

# Layered double hydroxides as catalysts for the efficient growth of high quality single-walled carbon nanotubes in a fluidized bed reactor

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#### ABSTRACT

A family of layered double hydroxides (LDHs), such as Fe/Mg/Al, Co/Mg/Al, and Ni/Mg/Al LDHs, were used as catalysts for the efficient growth of single-walled carbon nanotubes (SWCNTs) in a fluidized bed reactor. The LDH flakes were agglomerated into clusters with sizes ranging from 50 to 200  $\mu$ m, and they can be easily fluidized with a gas velocity ranging from 2.3 to 24 cm/s. After calcination and reduction, small metal catalyst particles formed and distributed uniformly on the flakes. At the reaction temperature, the introduction of methane realized the growth of SWCNTs with the diameter of 1–4 nm. The loose structure of LDH agglomerates afforded a yield as high as 0.95 g<sub>CNT</sub>/(g<sub>cat</sub> h) of SWCNTs with a surface area of 930 m<sup>2</sup>/g. Compared with Fe/Mg/Al LDH, Ni/Mg/Al and Co/Mg/Al LDHs showed a better selectivity to SWCNTs. The highest selectivity for metallic SWCNTs was obtained using Co/Mg/AI LDHs as the catalyst.

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# 1. Introduction

Based on their unique structure, mechanical and electrical properties, single-walled carbon nanotubes (SWCNTs) have been explored for many potential applications in materials science, biology, electronics, and energy conversion/storage [1]. Controllable mass production of SWCNTs is the prerequisite for any large scale applications. In the past decade, many efforts have been made for low cost large scale synthesis of high purity SWCNTs. Various processes, such as arc discharge [2], floating catalyst process [3], high pressure carbon monoxide (HiPCO) process [4], and CoMoCat process [5], have been developed for this purpose. Catalysts are considered to play a crucial role in the processes mentioned above for the growth of CNTs. It is commonly accepted that the formation of small metal catalyst particles (0.5–5 nm) is the key factor for the efficient growth of SWCNTs [3,4]. High dispersion of metal particles can be effectively achieved by using MgO [6–8] and  $SiO_2$  [5] particles as the supports.

Up to now, the most efficient way for mass production of carbon nanotubes (CNTs) is fluidized-bed catalytic chemical vapor deposition (CVD) [9–12]. A pilot production of agglomerated multi-walled CNTs (MWCNTs) with high yield (15 kg/h) was achieved [13]. Agglomerated few-walled CNTs [14], SWCNTs [15], and aligned CNTs [16] have also been produced in a large scale in fluidized bed reactors. For SWCNT growth in a fixed bed reactor, impregnated, or co-precipitation catalysts, such as Fe/MgO, Co/Mo/SiO<sub>2</sub>, were widely used as catalysts. However, due to the existence of a large amount of hydrogen in the fluidized bed reactor, the metal catalyst particles are still easy to sinter. This usually causes the formation of MWCNTs. The development of fluidizable catalysts

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for mass production of SWCNTs in a fluidized bed reactor that can avoid the sintering of small metal particles even with the existence of hydrogen is still a challenge.

Layered double hydroxides (LDHs), also known as hydrotalcite materials, are a class of synthetic two-dimensional nano-structured anionic clays, which consist of brucite-like layers. The divalent cations originally coordinated octahedrally by hydroxyl groups are isomorphously replaced by trivalent cations, affording the positively charged layers in the presence of charge-balancing anions. Hydrogen bonded water molecules may also occupy the remaining free space between layers. LDHs can be represented by the general formula  $M_{1-x}^{2+}M_x^{3+}(OH)_2A_{x/n}^{n-} \cdot mH_2O$ , where  $M^{2+}$  (M = Fe, Co, Ni, Cu, Zn, or Mg) and  $M^{3+}$  (M = Al, Cr, Ga, Mn, or Fe) are di- and trivalent cations, respectively; x is defined as the molar ratio of  $M^{3+}$ /  $(M^{2+}+M^{3+})$  and generally with a value ranging from 0.2 to 0.33 [17]. Recently, the facile method for the controllable mass production of LDHs have been developed [17]. Numerous metals, such as Fe, Co, Ni, Cu, Zn, Mg, Al, and Ca, can be dispersed in the lamellar LDH flake at an atomic level with controllable component. This is contributed by the substitution of divalent metal cations by trivalent cations within the brucite-like layers. Compared with natural clay, the composition of LDHs is much simpler and can be controlled, which is of paramount importance for designing a catalyst, catalyst precursor and catalyst support. When LDH are calcined and reduced, metal particles can be formed and distributed uniformly on the calcined LDH flakes [18], which are good catalysts for the growth of CNTs. The sintering of small metal particles on LDH flakes can be controlled. Recently, a few works have been published reporting on the *in situ* growth of CNTs on LDHs in a fixed bed reactor [19–21]. However, agglomerated MWCNTs with diameters ranging from 10 to 50 nm and a specific surface area of less than 50 m<sup>2</sup>/g were synthesized [19–21]. Recently, we have found that SWCNTs can be synthesized using LDHs as catalysts in a fixed bed reactor [18]. In this contribution, we report the efficient growth of SWCNTs on a family of LDHs in a fluidized bed reactor. High quality SWCNTs with a high surface area and low defect density were produced over the fluidizable calcined LDH flakes.

# 2. Experimental

#### 2.1. Catalyst preparation

The Fe/Mg/Al LDH flakes were prepared using a urea assisted co-precipitation reaction.  $Mg(NO_3)_2$ · $GH_2O$ ,  $Al(NO_3)_3$ · $9H_2O$ , and urea were dissolved in 250.0 mL deionized water with  $[Mg^{2+}] + [Al^{3+}] = 0.15 \text{ mol/L}$ , n(Mg):n(Al) = 3:1, [urea] = 3.0 mol/L. Fe(NO<sub>3</sub>)<sub>3</sub>· $9H_2O$  was then dissolved in the solution with molar ratio of Fe to Al of 0.4. The as-obtained solution was kept at 100 °C under continuous magnetic stirring for 12 h in a flask (equipped with a reflux condenser) of 500.0 mL under ambient atmosphere. The obtained suspension was kept at 94 °C for another 12 h without stirring. After filtering, washing and freeze-drying, the final products of brown-yellow powder were obtained. The other kinds of LDH flakes were prepared through the same process, of which the compositions were



Fig. 1 – (a, b) The SEM images, (c) particle size distribution, and (d) XRD pattern of the Fe/Mg/Al LDH catalyst.

fixed as n(Co):n(Mg):n(Al) = 0.4:3:1, n(Ni):n(Mg):n(Al) = 0.4:3:1and n(Co):n(Al) = 2:1.

#### 2.2. SWCNT synthesis in a fluidized bed reactor

The apparatus used in the experiment is similar to that described in the previous report [22]. The fluidized bed reactor is made of quartz with an inner diameter of 20 mm and a height of 500 mm. A sintered porous plate is used as the gas distributor at the bottom of the reactor. The gas distributor also acts as the floor, which supports the solids in the reactor before they are suspended in gas flow. Here, the lamellar Fe/ Mg/Al LDH flakes, as well as Co/Mg/Al, Ni/Mg/Al, and Co/Al LDH flakes were used as the catalysts. About 1.0 g catalyst was fed into the reactor before the reaction. The gas mixture containing carbon source entered the bottom vessel of the reactor and then passed through the gas distributor, the fluidized bed units, and finally flowed out. The quartz fluidized bed reactor, mounted in an electrical tube furnace, was heated to 900 °C in Ar atmosphere at a flow rate of 500 mL/ min. The catalysts were pushed apart from one another due to the up-flow gas at a sufficient velocity. Once reaching the reaction temperature, H<sub>2</sub> with a flow rate of 50 mL/min was introduced into the reactor for the reduction. After 5 min, the flow rate of Ar was turned down to 100 mL/min and CH₄ (400 mL/min) was introduced into the fluidized bed, starting the reaction on the surface of the LDH flakes. Both the catalyst particles and the CNT products can be smoothly fluidized

in the reactor. After the reaction, the fluidized bed reactor was cooled down under Ar atmosphere. The as-grown products were then collected and characterized.

## 2.3. Characterizations

The size distributions of the suspended catalysts were obtained using particle characterization system (Malvern Mastersizer, Mioro-plus). The reliability of the agglomerate size and the morphology of the LDH flakes were further confirmed by scanning electron microscope (SEM) observations. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/ max-RB diffractometer at 40.0 kV and 120 mA with Cu K  $\!\alpha$  radiation. The Brunauer-Emmett-Teller (BET) specific surface area of all samples was measured by N<sub>2</sub> adsorption at liquid-N<sub>2</sub> temperature using Micromeritics Flow Sorb II 2300. Tests of H<sub>2</sub>-temperature programmed reduction (TPR) of the LDH catalysts were conducted using a fixed-bed continuousflow microreactor. To remove water vapor formed by the reduction of metallic oxide components of the catalyst sample, a KOH column and a 3A zeolite molecular sieve column were installed in sequence at the reactor exit. The ramp rate of temperature was 10 °C/min. Change of hydrogen signal was monitored by on-line GC (Shimadzu GC-8A) with a TCD detector. Fifty milligrams of LDH catalyst sample was first flushed by an Ar (of 99.999% purity, 20 sccm) stream at 673 K for 60 min to clean its surface, and then cooled down to room temperature, followed by switching to a N<sub>2</sub>-carried 5.24 vol.%



Fig. 2 – The TGA curves of the Fe/Mg/Al (a), Co/Mg/Al (b), and Ni/Mg/Al (c) LDH catalysts. (d) The TPR curves of the calcined Fe/Mg/Al, Co/Mg/Al and Ni/Mg/Al LDH catalysts.

 $H_2$  gaseous mixture (20 sccm) as reducing gas to start the TPR observation. The fluidization characteristic of the LDH catalyst and as-grown products was investigated under ambient condition in an experimental apparatus as reported by Zhang et al. [22].

The morphology of the as-obtained SWCNTs was characterized using a JSM 7401F SEM operated at 3.0 kV, and a JEM 2010 high-resolution transmission electron microscope (TEM) operated at 120.0 kV. The sample for TEM observation was prepared using a common sonication method. Raman experiments were performed with a Renishaw RM2000 Raman spectrophotometer. The calcination process of LDHs and the purity of SWCNTs in the as-grown product were obtained through thermogravimetric analysis (TGA) by Q500.

# 3. Results and discussion

#### 3.1. The LDH catalysts

Four kinds of LDHs with different compositions of Fe/Mg/Al, Co/Mg/Al, Ni/Mg/Al, and Co/Al LDHs were prepared as the catalysts for the synthesis of CNTs, respectively. Fe-based



Fig. 3 – The fluidization characteristic of the Fe/Mg/Al LDH catalyst.

catalyst has been extensively employed in the production of CNTs in fluidized bed reactors [12,13,16]. Compared with Ni/ Co-based catalysts, Fe-based catalyst is much cheaper, which is of paramount importance for the large-scale production of CNTs. Thus, the Fe/Mg/Al LDH was selected as the model catalyst to study the morphological, structural, thermal, and reductive characteristics of LDH catalysts. After freeze-drying and scrunching, LDH agglomerates with particle sizes ranging from 50 to 200 µm were obtained, as shown in Fig. 1a. The SEM image from the Fe/Mg/Al LDH (Fig. 1b) reveals that the LDH flakes are 1–2  $\mu$ m in size and tens of nanometers in thickness. The particle size distribution of the LDH agglomerates obtained from the particle characterization system is given in Fig. 1c. Typical powder XRD pattern for the as-prepared Fe/Mg/Al LDH is shown in Fig. 1d. The sharp and symmetric features of the diffraction peaks (0 0 3), (0 0 6), and (0 0 9) suggest that the as-produced LDH flakes have a high degree of crystallization. The diffraction peaks can be indexed as a rhombohedral structure with the refined lattice parameters of a = 0.3043 nm and c = 2.2858 nm for the Fe/Mg/Al LDH. Co/ Mg/Al, Ni/Mg/Al and Co/Al LDHs showed similar morphologies and structures with the Fe/Mg/Al LDH.

Before the introduction of carbon source, the LDH catalysts needed to be calcined and reduced for the growth of CNTs. TGA and TPR were carried out to investigate the calcination and reduction behavior of the LDH catalysts. TGA of the asprepared Fe/Mg/Al LDH catalyst under N<sub>2</sub> atmosphere shows five weight loss periods (Fig. 2a). The first weight loss period observed at around 92  $^{\circ}\text{C}$  with a weight loss of 2.0% in Fig. 2a can be attributed to the evaporation of free water existed in the LDH catalyst. A weight loss of 11.5% around 189 °C is resulted by the removal of physically adsorbed H<sub>2</sub>O on the LDH flakes. When the temperature rises up to around 297 °C, the decomposition of  $CO_3^{2-}$  in the inter-layer spaces of LDH flake causes a weight loss of 10.0%. The forth period with a weight loss of 13.2% appeared at around 425 °C can be explained by the decomposition of large amount of OH<sup>-</sup> in the LDH flakes. The last weight loss of 2.5% observed at around  $670 \,^{\circ}\text{C}$  is thought to be the removal of residual  $OH^-$  and CO<sub>3</sub><sup>2-</sup>. TGA of Co/Mg/Al and Ni/Mg/Al LDHs were also carried out for comparison, and similar weight loss periods were observed, as shown in Fig. 2b and c. These findings are in good



Fig. 4 – (a) SEM image of the as-grown products using Fe/Mg/Al LDH catalyst and (b) the fluidization characteristic of the asgrown products using Fe/Mg/Al LDH catalyst.

agreement of the thermal behaviors of various kinds of LDHs, such as Mg/Al-CO<sub>3</sub> [23], Co/Mg/Al-CO<sub>3</sub>/NO<sub>3</sub> [24], Ni/Mg/Al-CO<sub>3</sub>/NO<sub>3</sub> LDHs [24], reported in literatures.

Fig. 2d shows the TPR curves of the calcined Fe/Mg/Al, Co/Mg/Al and Ni/Mg/Al LDH catalysts. For Fe/Mg/Al LDH, the Fe atoms exist in Fe<sub>2</sub>O<sub>3</sub> phase or MgFe<sub>2</sub>O<sub>4</sub> spinel phase after the calcination [20]. During the reduction process, the Fe<sub>2</sub>O<sub>3</sub> is reduced to Fe<sub>3</sub>O<sub>4</sub>, to FeO, and to Fe in the temperature ranges of 300–470, 470–600, and 600–700 °C, respectively [25]. The previous two reduction peaks are clearly shown in

Fig. 2d. Fe in MgFe<sub>2</sub>O<sub>4</sub> spinel phase can be reduced at higher temperature (about 800–900 °C) [26]. For Co/Mg/Al LDH, the low temperature peaks around 330 °C and 540 °C correspond to the reduction of Co<sup>3+</sup> to Co<sup>2+</sup> and Co<sup>2+</sup> to Co, respectively [27]. The high-temperature peak around 750 °C can be attributed to the reduction of the spinal phase (CoAl<sub>2</sub>O<sub>4</sub>) [24]. Similarly, for Ni/Mg/Al LDH, the peak around 520 °C can be assigned to the reduction of Ni<sup>2+</sup> to Ni, while the peak around 800 °C can be attributed to the reduction of Ni<sup>2+</sup> to Ni, while the peak around 800 °C can be attributed to the reduction of NiAl<sub>2</sub>O<sub>4</sub> [24]. After the calcination and reduction, the morphology of



Fig. 5 - (a, b) SEM and (c, d) TEM images of the SWCNTs grown on Fe/Mg/Al LDH catalyst.

Catalyst	Products	Diameter (nm)	I <sub>D</sub> /I <sub>G</sub> ratio <sup>a</sup>	STY $(g_{CNT}/(g_{cat} h))^{b}$	Ref.
Co/Al-LDH	MWCNTs	25	1.1	1.3	[19,21,28]
Co/Fe/Al-LDH	MWCNTs	11	0.72	2.3	[30]
Ni/Mg/Al-LDH	MWCNTs	10	1.2	5.7	[31,32]
Fe/Mg/Al-LDH	SWCNTs	1.1	0.25	-	[20]
Fe/Zn/Al-LDH	MWCNTs	30	-	-	[20]
Co/Zn/Al-LDH	MWCNTs	14–30	-	0.1-0.2	[29]
Ni/Al-LDH	CNFs	200–700	0.79	-	[40]
Fe/Mg/Al-LDH	SWCNTs	1.0-6.0	0.06	0.95	This work
Co/Mg/Al-LDH	SWCNTs	1.0-3.0	0.09	-	
Ni/Mg/Al-LDH	SWCNTs	1.0-4.0	0.14	-	
Co/Al-LDH	S/MWCNTs	2.0-80	0.41	-	

the obtained LDH flakes can be well preserved, and the as-obtained LDH agglomerates exhibited similar particle size distribution with that before the calcination and reduction.

# 3.2. Fluidization behavior of the catalyst and as-grown products

It is important to choose a proper operating gas velocity domain according to the fluidization behavior of the catalysts and the as-grown products. Fig. 3 shows the fluidization characteristic of the Fe/Mg/Al LDH catalyst. The intrinsic density of the LDHs is *ca*. 2000 kg/m<sup>3</sup>, while the bulk density of the as-obtained LDH agglomerates after calcination and reduction is 380 kg/m<sup>3</sup>. According to the density and size distribution, the LDH agglomerates can be considered as A particles according to Geldart particle classification, exhibiting good fluidization behavior. Once the catalysts are exposed to an up-flow gas, the pressure drops and bed expansion raises when gas flow rate increases. The minimal fluidization velocity ( $u_{mf}$ ) of the LDH catalyst is 2.3 cm/s. The catalyst is then in fluidized state when the gas velocity is over  $u_{mf}$ . Several flow regimes are identified as particulate fluidization, bubbling

Catalyst	Products	Diameter (nm)	I <sub>D</sub> /I <sub>G</sub> ratio <sup>a</sup>	STY (g <sub>CNT</sub> /(g <sub>cat</sub> h)) <sup>b</sup>	Ref.
Fe(CO)₅	SWCNTs	0.9	-	0.079	[4]
Co/Mo/SiO <sub>2</sub>	SWCNTs	0.9	0.05	0.30	[5]
Ferrocene	S/MWCNTs	2.0	-	8.0	[3]
Fe/MgO	SWCNTs	1–3	0.06-0.2	0.30	[41]
Fe/Mg/Al/O	DWCNTs	1.7–3.0	0.2	0.15-0.25	[42]
Fe/Mo/MgO	S/MWCNTs	1–10	0.1-0.4	-	[43]
Fe/Mg/Al-LDH	SWCNTs	1.0-6.0	0.06	0.95	This work
Co/Mg/Al-LDH	SWCNTs	1.0-3.0	0.09	_	

<sup>b</sup> The STY of CNTs was obtained by TGA.



Fig. 6 – (a) SEM and (b) TEM image of the SWCNTs grown on Co/Mg/Al LDH catalyst; (c) SEM and (d) TEM image of the SWCNTs grown on Ni/Mg/Al LDH catalyst.

fluidization, and turbulent fluidization with an increasing gas velocity. The pressure drop tends to be stable when the gas velocity is larger than 10.1 cm/s, indicating the beginning of bubbling fluidization. If the gas velocity further increases, turbulent fluidization, fast fluidization, and the pneumatic conveying regimes will be achieved. It is concluded that the stable fluidization state of the LDH catalyst can be maintained within a large gas velocity domain from 10.1 to 22.0 cm/s.

After the growth of CNTs, the size of the as-grown particles expanded to *ca*. 200  $\mu$ m, as shown in Fig. 4a. The fluidization curve of the as-grown particles is shown in Fig. 4b. Compared with pristine LDH catalysts, the as-grown products are with slightly larger  $u_{mf}$  of 3.1 cm/s and smaller bubbling fluidization beginning gas velocity of 7.0 cm/s due to the larger particle size and smaller bulk density induced by the growth of CNTs. Therefore, the gas velocity was kept at about 11.4 cm/s in the reactor to ensure a good fluidization state during the whole CNT synthesis process.

#### 3.3. As-grown SWCNTs in the fluidized bed reactor

CH<sub>4</sub> was introduced into the fluidized bed reactor after the calcination and reduction process. Typical morphology of the as-obtained products is shown in Fig. 5a and b. It can be observed that with short growth duration, large amount of CNTs were produced among the Fe/Mg/Al LDH flakes. TEM images of the products shown in Fig. 5c and d indicate that the as-grown CNTs in the fluidized bed reactor were mainly SWCNTs.

We compare the structures and properties of the CNTs obtained in the present work with those reported by other groups. In literatures, mainly MWCNTs with much larger diameter and higher I<sub>D</sub>/I<sub>G</sub> ratio were usually obtained when using different LDHs as catalysts (Table 1), such as Co/Al, Co/Fe/Al, Ni/Mg/Al, Fe/Zn/Al LDHs [19-21,28-32]. MWCNTs could also be easily synthesized on various natural catalysts, such as montmorillonites [33], bentonites [34], vermiculites [35], lavas [36,37], and sands [38,39]. Zhao et al. successfully synthesized SWCNTs with small diameter of 1.1 nm using Fe/Mg/Al LDH in a fixed bed reactor [20]. Here, the SWCNTs produced on Fe/Mg/Al LDH catalysts in a fluidized bed reactor are with high quality and large yield (Table 1). They have a mean diameter of 3.0 nm and a specific surface area of 930 m<sup>2</sup>/g. The quality of the SWCNTs grown on LDH flakes in fluidized bed was also competitive with those obtained by other methods (Table 2) [3-5,41-43]. Compared with CNTs synthesized using Fe/MgO [41], Fe/Mg/Al/O [42], and Fe/Mo/ MgO [43] catalysts, the SWCNTs obtained on Fe/Mg/Al LDH catalyst are with much lower I<sub>D</sub>/I<sub>G</sub> ratio and higher yield though they are with similar diameter distribution. Though CNTs growth by the floating catalyst methods exhibits a high yield of CNTs [3], the purity of the as-obtained SWCNTs is low and the content of impurities, which are mainly composed of MWCNTs and amorphous carbon, can be as high as 40%.

SWCNTs can also be effectively synthesized on Co/Mg/Al and Ni/Mg/Al LDHs (Fig. 6). However, it is difficult to synthesize SWCNTs with high quality on Co/Al LDHs. The SEM images of the products obtained on Co/Al LDH were shown



Fig. 7 - (a, b) SEM and (c, d) TEM images of the CNTs grown on Co/Al LDH catalyst.

in Fig. 7a and b. It is noticed that the plate-like morphology of the LDH flake is detrimentally damaged into flakes with irregular shape, on which CNTs with large diameters can be found. Fig. 7c reveals that the as-grown CNTs were mainly composed of MWCNTs with a high defect density. Only small bundles of SWCNTs (Fig. 7d) can also be found in both the SEM and TEM images, as indicated by the white arrows in Fig. 7b and c.

The diameter and wall number distributions of CNTs grown on Fe(Co, Ni)/Mg/Al LDHs were obtained by measuring around 200 individual CNTs on high-resolution TEM images.



Fig. 8 – Wall number and diameter distribution of the CNTs on different LDH catalysts: (a) Fe/Mg/Al; (b) Co/Mg/Al and (c) Ni/Mg/Al.

As shown in Fig. 8, when Fe/Mg/Al LDH was used as the catalyst, 54.0% of the as-obtained CNTs corresponded to SWCNTs with diameters ranging from 1.0 to 5.0 nm. The others were double walled carbon nanotubes (DWCNTs) with diameters distributed from 1.0 to 6.0 nm and few MWCNTs were found. The proportion of DWCNTs decreased significantly to 11.4% when Co/Mg/Al LDH was used as catalyst. The diameter of the as-obtained SWCNTs also decreased to a range from 1.0 to 3.0 nm. Ni/Mg/Al LDH catalyst exhibited higher selectivity to SWCNTs with the proportion of DWCNTs as low as 1.9%, and the diameters of SWCNTs were with similar distribution with that of Fe/Mg/Al LDH. Thus, it is concluded that both the wall number and diameter of the obtained CNTs can be tuned by changing the composition of LDHs.

Raman spectra of the as-obtained SWCNTs on Fe/Mg/Al LDH excited by lasers with different wavelength (488, 514, 633, 785 nm) were recorded. Fig. 9a shows the radial breathing mode (RBM) peaks for the SWCNTs grown on Fe/Mg/Al LDH catalyst, and the Kataura plot [44,45] directly showing the regions of metallic (blue spots) and semiconducting (black spots) nanotubes is attached as well. No RBM peak can be found in the Raman spectra excited by the 488 wavelength laser. In the Raman spectra excited by the 514 wavelength laser, typical RBM features for semiconducting nanotubes in the region of 122–184 cm<sup>-1</sup> are illustrated. There are still special features at around 119 and 258 cm<sup>-1</sup>, which confirmed the existence of metallic nanotubes. When the CNTs grown on Fe/Mg/Al LDH are excited by the 633 nm wavelength laser, the RBM peaks at around 190 and 218 cm<sup>-1</sup> are much stronger, indicating there are more metallic nanotubes showing Raman activity at this wavelength. The ratio of metallic to semi-conductive bands is estimated to be about 2:5 for 514 nm wavelength laser and 3:1 for 633 nm wavelength laser, according to the integral intensities of the relative peaks. The



Fig. 9 – Raman spectra of the as-obtained SWCNTs on Fe/Mg/Al-LDH excited with 488, 514, 633, and 785 nm lasers: (a) RBM peaks and (b) D and G peaks.

RBM mode recorded with a 785 nm laser shows extensive signals of semiconducting nanotubes as only semiconducting nanotubes are Raman active at this particular excitation wavelength [46]. For the SWCNTs grown on Co/Mg/Al and Ni/Mg/Al LDHs, RBM peaks are also found in the Raman spectra excited with 633 nm laser (Fig. 10a). However, the number of the RBM peaks decreases significantly, indicating the concentrated diameter distribution and the increasing content of SWCNTs. Besides, it is observed that the intensity of peaks at higher wave number (190, 213 cm<sup>-1</sup>) for SWCNTs on Co/ Mg/Al LDHs are much stronger than that on Ni/Mg/Al LDHs, indicating that the SWCNTs on Co/Mg/AL LDHs are of smaller diameters, which is in good agreement with the diameter distribution shown in Fig. 8. The ratios of the integral intensities of RBM features for semiconducting nanotubes to those for metallic nanotubes are 0.23, 1.1 and 0.34 for SWCNTs grown on Co/Mg/Al, Ni/Mg/Al and Fe/Mg/Al LDHs, respectively. This indicates that Co/Mg/Al LDHs exhibit the highest selectivity to metallic nanotubes [47,48]. The preferential growth of SWCNTs is still an issue to be explored. The values of  $I_D/I_G$ for SWCNTs on Fe/Mg/Al, Co/Mg/Al and Ni/Mg/AL LDH are 0.06, 0.09 and 0.14, respectively (Figs. 9b, 10b and Table 1). The low  $I_D/I_G$  value indicates that the as-obtained SWCNTs are all of high quality.

Up to now, it has been demonstrated that Fe/Mg/Al LDH, as well as Co/Mg/Al and Ni/Mg/Al LDHs are good catalysts for the efficient growth of SWCNTs in fluidized bed. The fluidized bed has great advantages in terms of enough growth space, excellent diffusion and heat transfer, easiness in scaling up and continuous operation for CNT production [9–13,16,49–51]. The metal particles with high density and good dispersion can be easily modulated by the composition of LDH catalysts, which are quite important to modulate the structure of CNTs. Based on the extensive strategies for growth, SWCNTs with high surface area and good graphitization can be produced in large scale to facilitate the applications in the area of composites, fuel cells, supercapacitors, lithium ion secondary batteries, and energy absorbing materials [1,33–36,52].



Fig. 10 – Raman spectra of the as-obtained SWCNTs on Co/ Mg/Al and Ni/Mg/AL LDHs excited with 633 nm laser: (a) RBM peaks and (b) D and G peaks.

### 4. Conclusions

Efficient growth of high quality SWCNTs was achieved by fluidized-bed CVD using Fe/Mg/Al, Co/Mg/Al and Ni/Mg/Al LDHs as the catalysts. The LDH flakes exhibited good fluidization characteristics due to the agglomeration caused by van der Waals interaction. Large amount of SWCNTs with diameters of 1–4 nm can be synthesized on the surface of LDH flakes due to the loose structure of LDH agglomerates. Co/Mg/Al and Ni/Mg/Al LDHs gave a better selectivity to SWCNT synthesis compared with Fe/Mg/Al LDH catalyst, and the Co/ Mg/Al LDH exhibited the best selectivity to metallic SWCNTs based on the results of Raman spectra. Large-scale production of SWCNTs with high surface area and good graphitization can be achieved on LDH flakes in fluidized bed reactor for further applications in the area of composites, energy conversion, catalysis, and devices.

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