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# Enhanced growth of carbon nanotube bundles in a magnetically assisted fluidized bed chemical vapor deposition



arbor

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#### ABSTRACT

The efficient fabrication of carbon nanotube (CNT) bundles is the prerequisite for their bulk applications. However, the poor fluidization behavior of metal nanoparticle catalysts hinders the effective growth of high quality CNT bundles. Herein magnetically assisted fluidized bed (MFB) chemical vapor deposition was proposed for bulk growth of long CNT arrays. By introducing a uniform magnetic field into the fluidized bed reactor, the fluidization behavior of the ultrafine catalyst particles derived from FeMgAl layered double hydroxides (LDHs) was significantly improved with reduced bed pressure drop and increased bed expansion. Possibly, the magnetic LDH-catalyst flakes were arranged orderly in a magnetic field, which facilitated the steady and durative growth of CNT bundles. Compared with the CNT products grown in a routine fluidized bed reactor, the as-produced CNTs in the MFB reactor were with a much higher yield of 9.1  $g_{CNT/g_{catal}}$ , improved graphitic degree, increased length up to ~100  $\mu$ m, together with smaller diameters and narrower diameter distribution as well. A gradient-magnetically assisted fluidized bed reactor was also explored for facile fabrication of very long CNT bundles over 100  $\mu$ m.

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## 1. Introduction

Carbon nanotubes (CNTs) have been strongly considered in the past decades [1–3]. As carbon atoms in CNTs are bonded with each other in sp<sup>2</sup> hybridization, CNTs afford extraordinary electrical and thermal conductivities, superb mechanical properties, tunable nanostructures that bring about the wide applications in various fields such as high-performance composites [4,5], electronics [6], catalysis [7,8], and energy conversion and storage [9,10]. In particular, CNT bundles, in which individual CNTs are aligned orderly in the same direction, are generally favored for the practical applications, stemming from the facts that aligned CNTs are more easily dispersible and usually with higher aspect ratios in contrast with the entangled CNT agglomerates. The mass production of long CNT bundles is the prerequisite for their practical applications.

Until now, the fluidized-bed catalytic chemical vapor deposition (CVD) method is commonly believed as the most efficient for the mass production of CNTs due to the advantages of large operation capacity, superior mass/heat transfer, easiness in scaling up, and

\* Corresponding author. E-mail address: zhang-qiang@mails.tsinghua.edu.cn (Q. Zhang). continuous operation. Particularly, the industrial production of agglomerated multi-walled CNTs has been achieved using fluidized-bed CVD method [4]. In the case of aligned CNT bundles, they were easily fabricated in fixed bed reactors using supported catalysts on flat substrates, such as Si/SiO<sub>2</sub> wafer [11], guartz [12], and so on. However, these supported catalysts with limited surface area hindered the mass production of CNT bundles, which were also ill-suited in a fluidized bed reactor due to the bad fluidization behavior. Much effort has therefore been devoted to developing better catalysts and reactors to improve the aligned CNT productivity. We previously used vermiculite-supported catalyst to produce vertically aligned CNTs with the length of  $10-20 \ \mu m$  in a fluidized bed reactor [13] and realized the mass production of CNT arrays (3.0 kg h<sup>-1</sup>) in a pilot plant fluidized bed reactor [14]. Noda and coworkers successfully used ceramic beads as the catalyst carrier in a fluidized-bed process and produced sub-millimeterlong CNT arrays with acetylene as the carbon source [15,16]. Because the ceramic beads as the catalyst carrier had high density of 3.89 g cm<sup>-3</sup> and were sufficiently active with Fe/AlO<sub>x</sub> catalyst layers, high gas velocity was employed to achieve a well-designed repetitive process for CNT growth. Furthermore, to cope with the problems of insufficient heat transfer in bead bed and the



distributor stacking during the recycle process, they firstly proposed a new fluidized bed reactor with an internal heat-exchange and preheating zone to produce sub-millimeter-long CNT arrays at high space velocity ( $3600 h^{-1}$ ) [2].

Recently, we developed the efficient fabrication of double helical CNT bundles over 1.0 mm long in a fixed bed reactor with layered double hydroxide (LDH) derived catalyst [17]. As typical synthetic two-dimensional nano-structured anionic clavs. LDHs are constituted by charge-balancing anions like  $CO_3^{2-}$  and positively charged layers composed of di- and trivalent metal cations coordinated octahedrally by hydroxyl groups [18]. The lateral size of one LDH flake is ranging from several nanometers to micrometers while the thickness is usually with a size of less than 30 nm. The metal cations are dispersed in the lamellar LDH flakes at an atomic level, which facilitates the formation of highly-dispersed metal NPs after calcination and reduction. Moreover, the calcined and reduced LDHs remain the plate-like morphology in microscale and the active metal NPs are partly and/or totally embedded in the lamellar substrate comprised of metal oxides [19]. The strong interactions between the metal NPs and the substrate render the metal NP catalysts with high thermal stability through restraining the severe sintering and coalescence at high temperature. In addition, uniform distribution for active metal NPs in the relatively flat substrate is of paramount importance for the growth of CNT bundles [20-22]. As a result, LDHs are the desired catalysts for efficient production of CNT arrays. However, in spite of the advantages mentioned above, the nano-structured LDH derived catalysts suffer from poor fluidization behavior due to the cohesiveness of ultrafine particles when they are applied in fluidized bed CVD.

The introduction of external force through vibration [23], magnetic field [24,25], and acoustic field [26] is very effective to tune the fluidization behavior of ultrafine particles. Among them, a magnetically assisted fluidized bed (MFB) combining the advantages of both fixed bed and fluidized bed is expected to enhance the gas-solid fluidization quality in many aspects, such as suppressing the back-mixing to narrow the residence time distribution, inhibiting the formation and expansion of bubbles and channeling, decreasing the bed pressure drop, and increasing the operation capacity [25,27,28]. As so far, MFB reactors have been widely applied in the fields of environmental protection [29], separation [30], and heterogeneous catalysis [31], etc.

In this contribution, an effective and efficient strategy based on the magnetically assisted fluidized bed CVD was developed to achieve the bulk growth of long CNT arrays using FeMgAl LDHs as the catalyst precursor. The fluidization behavior of magnetic catalyst particles derived from FeMgAl LDHs was evaluated in the uniform-magnetic-field assisted fluidized bed reactor and in the routine fluidized bed reactor firstly. Then the growth of CNT arrays was performed and the structural difference of the CNT products was subsequently investigated in detail. A non-uniform magnetic field was also built up, in which the gradient-magnetically assisted fluidized bed reactor was effective in the synthesis of long CNT arrays. The magnetically assisted fluidized bed CVD is a promising method for the controllable fabrication of CNT bundles for versatile applications.

### 2. Experimental

#### 2.1. Preparation of the catalyst precursor

The flake-like FeMgAl LDHs were employed as the catalyst precursors to grow CNT bundles in this contribution. The LDHs were fabricated *via* a routine urea assisted co-precipitation method as reported by our previous publications [32]. Briefly,  $Al(NO_3)_3 \cdot 9H_2O$ ,  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $Mg(NO_3)_2 \cdot 6H_2O$ , and urea were

dissolved in 1.0 L deionized water with a molar ratio of n(Al): n(Fe): n(Mg) = 1: 0.8: 2, and molar concentrations of  $[Al^{3+}] + [Fe^{3+}] + [Mg^{2+}] = 0.19 \text{ mol } L^{-1}$ ,  $[urea] = 3.0 \text{ mol } L^{-1}$ . The solution was kept at 100 °C under continuous magnetic stirring for 12.0 h in a 2.0 L flask, equipping with a reflux condenser. Then the as-derived suspension was kept at 94 °C for another 12.0 h without magnetic stirring. Afterwards, the suspension was further filtered, washed by deionized water for 5 times, and freeze-dried to achieve the final FeMgAl LDH catalyst precursors.

### 2.2. Growth of CNT bundles in MFB

Fe NPs derived from FeMgAl LDHs were served as the metal catalysts for the bulk growth of CNT arrays. The growth of CNT bundles was performed in a magnetic field assisted fluidized bed reactor using the catalytic CVD. The main apparatus is a quartz tube reactor with an inner diameter of 14 mm and a height of 500 mm. Four parallel copper solenoids surrounded the quartz reactor and the furnace to generate axial uniform magnetic field. The intensity of the magnetic field (H) was tuned by the current of the power supply to the copper solenoids. 0.20 g LDHs were loaded into the reactor and the catalytic reaction was carried out at 700 °C for 40 min with 70/40/40 mL min<sup>-1</sup> N<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>6</sub> as the protective gas, reductive gas, and carbon source, respectively. After aligned CNT deposition, the reactor was cooled down to room temperature under N<sub>2</sub> protection.

# 2.3. Characterization

The microstructure and morphology of the catalysts and the asgrown CNT products were observed by a scanning electron microscope (SEM, JSM 7401F) operated at 3.0 kV and a high-resolution transmission electron microscope (TEM, JEM 2010) operated at 120.0 kV. The X-ray diffraction (XRD) pattern of the LDH-based catalysts was recorded on a Bruker D8 Advance X-ray diffractometer. The magnetic hysteresis loops of the reduced LDO catalyst was measured with a LakeShore 7307 vibrating sample magnetometer. Raman spectra of the CNT products were collected with He-Ne laser excitation at 633 nm using Horiba Jobin Yvon LabRAM HR800 Raman spectrophotometer. The thermogravimetric analysis (TGA) was performed using Mettler Toledo TGA/DSC-1 under O2 atmosphere with a temperature increasing speed of 20 °C min<sup>-1</sup>. In order to calculate the yield as precise as possible, calcination tests were carried out by calcining the as-produced CNTs (~50 mg) at 800 °C in O<sub>2</sub> atmosphere for 30 min. During the calcination, CNTs were burned into CO<sub>2</sub> and the residues were oxidized catalysts. Therefore, the yield of CNT products is calculated as follows:

$$Yield = Weight_{loss} / Weight'_{residue}$$
(1)

Herein, Weight'<sub>residue</sub> refers to the unoxidized catalyst weight, which was converted from the weight of the residues. The calcination tests were performed 3 times for each sample and calculated the average value.

### 3. Results and discussion

# 3.1. Structure and fluidization characteristics of the LDH based catalyst

FeMgAl LDH based catalyst was used for the CNT growth in this work. Firstly, the as-prepared FeMgAl LDHs were calcined and reduced under  $H_2/Ar$  atmosphere at 700 °C for 30 min. After calcination, the lamellar LDH flakes were topotactically transformed into layered double oxides (LDOs) that also exhibited plate-

like morphology. The LDOs were mainly composed of Fe<sub>2</sub>O<sub>3</sub>, MgO, and spinel MgAl<sub>2</sub>O<sub>4</sub> phases. The iron oxides were reduced into Fe NPs by H<sub>2</sub>. The reduced FeMgAl LDO catalysts retained the plate-like flakes with a lateral size of 1–2  $\mu$ m (Fig. 1a & b). The tiny Fe NPs with an areal density as high as 10<sup>15</sup> m<sup>-2</sup> were uniformly distributed on the LDO flakes [33]. The XRD profile in Fig. 1c exhibited the characteristic peaks assigned to Fe, MgO, and MgAl<sub>2</sub>O<sub>4</sub> spinel.

To investigate the magnetic property of the reduced FeMgAl LDO catalyst, a vibrating-sample magnetometer was applied to collect the magnetic hysteresis loop as shown in Fig. 1d. The saturation magnetization/unit mass was about 22 emu g<sup>-1</sup> and the remanence was about 6 emu g<sup>-1</sup>. The coercivity of the reduced FeMgAl LDOs was around 473 Oe, which was much higher than that of bulk iron (~0.15 Oe) due to the small size effect of magnetic particles [34,35].

Both the high density metal NPs  $(10^{15} \text{ m}^{-2})$  and the flat morphology of the reduced LDO catalyst are prerequisites for the efficient growth of CNT bundles. The LDOs were with a lateral size of *ca*. 1–2 µm, a thickness of *ca*. 20 nm, and a low bulk density of 380 kg m<sup>-3</sup> after calcination and reduction. Consequently, the individual LDO particles are classified as Geldart group C particles. Most of Geldart group C particles can hardly be fluidized steadily as the interparticle interactions dominate the aggregate formation while the gas fluid drag forces are very weak in this case. As the result of low density of Geldart group C particles and negligible slip velocities, channeling and arbitrary aggregation of nano-particles are always observed, leading to the poor fluidized behavior. In addition, the back-mixing, disturbance, and disorder of the reduced LDO flakes are destructive to the growth of long CNT arrays.

It should be noticed that the reduced FeMgAl LDO catalyst exhibited a magnetic sensitive property. If these catalyst particles are laid into a magnetic field, the aggregates formed from the intrinsic and magnetically induced interparticle forces are under control. Therefore, the use of external magnetic-field assisting fluidized beds allows modulating the behavior of fluidized magnetic particles in a working condition [36–38]. Herein, the extra assistance of magnetic field is expected to promote the fluidization of LDH-based catalysts and enhance aligned CNT growth.

A cold-model test was carried out to investigate the fluidization characteristics of the reduced FeMgAl LDO catalyst in a MFB reactor. The intensity of the magnetic field H was controlled to be 222 Oe. For comparison, the fluidization behavior in a routine fluidized bed reactor without magnetic field was also investigated as a control test. As shown in Fig. 2, compared with the routine fluidized bed, the bed pressure drop in the MFB reactor was significantly decreased. Furthermore, when the gas velocity was larger than 4.1 cm s<sup>-1</sup>, the bed pressure drop in the MFB reactor approached a plateau while still up-going in the routine fluidized bed reactor. Besides, the maximum bed expansion (h/h<sub>o</sub>) was increased from 1.9 to 2.3 after the introduction of magnetic field. The fluidization quality of the LDH-based catalysts was significantly improved with



Fig. 1. The FeMgAl LDH based catalyst after calcination and reduction at 700 °C for 30 min: (a) SEM and (b) TEM image, (c) XRD pattern, and (d) magnetic hysteresis loop of the reduced catalyst for aligned CNT growth.



**Fig. 2.** The fluidization characteristics of reduced FeMgAl based catalysts in a MFB reactor. (A colour version of this figure can be viewed online.)

the assistance of magnetic field. The magnetic particles were aligned along the magnetic lines of force to form magnetic chains in the MFB reactor as previously reported probably [25]. On one hand, the magnetic chains are supposed to serve as small vertical internals to penetrate into the bubbles and split them into smaller ones, leading to enhanced mass transfer of feedstocks, products, and exhausts. On the other hand, the presumably ordered arrangement of reduced LDO flakes restrained the back-mixing and disturbance to some extent which was beneficial for the efficient growth of long CNT arrays. Accordingly, producing long CNT bundles in MFB reactor with LDH-based catalysts was quite promising.

# 3.2. CNT bundle growth with and without the assistance of magnetic field

The CNT products grown in a routine fluidized bed reactor and in the MFB reactor were labelled as R-CNTs and M-CNTs, respectively. A uniform magnetic field in a fluidized bed reactor was applied by matching the furnace and reactor in the center of the copper electromagnet coils. SEM images in Fig. 3 exhibited that R-CNTs were loosely compacted CNT arrays with a length of several micrometers (less than 10  $\mu$ m). In comparison, M-CNTs were aligned tightly into quite long curving bundles with the length of tens of micrometers and even over 100  $\mu$ m under conservative estimation (Fig. 3b). Even the prototype of double helical CNT arrays (Fig. 3d) was observed in M-CNTs. The effective confined growth of long helical CNT bundles [39] was contributed by the relatively steady and ordered arranged LDH-catalyst flakes in a magnetic field.

To determine the quality of carbon grown in a routine and magnetic field assistant fluidized bed, TGA was carried out. As presented in the differential thermogravimetric (DTG) curve, the majority weight loss of the M-CNT sample took place at a temperature of 615 °C (Fig. 4a), which is about 30 °C higher than that of the R-CNT. The thermal stability of M-CNTs was a bit improved.



Fig. 3. Morphology and microstructure of (a, c) the R-CNTs produced in a routine fluidized bed and (b, d) the M-CNTs grown in a magnetically assisted fluidized bed. R-LDO in (c) stands for the Fe catalysts based on the reduced LDOs. (A colour version of this figure can be viewed online.)



**Fig. 4.** Characterization of R- and M-CNT products: (a) TGA and DTG curves, (b) Raman spectra. (A colour version of this figure can be viewed online.)

The yields of the CNT products were calculated based on the mass ratio of weight loss to the residuals (converted to the unoxidized R-LDO catalysts) in the calcination tests. Particularly, the yield of M-CNTs was significantly improved to 9.1 g<sub>CNT</sub>/g<sub>catal</sub>, in comparison with that of R-CNTs (3.3 g<sub>CNT</sub>/g<sub>catal</sub>). Furthermore, Raman spectra were applied to determine the graphitic degree of the CNT products. As presented in Fig. 4b, D band at around 1325 cm<sup>-1</sup> is known to be characteristic for disordered graphitic carbon and G band around 1580 cm<sup>-1</sup> is corresponding to the ideal graphitic lattice vibration mode with  $E_{2g}$  symmetry. The intensity ratio  $I_D/I_G$  of D band to G band is widely accepted as a macroscopic evaluation criterion of the graphitic degree for nanocarbon. By introducing a

magnetic field into a fluidized bed reactor during CVD growth of CNT bundles, the  $I_D/I_G$  ratio of the CNT products was reduced from 1.57 to 1.23, indicating the higher graphitic quality of M-CNTs. Since the higher graphitic degree renders the carbon with better thermal stability in  $O_2$ , the results indicated by Raman spectra were consistent with the TGA characterization.

Moreover, TEM was employed to investigate the microstructure of aligned CNT products grown with and without the assistance of magnetic field. As illustrated in Fig. 5, both R-CNTs and M-CNTs displayed a tubular-like structure. There are intrinsic defects distributed on CNTs, which induced the curve structures. From the high-resolution TEM images in Fig. 5, it is illustrated that M-CNTs were thinner than R-CNTs with smaller diameter and fewer walls. CNT diameter distribution for both samples was obtained by measuring over 200 individual CNTs of each sample in highresolution TEM images and the statistical results were shown in Fig. 5e. It was illustrated that the diameters of M-CNTs were mainly ranged from 5 to 15 nm, while diameter distribution for the majority R-CNTs was in the range of 7-19 nm. Consequently, by introducing magnetic field into the fluidized bed reactor, the asproduced M-CNTs were with decreasing diameters and narrower diameter distribution.

## 3.3. Various CNT products in non-uniform magnetic field

By shifting down the copper electromagnet coils to only surround the bottom half part of the fluidized bed reactor, a nonuniform magnetic field was achieved with a magnetic field gradient from bottom to the top of the reactor. In this case, the magnetic field at the bottom part is stronger and particles are supposed to compact tightly due to the extra downward magnetic force, while the ones at the top part are randomly floating presumably. Therefore, the CNT products at the bottom and top parts were quite different from each other.

SEM images in Fig. 6 showed the morphology of the different CNT products. The CNT products in the surface was short slackly aligned CNTs with up to 2 µm in length (Fig. 6a), which was similar with the CNTs produced in a routine fluidized bed reactor. However, the CNT product at the bottom part was tightly packed CNT arrays as long as 60 and even over a hundred micrometers (Fig. 6b). At the bottom of the reactor, even some CNTs clung to the wall and the gas distributor. When peeling off, the root of the CNT arrays was rather smooth just as the aligned CNTs grown on a very flat substrate in a fixed bed reactor (Fig. 6c). Catalyst films were also found which were formed by the ordered arranging reduced LDO flakes as illustrated in Fig. 6d. In this gradientmagnetically assisted fluidized bed reactor, facile growth of CNT arrays with ~100 µm in length was achieved using ultra-light LDHbased catalysts. Therefore, it's an another promising choice to design a multistage gradient-magnetically assisted fluidized bed reactor for high efficient production of long CNT arrays which should be further explored.

# 3.4. Discussion on CNT growth in a magnetic field assisted fluidized bed

The use of magnetic field is an effective routine to tune the CNT nanostructures and intensify the CNT growth. For example, Doherty et al. [40] reported the magnetic field can spread and stabilize the plasma enabling the use of larger electrodes in an arc-discharge process. Keidar et al. found the magnetic field increase the plasma density during an arc-discharge process. The average length of single walled CNTs increases to 5  $\mu$ m by magnetic enhanced arc-discharge growth, which is double of CNTs grown without magnetic field [41]. The good combination of arc discharge and a weak



Fig. 5. TEM images and high-resolution TEM images of the CNT products grown in a routine fluidized bed reactor (a, b), a magnetically assisted fluidized bed reactor (c, d), and (e) the corresponding diameter distributions of the CNT products. (A colour version of this figure can be viewed online.)



**Fig. 6.** Growth of aligned CNTs in non-uniform magnetic field assisted fluidized bed: (a) Morphology of the aligned CNT products in the upper surface of the bed; morphology of (b, c) the long CNT arrays and (d) the catalysts peeled off from the bottom wall of the reactor. (A colour version of this figure can be viewed online.)

magnetic field of 0.56 T allows direct fabrication of aligned singlewall CNT films [42]. Besides the arc-discharge synthesis, magnetism-assisted CVD for CNT growth was also researched. Wei et al. [35] reported the synthesis of branched or iron-encapsulated CNTs in a magnetically assisted fixed bed reactor. During the CVD process, the external magnetic field with 50 mT cm<sup>-1</sup> gradient can promote the coalescence or division of the catalyst particles, causing the formation of branched or encapsulated nanostructures. Ohmae [43] and Luo et al. [44] both reported that the magnetic field can control the growth direction and morphology of CNTs or carbon nanofibers during the CVD growth.

The addition of magnetic field applied external interactions with metal nanoparticles. For instance, the ferromagnetic Fe/Co/Ni nanoparticles experience a controllable force in the magnetic field, and tend to drive the CNT grown in the direction where the magnetic field lines get stronger if the CNTs were grown from the catalyst tip. If we consider an individual metal catalyst, attributed from the diamagnetism of C atoms, the magnetic torque of C atoms was opposite to the external magnetic field line. This created a repulsive force on it and the C atoms preferred to precipitate along the opposite direction of the field line. Consequently, a compressive stress was achieved at the bottom of the metal catalysts, inducing the molten metal particle becoming a cone shape [44]. Therefore, a tip growth of CNT under magnetic field induced the large diameter of CNTs.

Herein, we applied the magnetic field on LDH derived catalysts in a fluidized bed. The reason we selected fluidized bed reactor is attributed from their advantages of enough space for carbon deposition, excellent heat and mass transfer, continuous operation, and the ability to produce CNTs at an industrial scale [2,16,45–47]. However, direct growth of very high quality CNT bundles in a continuous way [13,15,48,49] is still a grand challenge. In this contribution, metal nanoparticles embedded into oxide support were selected as model catalyst, in which the catalyst nanoparticles afford strong binding with the substrates [33]. The strong metal-support interaction renders the catalyst with a very high areal density over  $10^{15}$  m<sup>-2</sup>. The external magnetic field applied on the fluidized bed reactor resulted in external forces on the ferromagnetic Fe nanoparticles, which can tune the aggregate formation in a gas flow. The well match of intrinsic and magnetically induced interparticle forces brings about the smooth fluidization of reduced LDO in this work. The large bed expansion and smooth fluidization afford enough space for CNT deposition. This provides a very stable operation of aligned CNT growth. In contrast to Fe on Si wafer in which the external magnetic field promotes the coalescence or division of the Fe particles [35], tiny Fe nanoparticles are strongly anchored by the LDO supports, the size of Fe nanoparticles is almost constant. The uniform distribution of catalyst, stable mass transfer of feedstock, as well as bubble-free flow in the MFB guarantee the synchronous growth of CNT bundles in high graphitization degree. Otherwise, the unstable operation and strong collision among catalyst nanoparticle renders the CNT growth with complex conditions. This is also confirmed by the results reported in Section 3.2, in which CNTs with different nanostructures were grown on the same catalyst with/without magnetic field. We didn't observe the growth of branched CNTs in our work. However, we agree the possibility of magnetic field promoted coalescence or division of metal catalyst particles for controllable fabrication of branched or metalencapsulated CNTs if the metal-support interaction becomes weak. Hereby, the proof-of-concept that introduction of magnetic field into fluidized bed CVD benefits the high yield, morphologycontrolled growth of CNT bundles is unambiguously verified. This magnetically assisted fluidized bed CVD system affords a new perspective for the mass production of long CNT arrays.

#### 4. Conclusions

A unique and facile method of the magnetically assisted fluidized bed through CVD was developed for the efficient growth of long CNT bundles. By introducing the magnetic field into the fluidized bed, the fluidization quality of the LDH based catalyst was significantly improved with less bed pressure drop and increased bed expansion. Besides, the tiny magnetic catalyst particles were supposed to be arranged more orderly in the magnetic field, which was beneficial for the steady and continuous growth of long CNT arrays. As a consequence, in comparison with the CNT yield in the routine fluidized bed reactor, the yield of CNT products in the magnetically assisted fluidized bed reactor increased from 3.3 to 9.1 g<sub>CNT</sub>/g<sub>catal</sub>. CNT array products grown in the MFB reactor were with improved length up to  $\sim 100 \,\mu m$  and enhanced graphitic degree as well. Furthermore, the diameter distribution became narrower and shifted towards small diameter for the as-produced CNTs in MFB reactor compared with that for the routinely produced CNTs. In addition, it was interesting to observe that quite different CNT products were obtained when the uniform magnetic field was tuned to be non-uniform. In the gradient-magnetically assisted fluidized bed reactor, magnetic catalyst flakes could be compacted into flat films at the bottom part of the reactor which facilitated the growth of straight long CNT arrays. In this case, a multistage gradient-magnetically assisted fluidized bed reactor was supposed to be also efficient for producing CNT bundles over 100  $\mu$ m – long in large scale when further exploration was carried out. Therefore, the magnetically assisted fluidized bed CVD method is a prospective growth technology for the production of long CNT arrays in large scale. This is an emerging method to controllable fabrication of CNT bundles with high quality for their bulk applications in various fields such as high-performance composites, environmental protection, and energy conversion and storage.

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