Available online at www.sciencedirect.com
ScienceDirect

Journal of Energy Chemistry 22(2013)136–144

JEC JOURNAL OF ENERGY CHEMISTRY
www.elsevier.com/journals/
journal-of-energy-chemistry/2095-4956
www.elsevier.com/locate/jngc

Remarkable carbon dioxide catalytic capture (CDCC) leading to solid-form carbon material via a new CVD integrated process (CVD-IP): An alternative route for CO_2 sequestration

Wei Chu[a,c*], Maofei Ran[a], Xu Zhang[a], Ning Wang[a], Yufei Wang[b], Heping Xie[b], Xiusong Zhao[d,e*]

a. Key Laboratory Green Chemistry & Technology of Ministry of Education (MOE), College of Chemical Engineering, Sichuan University, Chengdu 610065, Sichuan, China; b. State Key Laboratory of Hydraulics and Mountain River Engineering, Sichuan University, Chengdu 610065, Sichuan, China; c. SABIC Technology Center Riyadh, P. O. Box 42503, Riyadh, Kingdom of Saudi Arabia; d. Department of Chemical and Biomolecular Engineering, National University of Singapore, Engineering Drive 4, 117576, Singapore; e. University Queensland, School Chemical Engineering, Brisbane 4072, Australia

[Manuscript received December 10, 2012; revised December 20, 2012]

Abstract

Through our newly-developed "chemical vapor deposition integrated process (CVD-IP)" using carbon dioxide (CO_2) as the raw material and only carbon source introduced, CO_2 could be catalytically activated and converted to a new solid-form product, i.e., carbon nanotubes (CO_2-derived) at a quite high yield (the single-pass carbon yield in the solid-form carbon-product produced from CO_2 catalytic capture and conversion was more than 30% at a single-pass carbon-base). For comparison, when only pure carbon dioxide was introduced using the conventional CVD method without integrated process, no solid-form carbon-material product could be formed. In the addition of saturated steam at room temperature in the feed for CVD, there were much more end-opening carbon nano-tubes produced, at a slightly higher carbon yield. These inspiring works opened a remarkable and alternative new approach for carbon dioxide catalytic capture to solid-form product, comparing with that of CO_2 sequestration (CCS) or CO_2 mineralization (solidification), etc. As a result, there was much less body volume and almost no greenhouse effect for this solid-form carbon-material than those of primitive carbon dioxide.

Key words

carbon dioxide catalytic capture (CDCC); carbon nanotubes (CNTs); chemical vapor deposition integrated process (CVD-IP); solid-form carbon material; debating greenhouse gases (GHG) effects

1. Introduction

While the consumption of fossil sources produces a huge amount of carbon dioxide (CO_2) greenhouse gas, the effects of greenhouse gases have resulted in a lot of emerging abrupt changes of the global climate and often extreme weather, then significant inconveniences to the living conditions in many areas [1−7]. The abatement of greenhouse gases (mainly CO_2) requires a significant decrease of carbon dioxide emissions and also efficient approaches of CO_2 sequestration and feasible utilization (CCS, CCUS) at large scale and conveniently low cost [3−7], which are very challenging throughout the world.

In the last twenty years, carbon dioxide has attracted more and more interests, while the scientific research has established a direct link between the increases in CO_2 emissions with the rise in global average temperature [6], which has led the governments and industries around the world to actively work on solutions to reduce carbon dioxide emissions. The research activities include capturing CO_2 either directly from the flue gas emitted by power plants and heavy industry through amine absorption [8], or by binding it in inorganic oxides [9,10], which is followed by recovery and sequestration of carbon dioxide gas.

While there are still a number of great challenges in advancing the development of CO_2 abatement and utilization, a few technologies have been reported for CO_2 abatement via both physical and chemical means [11−17], such as carbon dioxide capture and sequestration (CCS), carbon dioxide capture and utilization (CCU), as well as carbon dioxide capture

---

* Corresponding authors. Tel: +86-28-85403836; Fax: +86-28-85461108; E-mail: chuwei1965@foxmail.com (W. Chu), george.zhao@uq.edu.au (X. S. Zhao)

This work was supported by the National 973 Program of Ministry of Sciences and Technologies of China (2011CB201202) and the National Natural Science Foundation of China (20776089).

and utilization and storage or sequestration (CCUS). CCS technology is an approach to abating carbon dioxide, especially in dealing with CO_2 from power-generation plants, besides, CCUS provided an alternative way. Chemical conversions of carbon dioxide to value-added products are among the developing approaches for CO_2 utilization [11−19]. Several processes of chemical transformations of carbon dioxide have been developed, such as the synthesis of methanol [11] and dimethyl carbonate (DMC) [15], production of cyclic carbonate or CO_2-derived poly-carbonate-esters [16].

Rather than viewing CO_2 as a waste material, using the geological sequestration of carbon dioxide in the underground reservoirs, alternative approaches have also looked at the photochemical, electrochemical or thermochemical conversion of carbon dioxide, like a chemical feedstock, to more valuable hydrocarbons [6]. At present, however, the electrochemical and photochemical CO_2 conversions to hydrocarbons (HC) are still in its research period and have major drawbacks. The catalysts based on Fischer-Tropsch synthesis (FTS) technology could produce directly hydrocarbons, and there were higher conversions of CO_2 and yields for desired products in comparison with those of methanol catalysts for converting CO_2 [20−25]. In the reported work of Dorner et al. [21], catalytic CO_2 conversion via Fischer-Tropsch synthesis route has been proven to produce hydrocarbons above methane at high conversion of carbon dioxide and products yields.

Recently, several aspects of CO_2-related issues and those of production of CNTs and its catalytic applications have been investigated in our group [17−19,26,27], such as cyclic adsorption and desorption for CO_2 separation and capture, mineralization of CO_2, synthesis of methanol from CO_2, dry reforming of methane with CO_2, carbon nanotubes production, and hydrogen storage in metal-improved CNTs, etc. We have also developed several catalysts for the production of CNTs via conventional CVD method, and we investigated the CNTs applications for hydrogen storage and heterogeneous catalysis.

In this work, it was reported that our newly-developed "chemical vapor deposition integrated process (CVD-IP)" using carbon dioxide (CO_2) as the raw material and only carbon source introduced, CO_2 could be catalytically activated (CO_2 catalytic hydrogenation to methane reaction) and then the product mixture of the 1st step was flowed into the 2nd reactor and converted to a new solid-form carbon-product in a 2nd step (integrated two-steps new process technology), i.e., carbon nanotubes (CNT-C1, CO_2-derived) at a quite high carbon-yield. In addition, with a further cheap additive (simplified as "E", steam vapor, it is "Eau" in French language) in CVD-IP process of the carbon nanotubes growth, new-type high quality carbon nanotubes (with many tube-end-opening) have been also produced, for which there were much more tube-end-opening CNTs. CO_2-derived solid-form carbon-product (carbon nanotubes) of the above two main types (CNT-C1, CNT-C2) have been characterized by several physicochemical techniques such as TEM, XRD, Raman, FT-IR, TG-DTG. This new integrated process technology was illustrated using a DFT-drawing illustration.

2. Experimental

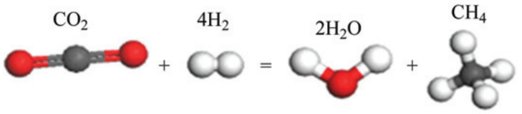
2.1. Carbon dioxide catalytic capture leading to solid-form carbon-material

Using an facile chemical catalytic activation and conversion route with carbon dioxide as the only carbon source introduced, i.e., CO_2 was activated and hydrogenated to methane, and then the product mixture of the 1st reactor was flowed into the 2nd reactor and converted to a solid-form carbon-product (integrated two-steps new process technology), CO_2 could be easily catalytically captured to solid-form carbon-material (in this case, CNTs). In this newly developed way which was called "chemical vapor deposition integrated process (CVD-IP)", carbon dioxide (CO_2) raw material could be catalytically captured easily and converted to a solid-form carbon-product.

The experiments of carbon dioxide catalytic capture and conversion to CNTs was described as follows: nickel-based catalyst for CVD process was synthesized by citric acid combustion method, in the form of powders. 150 mg CVD catalyst in a ceramic boat was placed in the quartz reactor, followed by a reduction in pure hydrogen at 550 °C. Then the CVD process was through the catalyst bed at 650 °C. The inlet carbon dioxide was fed at a flow-rate of 900 mL/h with stoichiometric hydrogen (3600 mL/h) in the 1st reactor, and the product mixture of the 1st reactor was flowed into the 2nd reactor and converted to solid-form carbon-product using CVD method. CO_2-derived new carbon nanotubes of type I (CNT-C1, from CO_2) has been obtained directly using the product mixture of the 1st reactor through a silica-gel trap for water, without further additive via the above new procedure.

The involved main chemical reactions are illustrated as follows:

(1) $n\mathrm{CO_2}+4n\mathrm{H_2} \longrightarrow n\mathrm{CH_4}+2n\mathrm{H_2O}$



(2) $n\mathrm{CH_4} \longrightarrow \mathrm{CNTs}+2n\mathrm{H_2}$

In total, net reaction:

$n\mathrm{CO_2}+2n\mathrm{H_2} \longrightarrow \mathrm{CNTs}+2n\mathrm{H_2O}$

And then, when a cheap additive (E: Eau, i.e., steam vapor at room temperature) was supplied with the product mixture of the 1st reactor for the 2nd step in the above new process, carbon nanotube of type II (CNT-C2, from CO_2) has been synthesized, for which there were much more tube-end-opening nanotubes.

For comparison, conventional carbon nanotubes were prepared via CVD method from methane raw material (the carbon-product was labeled like "CNT-M1"), using CVD method described in our previous work [26]. Further purified sample, labeled as CNT-M2, has been obtained using the treatment of CNT-M1 in a concentrated HNO_3 (68 wt%)

and refluxed at 140 °C for 12 h in an oil bath. Four MWCNTs samples are grouped in Table 1 for a clear view.

Table 1. List of carbon nanotube samples

Sample code	Raw material	Synthesis method
CNT-C1	CO_2 derived	CVD-IP1
CNT-C2	CO_2 derived	CVD-IP2
CNT-M1	CH_4 derived	CVD
CNT-M2	CH_4 derived	CVD

The "CNTs productivity" was calcuated using the following equation:

$$\text{Productivity of CNTs} = (m_{\text{tot}} - m_{\text{cat}}) \times 100\% / m_{\text{cat}}$$

where, m_{cat} is the catalyst mass before reaction, and m_{tot} is the total mass of the solid carbon-product with catalyst of small amount, after four-hours' catalytic capture of carbon dioxide leading to solid-form carbon-product.

The "carbon yield of CNTs sample" was calcuated using the following equation:

$$\text{CNTs yield (in carbon-base)} = n_{\text{C}} \times 100\% / n_{CO_2}$$

where, n_{C} is the mole amount in CNTs produced; n_{CO_2} is the mole amount of inlet CO_2.

2.2. Characterization of CO_2-derived CNTs samples

The samples were characterized by several techniques using XRD, TEM, IR, TG-DTG etc. [28,29]. X-ray diffraction patterns were measured and collected on an XRD Bruker D8 diffractometer with Cu K_α radiation.

Transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2000 FX microscope at 200 kV in National University of Singapore (NUS). The samples were prepared by ultrasonic dispersion in an ethanol solution, placed on the TEM copper grid and the solvent was evaporated.

Scanning electron microscope (SEM) images were obtained on a Philips FEG XL-30 system. Room temperature micro-Raman scattering analysis was carried out with a Renishaw spectrometer using Ar laser excitation source.

FT-IR spectra of the samples were measured using KBr wafer in a Bruker Tensor-27 FT-IR spectrometer. The spectra were recorded in the range of 400–4000 cm^{-1}.

TG-DTG was performed to characterize the decomposition behavior and peak temperature for carbon nanotubes sample, while air was used as the carrier gas for reacting the sample with a heating rate of 20 °C/min in the temperature range of 50–800 °C.

3. Results

With our newly developed integrated procedure (CVD-IP1), CO_2 catalytic capture and conversion to CNTs has been achieved very remarkably (Figure 1). Carbon nanotubes (CNT-C1) has been produced at a high productivity and a relatively high carbon-based yield of CNTs (more than 30% in carbon-base at a single-pass catalytic capture to solid-form product, while CO_2 conversion was nearly 100%). In comparison, no CNTs product could be formed when only pure carbon dioxide was introduced and using the conventional CVD method (Figure 1).

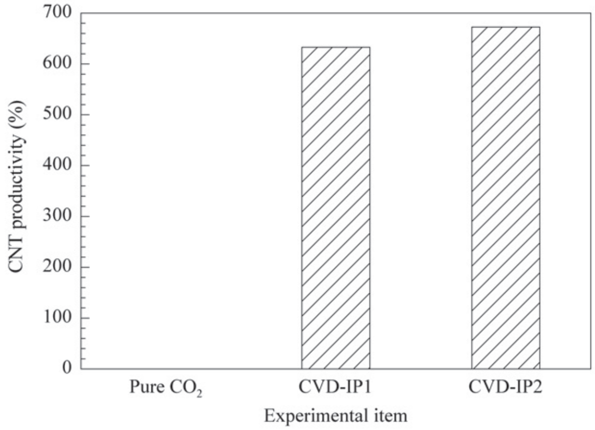


Figure 1. Productivity of carbon nanotubes (solid-form product) versus preparation item using CO_2 catalytic capture and CVD-IP new process

TEM image of the CO_2-derived CNTs was indicated in Figure 2(a). At a larger magnification, there were many straight carbon nanotubes (shown in Figure 2b), while the carbon nanotube-ends were mostly closed for this as-synthesized carbon nanotube sample, and the observation was similar to that of CNTs from conventional methane CVD process.

The above CO_2-derived carbon nanotubes of Type I (designated as CNT-C1) possessed similar properties to those of the sample prepared using conventional chemical vapor deposition (CVD) method with methane as the carbon source (labeled like CNT-M1). In our further experiments, a cheap additive (E) was added to the new integrated process to synthesis another new-type CNTs of better quality: such CO_2-derived CNTs of Type II was labeled as CNT-C2. It was found that in the presence of additive (E), CNT-C2 possessed much more end-opening nanotubes (Figure 3), than those of the sample prepared using the conventional CVD method (CNT-M1). This advantage property of CNT-C2 was desirable in many applications due to defined-field effects, especially in heterogeneous catalysis [30−32].

The representative transmission electron microscopy (TEM) images of CNT-C1 and CNT-C2 samples derivated from CO_2 are compared in Figures 2 and 3. It was seen from Figure 2 that CNT-C1 displayed a bamboolike morphology. At a larger magnification, there were many straight carbon nanotubes while the carbon nanotube ends were mostly closed. It was also seen from the high-magnification TEM image that the outer diameter of CNT-C1 was about 20 nm with wall thicknesses ranging from 5 to 6 nm and inner diameters in the range of about 7−10 nm.

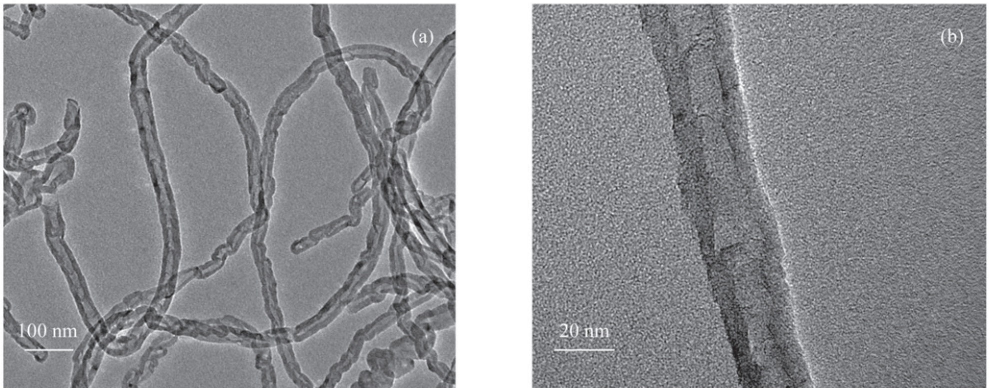


Figure 2. TEM (a) and HRTEM (b) images of CO_2-derived carbon nanotubes (CNT-C1) from CO_2 catalytic capture

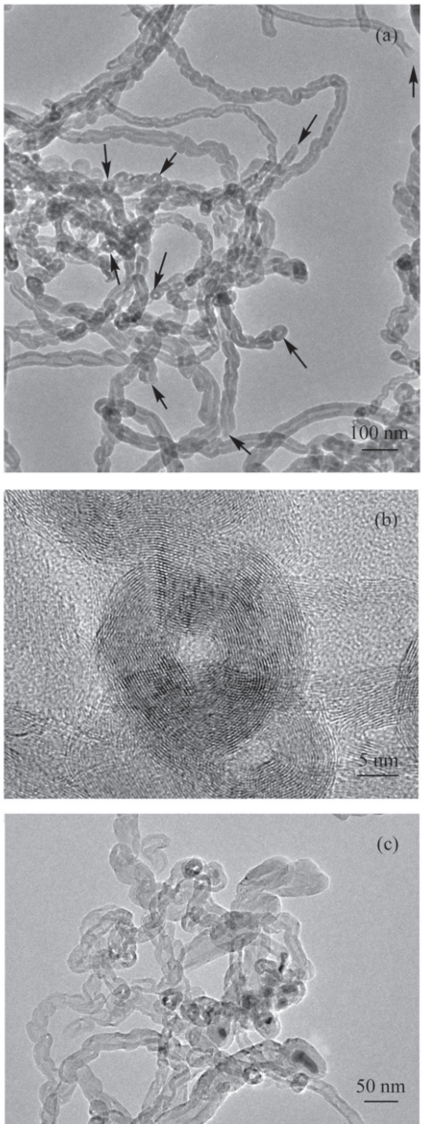


Figure 3. TEM (a,c) and HRTEM (b) images of CO_2-derived carbon nanotubes (CNT-C2) from CO_2 catalytic capture

XRD patterns of CO_2-derived CNT-C1 and CNT-C2 samples, together with that of a conventional carbon nanotubes sample prepared using the traditional CVD method (labeled as CNT-M1), are shown in Figure 4. There are two typical diffraction peaks at 26.0^{o} and 42.9^{o}, which are due to the (002) and (100) reflections respectively, corresponding to SP2-hybrid graphene carbon. There were also these two diffraction peaks for CNT-M1 sample produced using methane CVD process, but with a slightly lower peak intensity. The other diffractions peaks were due to metallic nickel and magnesium oxide, the support for nickel catalyst, on which CNTs sample grew [33].

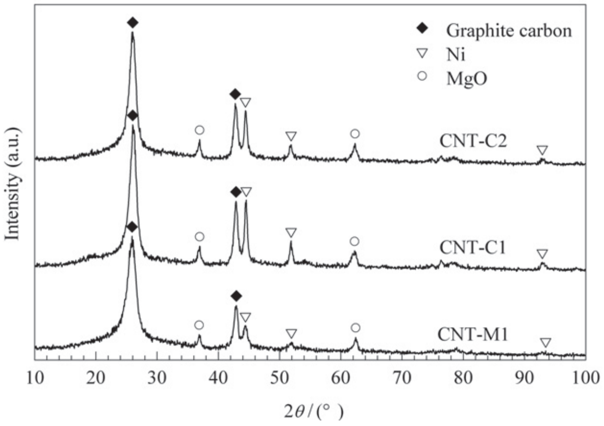


Figure 4. XRD patterns of three carbon nanotubes

Raman spectrum of sample CNT-C2 is shown in Figure 5. The two peaks at 1342 cm^{-1} and 1571 cm^{-1} were attributed to the D band and G band respectively for CNTs sample [34]. The intensity ratio (I_D/I_G) of the D band over the G band was utilized to evaluate the perfection degree of the synthesized carbon nanotube sample. I_D/I_G value of CNT-C2 sample was 0.907, indicating that this sample was of type multi-walls carbon nanotubes (MWCNTs) [34].

The mechanism for carbon dioxide catalytic capture and conversion to solid-form carbon-material is illustrated in Scheme 1. At the first step, carbon dioxide was catalytically activated to form an intermediate product (methane mixture), which was then transferred to solid-form product in the second step, i.e., carbon nanotubes were produced. The whole new procedure was a CVD integrated process (CVD-IP). Nickel-based CVD catalyst and the integrated CVD-IP procedure were both very important for a better realization of CO_2 catalytic capture and conversion to solid-form product.

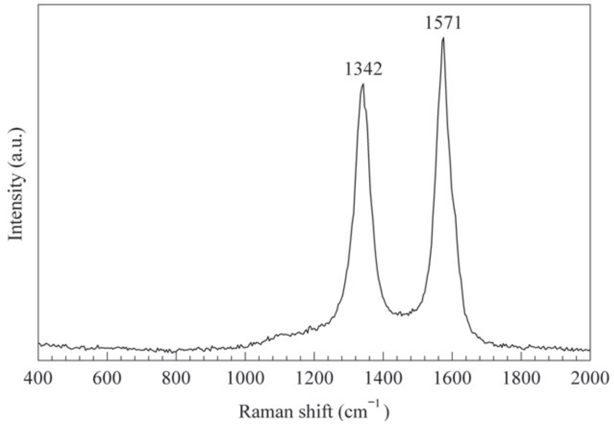
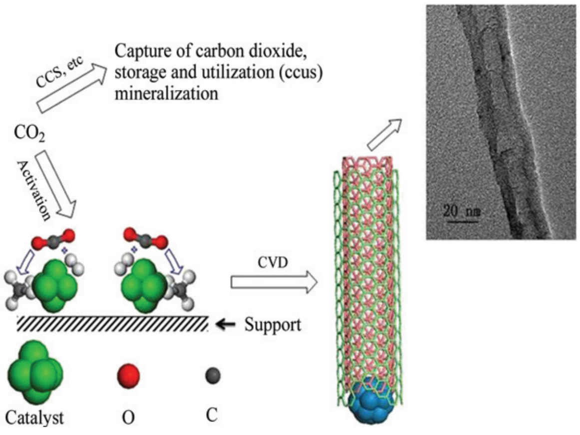


Figure 5. Raman spectrum of sample CNT-C2



Scheme 1. Mechanism for carbon dioxide catalytic capture and conversion to CNTs using CVD-IP procedure

The newly-developed route in this work opened an alternative approach for carbon dioxide sequestration and CO_2 catalytic capture. Besides, its solid-form product CNTs was a very useful new carbon material. This new procedure (CO_2 catalytic capture) with its very useful product production gave a remarkable and alternative approach for CO_2 sequestration or other ways of CO_2 mineralization, etc.

Figure 6 shows TG-DTG curves of CO_2-derived CNT-C1, and CNT-C2 samples as well as the conventional CNT-M1. The weight loss of the three samples after 800 °C was about 85 wt%. There were only slight differences of weight loss for these three samples. From DTG curves, it can be seen that there is only one peak of weight loss event occurred at around 690 °C, which was due to the oxidation of graphite carbon [35]. This further indicated that the solid-form carbon product was consisted only of SP2 hybrid graphene-type carbon. There was no weight loss event at about 400 °C, indicating that the samples did not contain amorphous carbon [35]. The above TG-DTG results demonstrated that the solid-form product from CO_2 catalytic capture was mainly carbon nanotubes, comparable with CNTs product using methane CVD process.

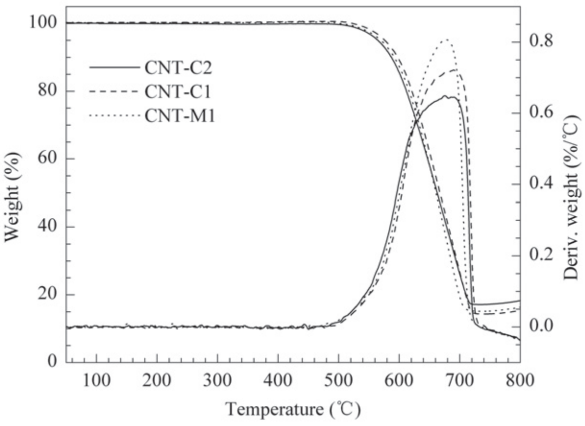


Figure 6. TG-DTG curves of samples

FT-IR spectra of three samples in the wavelength range of 1000−2000 cm^{-1} are shown in Figure 7. The main peak at 1630 cm^{-1} was due to the adsorbed water and potentially C = O group [36]. Besides, there were two more absorption bands at 1440 cm^{-1} and 1720 cm^{-1} for CNT-C2 and CNT-M2 samples (CNT-M2 sample was obtained after a treatment of CNT-M1 using 68 wt% nitric acid under quite severe conditions). These two absorption peaks were owing to the bending vibration of O−H in carboxylic acids and phenolic groups and the carbonyl C = O species in COOH, respectively [36,37]. This indicated that the cheap additive's impact on in-situ production of CNTs was very similar to that of CNTs post-treatment using a strong acid treatment under severe conditions, for the formation of surface groups in CNTs sample. The surface oxygen-containing groups such as O−H and COOH were formed owing to the reaction between surface carbon atoms with the strong acid in the post-treatment or the additive effect in the in-situ synthesis. The presence of such surface oxygen-containing groups plays an important role in the preparation of new efficient catalysts [30]. The above results demonstrated that the in-situ cheap additive functioned

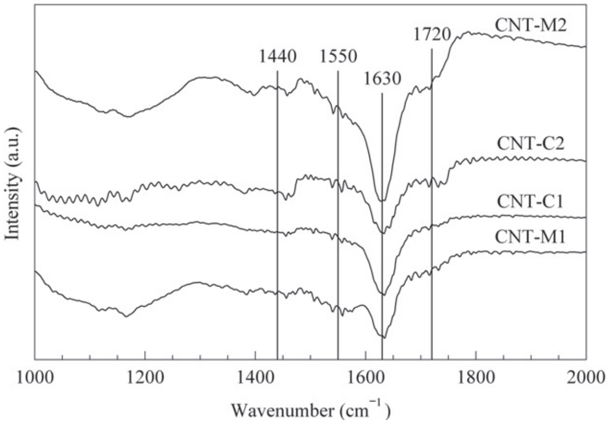


Figure 7. FT-IR spectra of four carbon nanotubes

as that of post-treatment nitric acid in terms of creation of surface functional groups on CNTs sample, while the new process was much more facile, cheaper and cleaner. There was not vibration band at 1550 cm $^{-1}$ (characteristic of carbon black [36]) for the samples, which is in good agreement with the results of TEM and TG-DTG measurements.

4. Discussion

4.1. Concerns of global warming and climate change due to more greenhouse gases emissions

From BBC News of 5 September 2010, the UK former prime minister Tony Blair said that politicians did not have to wait for chaotic climate change in order for them to act [7]. The risks of not cutting emissions, given the potentially massive consequences, were enough to justify action (Example 1: extreme weather events such as more floods disasters in several countries, heatwaves in Moscow and many other countries, etc; Example 2: the more and more melting of Himalayan glaciers and Antarctic Pole glaciers; there were a few pioneers who suspected that all those glaciers would melt in about 2050 and there would be more extreme whether). Mr. Blair has warned that world leaders may pay a heavy price in history if they fail to tackle global warming. Mr. Blair had also utilized the UK's G8 presidency in 2005 to push the issue of climate change.

From the BBC News in September 2010, the Committee on Climate Change (CCC) says that climate effects are already being felt in the UK in the form of higher temperatures and changing seasons [38,39]. Comparing with the value of 0.74 °C of the world average temperature rise for the past 100 years from 1898 to 1998, the UK's average temperature has already risen by 1 °C since the 1970s (only 40 years period). The UK government advisers warn and suggest that the UK needs to prepare itself quickly to deal with the impacts of climate change. The CCC uses projections from computer models of climate change to forecast a higher incidence of extreme weather events such as floods, heatwaves and droughts [38,39]. Lord Krebs suggested, the chairman of the CCC's adaptation sub-committee, that the UK must start acting now to prepare for climate change. The developments of more efficient routes abating the greenhouse gases emissions are very important for less worsening climate.

From the Guardian Journal of UK in July 2010, the global warming pushed 2010 temperatures to high record [40]. Global temperatures in the first half of the year were the hottest since the records began more than a century ago, according to two of the world's leading climate research centers [40]. Scientists have also released what they described as the "best evidence yet" of rising long-term temperatures. The report is the first one to collate 11 different indicators—from air and sea temperatures to melting ice—each one based on between three and seven data sets, dating back to between 1850 and the 1970s. The cause of the global warming was "dominated" by greenhouse gases emitted by human activities [38−42].

Global temperatures averaged during the first 6 months of 2010 were the warmest on record (since 1880) according to analyses produced by NOAA and NASA [41].

4.2. New opportunities for carbon dioxide catalytic capture

From the Copenhagen's Congress in December 2009, the world leading governments have being awared again to take more and more acts and find efficient approaches for the decrease of carbon dioxide emissions. Although the governments have taken some steps to raise awareness of the issue, few tangible changes have been resulted till now [42]. The Intergovernmental Panel on Climate Change (IPCC) would have more effects on the preventions of more global warming and extreme weathers [39−42].

Lord Krebs also suggested, the chairman of the CCC's adaptation sub-committee, that "It is not necessarily about spending more, but about spending smart and investing to save. If we get it right, we can save money in the short term and avoid large extra costs in the future".

Comparing with the other more costy routes of abating carbon dioxide emissions, the new route of CO_2 catalytic capture reported in this work could be a relatively cheap way for CO_2 capture and sequestration, while the derived product CNTs was a very useful and quite expensive carbon material. Following this inspiration and new approach, although there are still several steps for its enlarging and scale-up to a large-scale and also economically-feasible route, this new process would open an alternative and promising way for carbon dioxide catalytic capture, besides the route of carbon dioxide sequestration (CCS).

4.3. Benefits of magic CNTS production and applications

Since the first discovery of carbon nanotubes (CNTs) in 1991 [43], CNTs samples have been found many applications in materials engineering, electronics, energy storage, catalysis, etc [32,44−47], because of their chemical and mechanical stability, electrical conductivity and electro-magnetic properties. CNTs material could be produced from different carbon sources [33,48,49], such as natural gas, acetylene [33], alcohol [49], and so on.

There are many useful applications for carbon nanotubes materials, often better properties than those of the active carbon or carbon black, in the aspects of hydrogen storage, strength enhancement of the composite materials, catalyst support for selective hydrogenation, super-capacitor application, and in many other fields reported [27,30−37,44−46]. There were abundant well-defined hollow interior spaces for carbon nanotubes and they exhibited unusual mechanical and thermal properties as well as good electron conductivity.

In the works of Pan et al., when Rh and promoters were assembled inside the carbon nanotubes, forming a new nanoreactor catalyst, a striking enhancement of the catalytic activity of Rh particles confined inside nanotubes was reported for the conversion of CO and H_2 to ethanol [32]. The overall formation rate of ethanol (30.0 mol/($mol_{Rh}\cdot h$)) inside the nanotubes exceeds that on the outside of the nanotubes by more than an order of magnitude, although the latter is much more accessible. The "defined-field effects" explained the results [31,32].

5. Conclusions and outlook

In this work, through our newly-developed "chemical vapor deposition integrated process (CVD-IP)" using carbon dioxide (CO_2) as the raw material and only carbon source introduced, CO_2 could be catalytically captured and converted to solid-form carbon-product, i.e., carbon nanotubes (CNT-C1, CO_2-derived) at a quite high carbon-based yield (CO_2 conversion was nearly 100%, within more than 30% raw material was converted to carbon nanotubes at single-pass procedure). For comparison, when only pure carbon dioxide was introduced using the conventional CVD method, there was not any solid-form carbon-product formed.

In order to efficiently deal the global warming and climate change due to the effects of greenhouse gases (mainly CO_2), different technologies have been proposed to reduce the carbon dioxide emissions and their impacts on global warming, such as geological sequestration of carbon dioxide in underground reservoirs (CCS), and the chemical recycling conversion process of carbon dioxide gas into value-added chemicals, etc. The results in this inspiring work have illustrated an alternative and promising route for efficiently decreasing the global CO_2 emission when it would be enlarged in a huge scale-up and in giant industrial scale plants, supposing that the leading governments and the academic and industrial societies would pay more and more attention and joint-efforts for the research and developments of a more efficient and cheap process technology using similar and enlarged CVD-IP new technical route.

In addition, with a cheap additive (E) in CVD-IP process of the carbon nanotubes growth and production, new-type high-quality carbon nanotubes (CNT-C2, CO_2-derived) has been produced, in which there were a significant portion of end-opening carbon nanotubes. There are high potential applications due to "defined-field effects".

This work and initiatives opened a remarkable and alternative catalytic capture approach of carbon dioxide than that of CO_2 sequestration and other ways of CO_2 solidification (mineralization, etc). However, there are 10 open questions or issues in the technical and economical aspects (some of the tasks or issues are the similar or partly overlapped ones):

1. In this two-step integrated process of CO_2 catalytical capture to a solid-form carbon material, the reactants are carbon dioxide and hydrogen, the main products are solid-form carbon-material (especially carbon nanotubes, MWCNTs) and some percentage of methane, which could be further converted to solid-form non-green effect carbon material, with recycling conversion. The catalysts and process efficiency need to be enhanced, this becomes the 1st issue.

2. The total cost of this new process of carbon dioxide catalytic capture is composed of three main aspects: (1) operating cost including electricity consumption, (2) co-reactant hydrogen fee, (3) small amount catalyst consuming fee for the solid-form carbon-material production using CVD. If not considering the use of carbon-product (even high-quality MWCNTs with end-opening nanotubes), how to reduce each one cost of these three aspects, in order to make this new process of CO_2 catalytic capture in an economically-feasible way or quite cheap route?

3. Nickel-based catalyst has been utilized for CVD step in this pioneer attempt, which is not cheap comparing with the use of iron-based catalysts. While the iron-based catalysts were also reported to be efficient for MWCNTs production by similar CVD technique. So developing low-cost and more effective iron-based catalyst is the 3rd challenging task and issue.

4. The actual industrial hydrogen cost is about 1100 USD per ton hydrogen, could this be much reduced using the cheaper solar electricity of home-owned solar electricity plants with the leading governments supporting? The Germany government was one of the best examples for significantly developing the solar electricity. Therefore, with more leading governments initiatives and strong supports, could the hydrogen price be decreased to half or one third of the actual price? i.e., to be 550 USD or 370 USD per ton of hydrogen? The related technology development is the 4th opening task and issue.

5. With the stoichiometric consumption and total balance (re-using of formed hydrogen), for treating 44000 tons of carbon dioxide, 4000 tons of hydrogen was consumed, forming 12000 tons of solid-form carbon-material (MWCNTs, or other in which the process operating fee was cheaper?), some operating cost of electricity consumption, and about 120 tons of iron-based catalyst (supposing the carbon-material productivity was about 100 kg/kg_{cat}; while it was reported to reach a value of 300 kg/kg_{cat} or more in the literature). The related costs were:

(1) 4000 ton hydrogen: 4000 ton × 370 USD/ton = 1 480 000 USD;

(2) 120 tons of iron catalyst consumption: 120 ton × 2000 USD/ton = 240 000 USD;

(3) Capture of power plant CO_2 cost: 44000 ton × 25 USD/ton = 1 100 000 USD;

(4) The operating electricity fee: 44000 ton × 15 USD/ton = 660 000 USD;

The total of above 1 to 4 items was equal to: 3 480 000 (USD);

(5) As MWCNT was expensive, (2−3 USD/g, or 1000 USD/kg), 12 000 ton MWCNTs product would sale a huge benefit. Or, at least using it as the active carbon or carbon black, the related (much cheaper) price was about 5000 USD/ton, thus:

12000 ton × 5000 USD/ton = 60 000 000 USD

Therefore, a small part (10%) of the solid-form carbon material re-application (sale) would compensate the cost of carbon dioxide catalytic capture process technology;

(6) From CDM issue related to reducing CO_2 emissions, these 44 000 ton of CO_2 catalytic capture would equal to: 44 000 ton×30 USD/ton = 1 320 000 USD.

Based on the above analysis, the catalytic capture is theoretically feasible and technically feasible, as well as in the economical aspect.

In order to make this feasible catalytic capture of carbon dioxide new process technology more cheaper and easy to be operated in large scale, the investigations and improvements in the following three aspects constitute the 5th task and issue: (1) cheaper hydrogen production, (2) more efficient iron-based catalyst, and (3) solid-form carbon material more re-applications.

6. After treating 44 000 tons of carbon dioxide, about 12 000 ton of high quality MWCNTs could be produced. The use and sale of these deliver a huge benefit.

If we could develop other solid-form carbon-material products (like carbon nano-fibers, etc) and related process with cheaper operating cost, based on the similar catalytic capture approach? This is the 6th opening issue.

7. Could this catalytic capture new process technology be applied directly to the power plants emitted CO_2 mixture (glue gas, etc) after some brief PSA separation?

8. The development and new technologies on more efficient catalytic combustion of natural gas or so in power plants are also very important topics.

9. In order to significantly reduce the greenhouse gasses (GHG) effects for less degrading living atmosphere, the developments of more efficient De-NO_x, De-SO_x are also very important. This is the 9th opening task or issue.

10. Other related issues.

Acknowledgements

This work was supported by the National 973 Program of Ministry of Sciences and Technologies of China (2011CB201202) and the National Natural Science Foundation of China (20776089). The authors would like to thank Dr L. L. Zhang and Z. B. Lei for their assistances in TEM and Raman measurements; we also thank Dr. H. Zhang, Dr D. G. Tong, W. J. Sun and Z. Q. Wang for their assistances; we also express our appreciations to Prof. X. Y. Dai and Dr M. Liu for useful discussion and helps.

References

[1] Karl T R, Trenberth K E. *Science*, 2003, 302(5651): 1719
[2] Keith D W. *Science*, 2009, 325(5948): 1654
[3] Wilson E J, Friedmann S J, Pollak M F. *Environ Sci Technol*, 2007, 41(17): 5945
[4] Johnson T L, Keith D W. *Energy Policy*, 2004, 32(3): 367
[5] Anderson S, Newell R. *Annu Rev Environ Resour*, 2004, 29: 109
[6] Dorner R W, Hardy D R, Williams F W, Willauer H D. *Energy Environ Sci*, 2010, 3(7): 884
[7] Harrabin R, Blair T. 'Heavy price' for Climate Inaction, http://www.bbc.co.uk/news/science-environment-11181330, September 5, 2010
[8] Rochelle G T. *Science*, 2009, 325(5948): 1652
[9] Avalos-Rendon T, Casa-Madrid J, Pfeiffer H. *J Phys Chem A*, 2009, 113(25): 6919
[10] Nikulshina V, Gebald C, Steinfeld A. *Chem Eng J*, 2009, 146(2): 244
[11] Sakakura T, Choi J C, Yasuda H. *Chem Rev*, 2007, 107(6): 2365
[12] Pan Y X, Kuai P Y, Liu Y A, Ge Q F, Liu C J. *Energy Environ Sci*, 2010, 3(9): 1322
[13] Abe T, Tanizawa M, Watanabe K, Taguchi A. *Energy Environ Sci*, 2009, 2(3): 315
[14] Wambach J, Baiker A, Wokaun A. *Phys Chem Chem Phys*, 1999, 1(22): 5071
[15] Bhanage B M, Fujita S, Ikushima Y, Arai M. *Appl Catal A*, 2001, 219(1-2): 259
[16] Song C S. *Catal Today*, 2006, 115(1-4): 2
[17] (a) Wang N, Chu W, Zhang T, Zhao X S. *Chem Eng J*, 2011, 170(2-3): 457; (b) Wang N, Chu W, Zhang T, Zhao X S. *Int J Hydrog Energy*, 2012, 37(1): 19; (c) Wang N, Chu W, Huang L Q, Zhang T. *J Nat Gas Chem*, 2010, 19(2): 117
[18] (a) Yu X P, Wang N, Chu W, Liu M. *Chem Eng J*, 2012, 209: 623; (b) Zhu J Q, Peng X X, Yao L, Shen J, Tong D M, Hu C W. *Int J Hydrog Energy*, 2011, 36(12): 7094
[19] (a) Cai M D, Wen J, Chu W, Cheng X Q, Li Z J. *J Nat Gas Chem*, 2011, 20(3): 318; (b) Guo F, Chu W, Xu J Q, Zhong L. *Chin J Chem Phys*, 2008, 21: 481
[20] Dorner R W, Hardy D R, Williams F W, Davis B H, Willauer H D. *Energy Fuels*, 2009, 23(8): 4190
[21] Dorner R W, Hardy D R, Williams F W, Willauer H D. *Appl Catal A*, 2010, 373(1-2): 112
[22] Toyir J, de la Piscina P R, Fierro J L G, Homs N. *Appl Catal B*, 2001, 29(3): 207
[23] Kim J S, Lee S, Lee S B, Choi M J, Lee K W. *Catal Today*, 2006, 115(1-4): 228
[24] Xu L Y, Wang Q X, Liang D B, Wang X, Lin L W, Cui W, Xu Y D. *Appl Catal A*, 1998, 173(1): 19
[25] Li S Z, Krishnamoorthy S, Li A W, Meitzner G D, Iglesia E. *J Catal*, 2002, 206(2): 202
[26] (a) Ran M F, Liu Y, Chu W, Liu Z B, Borgna A. *Catal Commun*, 2012, 27: 69; (b) Ran M F, Sun W J, Liu Y, Chu W, Jiang C F. *J Solid State Chem*, 2013, 197: 517
[27] (a) Wen J, Chu W, Jiang C F, Tong D G. *J Nat Gas Chem*, 2010, 19(2): 156; (b) Zhang X W, Chu W, Zhuang H X, Xu S W. *Chem J Chin Univ (Gaodeng Xuexiao Huaxue Xuebao)*, 2005, 26(3): 493
[28] (a) Khodakov A Y, Chu W, Fongarland P. *Chem Rev*, 2007, 107(5): 1692; (b) Chu W, Wang L N, Chernavskii P A, Khodakov A Y. *Angew Chem Int Ed*, 2008, 47(27): 5052
[29] (a) Chu W, Chernavskii P A, Gengembre L, Pankina G A, Fongarland P, Khodakov A Y. *J Catal*, 2007, 252(2): 215; (b) Hong J P, Chu W, Chernavskii P A, Khodakov A Y. *J Catal*, 2010, 273(1): 9
[30] Chen W, Fan Z L, Pan X L, Bao X H. *J Am Chem Soc*, 2008, 130(29): 9414
[31] Pan X L, Bao X H. *Chem Commun*, 2008, (47): 6271
[32] Pan X L, Fan Z L, Chen W, Ding Y J, Luo H Y, Bao X H. *Nat Mater*, 2007, 6(7): 507
[33] Emmenegger C, Bonard J M, Mauron P, Sudan P, Lepora A, Grobety B, Züttel A, Schlapbach L. *Carbon*, 2003, 41(3): 539
[34] Wen Q, Qian W Z, Wei F, Liu Y, Ning G Q, Zhang Q. *Chem Mater*, 2007, 19(6): 1226
[35] Huang W, Wang Y, Luo G H, Wei F. *Carbon*, 2003, 41(13): 2585
[36] Yang H M, Liao P H. *Appl Catal A*, 2007, 317(2): 226
[37] Li C H, Yao K F, Liang J. *Carbon*, 2003, 41(4): 858

[38] Black R. Climate Change Advisers Urge UK to Prepare for Change, http://www.bbc.co.uk/news/science-environment-11322929, September 16, 2010

[39] Harrabin R. Call to Replace UN Climate Chiefs, http://www.bbc.co.uk/news/science-environment-11303686, September 14, 2010

[40] Jowit J. Global Warming Pushes 2010 Temperatures to Record Highs, http://www.guardian.co.uk/environment/2010/jul/28/global-temperatures-2010-record, July 28, 2010

[41] Hoerling M. Ongoing Scientific Assessment of the 2010 Western Russia Heatwave, http://www.esrl.noaa.gov/psd/csi/moscow 2010, September 3, 2010

[42] Sachs J. Obama Must Take a Lead on Climate Change–and Soon, http://www.guardian.co.uk/environment/cif-green/2010/jul/28/sachs-obama-climate-change, July 28, 2010

[43] Iijima S. *Nature*, 1991, 354(6348): 56

[44] Yoo E, Gao L, Komatsu T, Yagai N, Arai K, Yamazaki, T, Matsuishi K, Matsumoto T, Nakamura J. *J Phys Chem B*, 2004, 108(49): 18903

[45] Wong S S, Woolley A T, Joselevich E, Cheung C L, Lieber C M. *J Am Chem Soc*, 1998, 120(33): 8557

[46] Tans S J, Verschueren A R M, Dekker C. *Nature*, 1998, 393(6680): 49

[47] Arnold M S, Green A A, Hulvat J F, Stupp S I, Hersam M C. *Nat Nanotechnol*, 2006, 1(1): 60

[48] Piao L Y, Li Y D, Chen J L, Chang L, Lin J Y S. *Catal Today*, 2002, 74(1-2): 145

[49] Maruyama S, Kojima R, Miyauchi Y, Chiashi S, Kohno M. *Chem Phys Lett*, 2002, 360(3-4): 229