth temperature of 800°C and an H_2 flow rate of 1000 mL/min. As illustrated in Figure 6, the highest amount of nitrogen incorporation was obtained when the FcH concentrations were in the range of 2.5–5 mg/mL. The EDS results revealed a maximum N content of 14.5 at.%. As the concentration was increased, the nitrogen content decreased to about 10 at.%. It is clear that the nitrogen content varied over a relatively narrow range from 10 to 15 at.% at different FcH concentrations. As the FcH concentration is increased, the N/C atomic ratio in the source gas decreases, which could be the cause for the decreasing nitrogen content in the CNTs.

3.5. Chemical and Structural Characterization of the N-CNTs. Figure 7 shows XRD patterns of N-CNT and CNT samples. The N-CNTs were deposited using 5 mg/mL of FcH/ACN, an H_2 flow rate of 1000 mL/min, and a deposition temperature

FIGURE 6: Effect of the Fe catalyst concentration on the nitrogen content in N-CNTs grown at an H_2 flow rate of 1000 mL/min, a deposition temperature of 800°C, and a deposition time of 1 h.

TABLE 1: XPS determined elemental composition of N-CNTs (at.%) for low and high catalyst loadings.

Elements (at.%)	Fe	O	C	N	Si
Low catalyst loading (5 mg/mL)	0.6	3	92	3.8	1.3
High catalyst loading (15 mg/mL)	0.3	2	94	3.1	0.4

of 800°C, while the CNTs were deposited under identical conditions except that an FcH/para-xylene solution was used as the source of carbon. The deposition time for both samples was 1 h. It is worth noting that XRD data for the N-CNTs samples were similar regardless of the catalyst concentration, growth temperature, or H_2 flow rate used. The peak at $2\theta = 27.17^\circ$ is the characteristic of (002) line for hexagonal graphite ($d = 3.27 \text{ \AA}$) arising from the N-CNT carbon microstructure. This peak reflects the graphitic character of the CNTs. The peak in 42–48° range could be attributed to (101) plane of N-CNTs or to some trace of iron carbide or iron metallic catalyst. However, because of the presence of many nitrogen functionalities in the N-CNT microstructure, there is a small shift ($\Delta 2\theta = 0.945^\circ$) towards higher 2θ as compared to the diffraction data for nitrogen-free CNTs ($2\theta = 26.71^\circ$). This may be due to the incorporation of nitrogen in the structure of nanotubes that promotes the graphitic stacking and creates slight distortion in crystalline regularity along a or b direction by shorter C-N bonds [27].

XPS has been proven useful for quantifying the level and identifying the chemical environments of the incorporated nitrogen [4, 43–46]. Figures 8 and 9 show typical N1s XPS spectra between 394 and 410 eV for N-CNT samples grown with a low (5 mg/mL) and high (15 mg/mL) concentration of FcH/ACN at a growth temperature of 800°C.

The data analysis (see Table 1) showed that 3.8 and 3.1 at.% of nitrogen were incorporated into the N-CNTs at the low and high catalyst loadings, respectively. It is important to note that the amount of nitrogen determined by XPS (3.1–3.8 at.%) is lower than the values obtained with EDS (10–14 at.%), due to

FIGURE 7: XRD patterns of CNTs (red) deposited using 5 mg/mL of FcH/para-xylene and N-CNTs (blue) deposited with 5 mg/mL of FcH/ACN using the IV-CVD reactor. For both samples, the H_2 flow rate was 1000 mL/min, the deposition temperature was 800°C, and the deposition time was 1 h.

the fact that XPS is a surface sensitive technique providing elemental composition from a depth of 1–12 nm, while the depth in EDS is greater than 500 nm. Nevertheless, a similar trend is observed with both analysis techniques; that is, the percentage of nitrogen incorporated decreases with catalyst loading. Si and Fe impurities were also detected in both samples.

Nitrogen in four different chemical environments was identified in the N-CNTs with the relative ratio of the types depending on the concentration of FcH catalyst used. It has been reported that at least four types of nitrogen can be distinguished based on deconvolution of the N1s spectrum: pyridinic-N (398.6 eV), pyrrolic-N (400.1 eV), quaternary-N (401.1 eV), and pyridinic-N oxides (402–405 eV) [14, 17, 36, 40, 41, 47]. The literature peaks agree well with those seen in the deconvoluting of our spectra. As displayed in Figures 8 and 9, the distribution of the different types of nitrogen functional groups depends on the catalyst concentration/loading. Indeed, it should be noted that there are seven peaks in the low catalyst sample spectrum (Figure 8) and only four peaks in the high catalyst sample (Figure 9). In addition to the pyridinic, pyrrolic, quaternary, and pyridinic oxides nitrogen species, Kumar [31] detected more than six peaks of nitrogen species in the pyrolysis of mixtures of camphor, FcH, and dimethylformamide. They attributed the peak at 397.3 eV to the iron nitride in agreement with the results found by He et al. [16] and Hasan et al. [48]. The latter group assigned the N1s peak at 398.1 eV to the interaction between metal and pyridinic nitrogen. On the other hand, Ronning et al. [44] have reported the most nitrogen functional group forms present in carbonaceous materials and assigned the peak at 399.5 to pyrrolic or cyano-like groups and the peaks at (402.5–406.1 eV) to certain forms of oxidized nitrogen, like N-oxides of pyridinic-N. These results are, however, in contrast to

FIGURE 8: Deconvoluted XPS spectrum in the N1s region of an N-CNT sample grown with an FcH/ACH concentration of 5 mg/mL and 1000 mL/min of H_2 at 800°C using the IV-CVD reactor.

FIGURE 9: Deconvoluted XPS spectrum in the N1s region for an N-CNT sample grown with an FcH/ACH concentration of 15 mg/mL and 1000 mL/min of H_2 at 800°C using the IV-CVD reactor.

other reports [31, 47] that attribute the peaks at 403.3 and 404.3 eV to the molecular nitrogen trapped inside the tubes or intercalated into the graphite layers of the CNTs.

The formation of pyridinic oxides in our samples could be explained by the high reactivity towards oxidation via the transformation of quaternary nitrogen to pyridinic oxides at

TABLE 2: Major nitrogen functional groups identified in the N-CNTs grown with the low and high catalyst loadings.

Sample/N content (%)	N-Pyridinic (397–398.6 eV)	N-Pyrrolic (399.7 eV)	N-Quaternary (401 eV)	N-Pyridinic oxides (402–405 eV)
Low catalyst loading (5 mg/mL)	31	5	37	28
High catalyst loading (15 mg/mL)	48	7	31	15

high temperatures [40] in presence of oxygen traces dissolved in the mixture or impurities in the reactor. Table 2 compares the percentage of N-types incorporated into CNTs structure obtained from deconvolution and fitting results.

The comparison shows that the percentages of N-pyridinic and N-pyrrolic functionalities tend to increase and N-quaternary and N-pyridinic oxides groups tend to decrease with catalyst loading at the same growth temperature. It has been found that the dilution of nitrogen source affects the formation of nitrogen species. Ghosh et al. [32] injected different dimethylformamide concentrations in the presence of FcH and found that the peak areas of pyridinic, pyrrolic, and quaternary species increased with concentration of nitrogen source but at the same catalyst loading. However, in our study, the catalyst loading was increased leading to an increase in percentage of pyridinic and pyrrolic and decrease in quaternary and pyridinic oxides nitrogen species. Thus, we assume that increasing catalyst loading could promote the formation of N-pyridinic.

4. Conclusions

Nitrogen-doped carbon nanotubes were synthesized using a mixture of FcH and ACN in an inverted-vertical CVD reactor. The primary aim of this study was optimization of the synthesis parameters to prepare N-CNTs with high nitrogen content. Specifically, the effects of the synthesis conditions including hydrogen flow rate, growth temperature, and catalyst concentration were evaluated. The results showed that N-CNTs could be produced in an inverted-vertical CVD reactor with a high nitrogen incorporation of around 14 at.% using 2.5 to 5 mg/mL of FcH/ACN solution, a hydrogen flow rate of 1000 mL/min, and deposition temperature of 800°C. TEM images revealed that the N-CNTs have a bamboo-like structure consistent with the insertion of heteroatoms into the lattice. XRD patterns for the N-CNTs, as compared to CNTs with no nitrogen, revealed a shift toward lower d -spacing due to the formation of shorter N-C bonds as compared to C-C bonds. The former leads to less graphene sheet stacking. XPS was used to elucidate the effect of catalyst loading on the formation of different types of nitrogen in the CNTs structure. The results showed that nitrogen in four different chemical environments was formed when a high catalyst loading was employed while seven nitrogen types were found at a low catalyst loading. Finally, the results showed that the percentages of N-pyridinic and N-pyrrolic moieties increase and N-quaternary and N-pyridinic decrease with increased catalyst loading at the same deposition temperature. With the deposition parameters optimized for producing N-CNTs with a high nitrogen content, future work will involve scaling

up of the IV-CVD reactor for mass production as well as more detailed investigation of the N-CNT growth mechanism.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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