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Synthesis of carbon nanotubes using a novel catalyst derived from hydrotalcite-like Co–Al layered double hydroxide precursor

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In the present letter, for the first time, the efficacy of hydrotalcite-like layered double hydroxides (LDHs) materials as alternative and novel catalyst precursors for the synthesis of carbon nanotubes (CNTs) via catalytic chemical vapor deposition (CCVD) of acetylene was reported. Nanometer-sized cobalt particles were prepared by calcination of a single molecular LDH precursor containing cobalt (II) and aluminum (III) and following by a process of reduction. Multi-walled CNTs with uniform diameters were obtained using the as-synthesized catalyst in the reaction.

KEY WORDS: carbon nanotubes; chemical vapor deposition; layered double hydroxide.

1. Introduction

Since carbon nanotubes (CNTs) were first observed by Iijima in 1991 as a by-product of the fullerence synthesis [1], they have received much attention owing to their interesting and unique properties for many potential applications [2]. Various methods, such as arc-discharge [1], laser ablation [3], catalytic chemical vapor deposition (CCVD) [4] and hydrocarbon pyrolysis [5], have been used successfully in the synthesis of CNTs. Among them; the flexible CCVD method has great potential for scaling up the synthesis of CNTs at lower energy consumption compared to other synthesis methods. The formation of CNTs by CCVD routes occurs through the catalytic decomposition of a carbonaceous gas on nanometric metal particles, which are typically transition metals (iron, nickel, cobalt and their alloys) supported over materials with large surface area to disperse and stabilize metallic particles, such as metal oxides, silica and different types of zeolites [6–8]. Moreover, the precipitation of carbon from the saturated metal particles depends strongly on the characters of the catalyst. In order to control the growth of nanotubes with desired characteristics (structure, morphology and yield), many different catalysts have been investigated comprehensively. However, despite of the huge research a large number of technological and basic issues still remain to be resolved.

Layered double hydroxides (LDHs), are a class of synthetic anionic clays whose structure can be described as containing brucite ($Mg(OH)_2$)-like layers in which some of the divalent cations have been replaced by trivalent ions, giving positively charged sheets. This residual charge is balanced by the intercalation of anionic species with water molecules, stacked in such a way as to produce a hydrotalcite-like structure. A general formula which can represent this class of materials is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{n-}_{x/n} \cdot mH_2O$, where M^{2+} represents a divalent cation, M^{3+} a trivalent cation, and A^{n-} the intercalated anion. Furthermore, metal cations can arrange uniformly in the brucite-like layer of LDHs at an atomic level. By varying the di- and trivalent cations, their proportion, and the interlayer anion, a wide variety of LDHs can be obtained [9,10]. One particularly interesting aspect of LDHs chemistry is using them as catalysts after a controlled thermal treatment, generally around 450–500 °C [9]. At these temperature LDHs lose their layered structure and form mixed metal oxides with high thermal stability, high surface area, high dispersion of metal cations, and small crystal size.

Since metal particles could be obtained by the calcinations and the sequent reductions of the LDHs, it is possible to use cobalt-containing LDH materials as alternative catalyst precursors for the synthesis of CNTs by CCVD method. In the present letter, we report the use or an innovative and novel catalyst deriving from a layered double hydroxide containing Co^{2+} and Al^{3+} cations (CoAl-LDH) molecular precursor to catalyze the synthesized of CNTs. TEM and HRTEM measurements were used to follow the quality and nature of the synthesis of CNTs. The obtained preliminary results show to be attractive for making good quality and quantity multi-walled nanotubes (MWNTs).

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2. Experimental

2.1. Preparation of samples

Layered double hydroxide carbonate containing Co^{2+} and Al^{3+} in the brucite-like layers (CoAl-LDH) was synthesized by the coprecipitation method. $Co(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with the CO^{2+}/Al^{3+} molar ratio of 1.7 were dissolved in 100 mL of deionized water to give a solution with a total cationic concentration of 1.2 M. Then a mixed NaOH/Na_2CO_3base solution ($[CO_3^{2-}] = 2[Al^{3+}]$, $[OH^-] = 1.8(2[CO^{2+}] + 3[Al^{3+}])$ was added slowly to the salt solution up to $pH = 9.0 \pm 0.1$ under vigorous stirring at room temperature. The resulting suspension was aged at 60 °C for 6 h with stirring, recovered by four dispersion and centrifugation cycles in deionized water, and the final gelatinous precipitate was dried at 70 °C overnight, then the as-synthesized LDH was calcined at 500 °C in air for 5 h. The elemental analysis revealed that the Co/Al molar ratio in the final product (=1.73:1) was close to that in the starting reaction solution, and gave the following formula for CoAl-LDH:$[Co_{0.63}Al_{0.37}(OH)_2](CO_3)_{0.185} \cdot mH_2O$.

2.2. Characterization

Elemental analysis for metals was carried out using a Shimadzu ICPS-7500 inductively coupled plasma emission spectrometer (ICP-ES). Powder X-ray diffraction (XRD) patterns of the samples were recorded in the 2θ range 3–70 ° using a Rigaku XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, Cu Kα radiation ($\lambda = 0.15418$ nm). The specific surface area of sample was measured by the BET method using low-temperature nitrogen adsorption in a Quantachrome Autosorb-1C-VP system. Transmission electron microscopy (TEM) measurement was performed using a JEOL 2000FX electron microscope with the accelerating voltage of 160 kV. The sample was investigated by a JEOL 2010 type high-resolution transmission electron microscopy (HRTEM) operated at 200 kV. For the electron microscopy measurements the samples were prepared by dispersing the reaction product in ethanol by ultrasonication and placing a droplet onto the surface of a copper grid. Raman spectra were recorded on a Microscopic Confocal Raman Spectrometer (RM2000) using an argon ion laser at 633 nm. Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDX) analysis was performed using a JSM-630/F apparatus with the analytical software INCA. The accelerating voltage applied was 15 kV.

2.3. Synthesis of CNTs

CNTs were synthesized at 700 °C by catalytic chemical vapor deposition of acetylene. Particularly the calcined CoAl-LDH sample was placed in a vertical quartz flow reactor of a tubular furnace equipped with temperature and gas-flow controls, and first heated up to 500 °C under a gas mixture consisting of hydrogen and nitrogen for 90 min; subsequently, hydrogen was turned off and acetylene was introduced into the system, temperature was elevated to 700 °C for 90 min. After the reaction, the reaction gas was replaced by N_2 and the furnace cooled to room temperature. To purify the CNTs formed, the obtained mixture was dissolved in an aqueous HCl solution, and then the resulting suspension was filtered and washed with deionized water until neutrality. The final sample was dried at 80 °C overnight in air.

3. Results and discussion

The typical SEM images of the nanotubes grown in our system are shown in figures 1a, b. It can be found that the CNTs have been obtained successfully over the novel catalyst. Figures 2 and 3 illustrate the length and diameter distributions of more than 100 CNTs produced in this way, respectively. Note that the lengths of nanotubes range from 0.5 to 8.5 μm with an average length of 6.0 μm, and the tubes are relatively uniform in

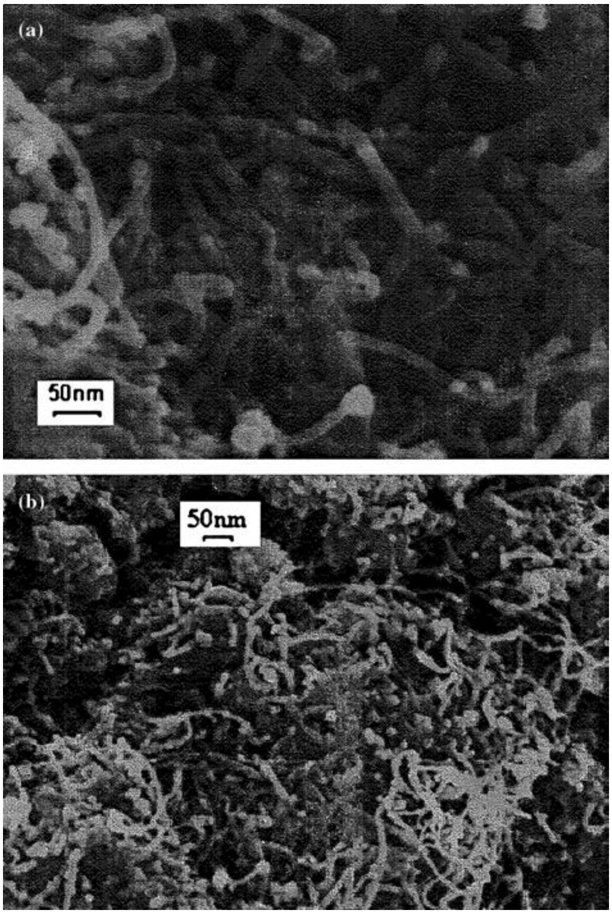

Figure 1. SEM images for the CNTs obtained on the catalyst at 700 °C.

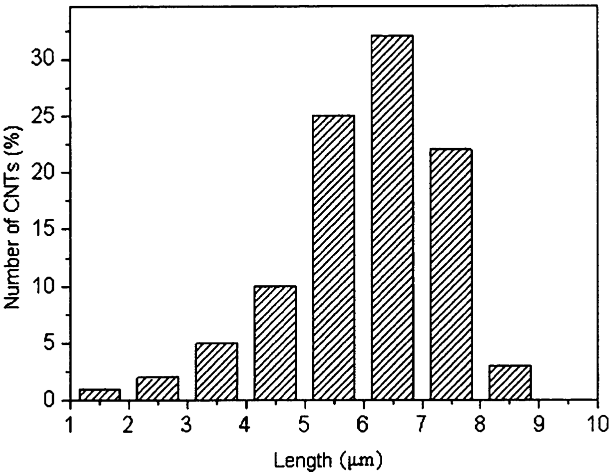

Figure 2. Length distribution of CNTs obtained on the catalyst at 700 °C.

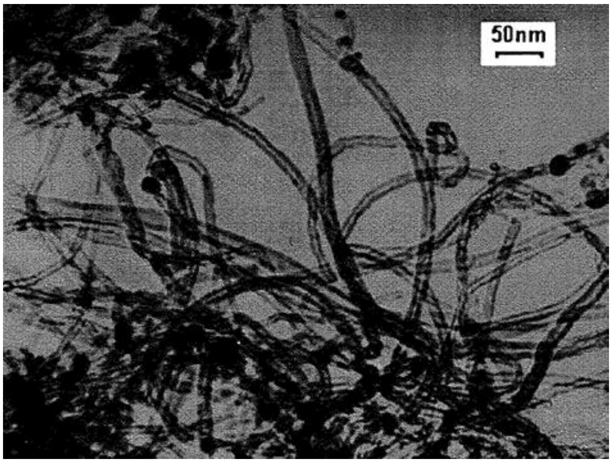

Figure 4. TEM images for the CNTs obtained on the catalyst at 700 °C.

diameter mainly ranging from 20 to 30 nm. Furthermore, it is seen from the TEM image of the CNTs shown in figure 4 that all the one-dimensional solid-state CNTs here are to be provided with thin and hollow core, similar to the tubes reported by Lee and coworkers [11]. Meanwhile, spherical catalyst particles with diameters of ca.15 nm are encapsulated in one termination of the tubes as a common characteristic. Besides, the walls of the obtained CNTs are well graphitized, and only a small amount of amorphous carbon is found among the deposits. Also it is interesting to note that in our cases the density of tubes is quite high, and the yield of carbon is greatly high (about 188 wt.%). The EDX spectrum (figure 5) shows C, Co, Al and O peaks. The Co signals mainly originated from catalyst particles, while C signals with high intensity originated from the CNTs. The results indicate that abundant CNTs were grown on the catalysts.

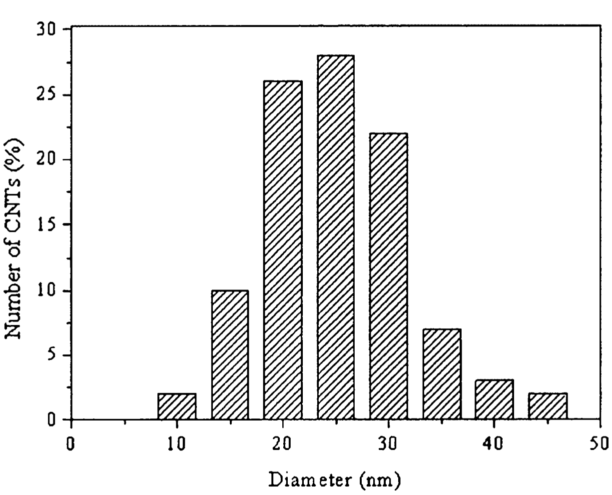

Figure 3. Diameter distribution of CNTs is obtained on the catalyst at 700 °C.

A high-resolution TEM micrograph of the walls of nanotubes is shown in figure 6. The tubes exhibit clearly the typical multi-walled structure with essentially concentric single walled tubes composing about 18 graphite layers. The interlayer spacing between the graphite planes is estimated to be 0.34 nm, as expected from turbostratic graphite. It is also seen that the thickness of the hollow core region and the tube walls are ca. 7 and 5 nm, respectively. The above result indicates that the as-synthesized cobalt nanoparticles deriving from the single CoAl-LDH precursor are very active and effective in the generation of MWNTs.

Figure 7 shows Raman spectrum of the CNTs grown over the novel catalyst. The two strong peaks at 1326 and 1598 cm^{-1} corresponding to the 'D' band and the 'G' band of the typical Raman peaks of graphitized CNTs respectively. The peak at 1598 cm^{-1} corresponds to an E_{2g}mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a 2-dimensional hexagonal lattice, indicating the presence of crystalline graphite carbon in multi-wall CNTs [12]; while the band at 1326 cm^{-1} is attributed to disordered graphitic materials [13]. Ratios of the D peak to the G peak have been used as an indicator of the amount of disorder within carbonaceous materials and nanotubes [14]. The D peak in our study is quite high indicating that there still exists two-dimensional disordered graphite carbon in product.

The powder XRD patterns for CoAl-LDH, calcined CoAl-LDH, and the extractive CNTs product are shown in figure 8, respectively. It can be noted that the XRD pattern for the CoAl-LDH (see figure 8a) exhibit the characteristic diffractions of a hydrotalcite-like layered double hydroxide material (JCPDS file 38–0487) [15] and no other crystalline phases are present. The XRD pattern gives a series of peaks, such as 003 and 006, appearing as narrow symmetric at low 2θ angle corresponding to the basal spacing and higher order diffractions, and indicates that the sample consists of a

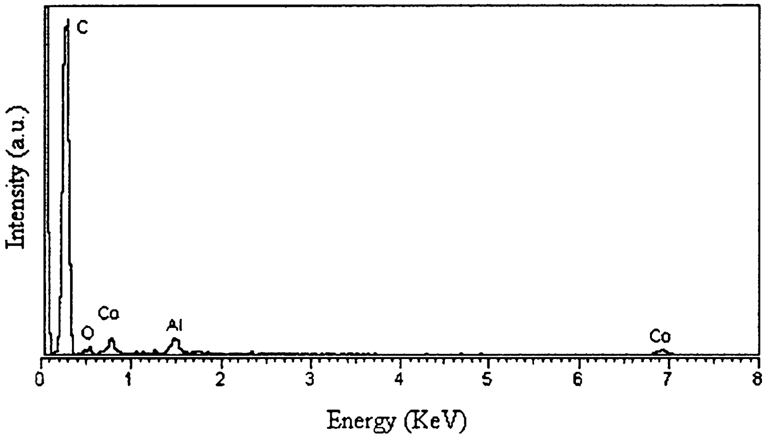

Figure 5. EDX spectrum of CNTs obtained on the catalyst at 700 °C.

well crystallized single phase with large constituting crystallites. Obviously, calcination has destroyed the layered structure of the CoAl-LDH, as no characteristic diffractions of LDH are present in the XRD pattern for the calcined CoAl-LDH (see figure 8b), and the new characteristic diffractions in the pattern exhibit the presence of spinel-like metal oxide phases containing cobalt cations such as Co_3O_4 and/or $CoAl_2O_4$. However, it is rather difficult to distinguish between these mixed oxide phases due to their almost identical positions of the characteristic diffractions. Furthermore, J. Pérez-Ramírez *et al.* [16] have reported that a part of Co^{3+} could he substituted by Al^{3+} in the Co_3O_4 phase, and thus another kind of stable spinel-like Co^{2+} $(Co^{3+}, Al)_2O_4$ phase consequently presented in calcined product of Co–Al hydrotalcite. Although, Co and Al mixed oxides usually lead to normal spinels, $CoAl_2O_4$-type, where Co^{2+} occupies tetrahedral positions and Al^{3+} fills the octahedral positions. In any case, the nanometric cobalt particles could be obtained by reducing the starting mixed oxides obtained by calcination of CoAl-LDH precursor, as has been proven by the presence of a CNT -containing mixture power with dispersion of the CNTs around the substrate grains in figure 4. Furthermore, the XRD pattern for the purified CNTs (see figure 8c) shows a broad peak around $2\theta = 25.6°$, corresponding to the (002) diffraction of graphitic carbon ($d = 0.348$ nm) and the characteristic diffraction of the metal Co around $2\theta = 44.4°$ ($d = 0.204$ nm). This is because under the mild acidic treatment of the purification of the CNTs, only the retaining mixed metal oxides and unprotected metal particles, the amount of which is about 30% of the whole sample weight, have been eliminated. Moreover, owing to the fact that the amount of the impurities is 35% of the whole sample weight before purification, it thus can be inferred that after acidic treatment, the only significant impurities were some metal Co particles embedded by carbon walls. However, the wider root of the (002) diffraction trace of carbon shows the characteristics of the disordered and/or amorphous carbon. In addition, according to the Scherrer equation, the

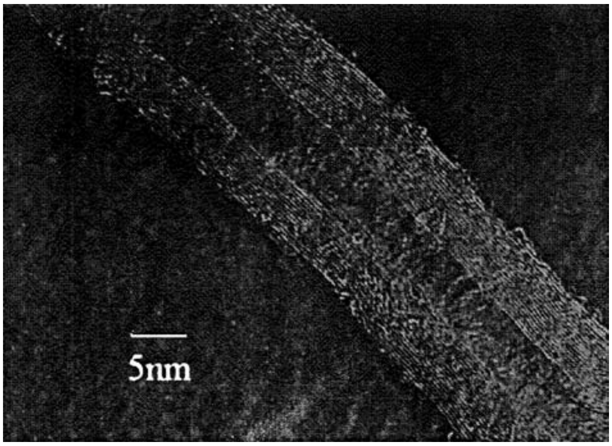

Figure 6. HRTEM images for a multi-walled carbon nanotube on the catalyst.

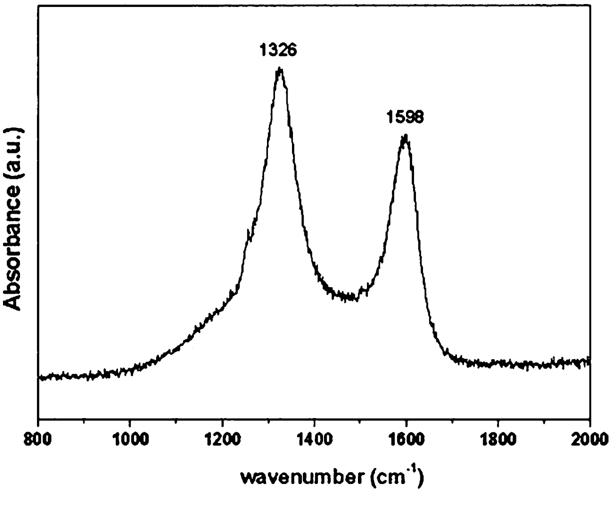

Figure 7. Raman spectrum of CNTs grown over the novel catalyst.

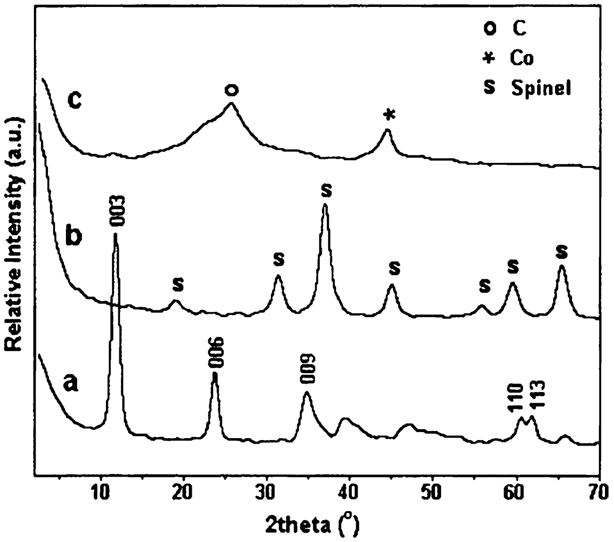

Figure 8. Powder XRD patterns for CoAl-LDH (a), calcined CoAl-LDH (b), and the purified CNTs (c).

average crystallite size of the metal Co is calculated to be 16.3 nm, as expected to be consistent with the outer diameter of CNTs formed. On the other hand, the distribution of cobalt centers also can be characterized by the EDX images of different samples shown in figure 9, where the bright spots in the diagrams represent cobalt elements. It can be found that active components in two cases of metal cobalt particles and calcined CoAl-LDH over the surface samples are dispersed highly, as should originate from uniform distribution of metal cations on the brucite-like layers of the CoAl-LDH precursor.

The specific surface area of the samples in different states is shown in table 1. It is seen that calcination has a marked effect on the specific surface area of CoAl-LDH precursor, which is much smaller than that of calcined CoAl-LDH. This is because initially water and, subsequently, carbon dioxide are released from LDH precursor through cratering effect resulting in the considerable increase in the surface area upon calcinations. After synthesis reaction of CNTs the surface area of obtained CNTs deposits is a little larger than that of calcined CoAl-LDH, as attributed to the formation of CNTs over the catalyst. Moreover, a remarkable increase in the surface area of CNTs after purification further indicates the success of the purification.

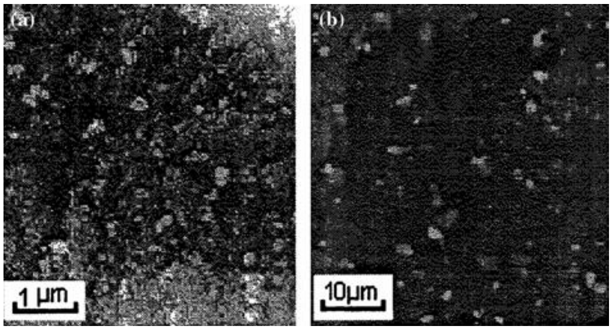

Figure 9. EDX images of calcined CoAl-LDH (a) and the CNTs with catalyst particles (b).

Table 1
Specific surface area of the samples in different states

Sample	CoAl-LDH	Calcined CoAl-LDH	Obtained CNTs	Purified CNTs
Surface area (m^2/g)	77.6	131.3	140.2	215.6

All of the facts mentioned above show that the resulting CNTs are rather good both in quality and quantity, indicating excellent catalytic effect of the novel catalyst on the CNTs growth. Here, a tentative explanation has been proposed. In the single CoAl-LDH molecular precursor, all metal cations lying in the brucite-like layers arrange uniformly at an atomic level [17]. Accordingly, after calcination the reducible Co-containing oxide phases under the experimental conditions can also disperse highly on the surface of the substrate formed with a big specific surface area of 131.3 m^2/g, as prevent the metal Co nanoparticles obtained aggregating and sintering under high temperatures; another one, the small size of metal Co nanoparticles deriving from the CoAl-LDH precursor explains the reason why the diameter of CNTs grown over the novel catalyst is relatively small according to the growth mechanism of CNTs [7,8]. On the basis of the obtained results, it is concluded that cobalt-containing LDHs as catalyst precursors are shown to be attractive for the formation of CNTs in good quality and high yield. Since the character of metal catalyst particles is related to that of LDH precursors, we should be able to tailor and govern CNT's morphology and structure by modifying the nature of LDH precursors.

4. Conclusion

CNTs could be synthesized successfully at 700 °C by CCVD of acetylene using the nanometer-sized Co-catalyst deriving from a single layered double hydroxide containing Co^{2+} and Al^{3+} molecular precursor. The results have shown obviously the high efficacy of the catalyst in the formation of the good quality and quantity multi-walled CNTs. Further investigations are needed to elucidate the effect of different types of LDHs materials containing active transition metal cations (Co, Ni and Fe cations) as catalyst precursors for the growth of nanotubes.

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