CO_2 enhanced carbon nanotube synthesis from pyrolysis of hydrocarbons†

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We report on the role of CO_2 in improving carbon nanotube yield and crystallinity from catalytic chemical vapor deposition of hydrocarbons.

As carbon nanotubes (CNTs) find applications in more and more fields, high quality CNTs in large quantities are increasingly in demand. Chemical vapor deposition (CVD) is one of the most promising methods for large-scale production of high-quality CNTs at relatively low cost. It also allows a close control of the nanotube structural characteristics by employing a suitable catalyst, carbon sources, and thermodynamic reaction conditions. It is commonly believed that CNT growth is initiated once a carbon monolayer covering a catalyst particle becomes unstable due to the incorporation of additional carbon atoms or thermal vibrations.[1,2] The interaction of the catalyst with the support affects both the size and the shape of the catalyst particles. A large portion of the catalyst particles is covered by a layer of carbon or the growing CNT, further hindering the catalytic decomposition of the carbon feedstock at the surface of the catalyst particles. Therefore, in order to improve the synthesis yield and quality of CNTs, it is desirable to disperse the metal particles uniformly on the oxide support, and keep the catalyst active as long as possible.

So far, many approaches have been developed to increase CNT yields, such as water assisted growth,[3] alcohol growth,[4] oxygen assisted growth in PECVD.[5] The increase in quality and yield is ascribed to efficient etching of amorphous carbon from the catalyst surfaces. Here we utilized CO_2 to improve CNT growth by CVD from hydrocarbons. CO_2 acts as an oxygenate so as to remove the amorphous carbon, and also as a new type of carbon source after reaction with the hydrocarbon.

The single-wall carbon nanotubes (SWNTs) were produced from the pyrolysis of CH_4 on a MgO supported Fe–Mo bimetallic catalyst, which has many advantages over the monometallic catalysts.[6] The choice of methane, catalyst composition, and type of support are the key to produce high quality SWNTs.[7] MgO was selected as the support since it provides a suitable interaction with the catalyst and it is also easily removed during purification. The SWNT synthesis was performed at 900 °C (see ESI†).[8] As shown in Fig. 1, the CNT yield varies with the $CO_2 : CH_4$ ratio in the feedstock. Without the assistance of CO_2, only 38 mg of SWNTs can be obtained from 100 mg of the catalyst. Adding the appropriate amount of CO_2 into the hydrocarbon feedstock can significantly increase the yield. At a $CO_2 : CH_4$ ratio of about 1 : 20, the yield increased by more than 60% than without CO_2 assistance. However, a further increase of CO_2 in the feedstock could cause a significant decrease in the nanotube yield.

The TGA profiles (Fig. 2(a)) of the purified tubes indicate that it is relatively easier to achieve high purity for the tubes produced with CO_2 assistance. CO_2 might be also responsible for keeping the metal particles clean, which can therefore be easily removed by the acid treatment during the purification. Additionally, the combustion temperature obtained from the derivative TGA (dW/dT) also increases with the concentration of CO_2 in the feed until reaching a $CO_2 : CH_4$ ratio of 1 : 10, suggesting that the addition of a suitable concentration of CO_2 can also improve the crystallinity of CNTs. But a too high concentration of CO_2 in the feed would lead to poor crystallinity, most likely due to the strong etching of the graphitic walls by the CO_2 molecules. The much broadened derivative TGA peak of the sample obtained at $CO_2 : CH_4 = 10 : 50$ also confirms this point (see the inset of Fig. 2(a)).

The Raman scattering data of the CNT products clearly exhibits radial breathing mode (RBM) bands which are the characteristic feature of few-wall CNTs (see Fig. 2(b)). Interestingly, the introduction of CO_2 into the reaction does not

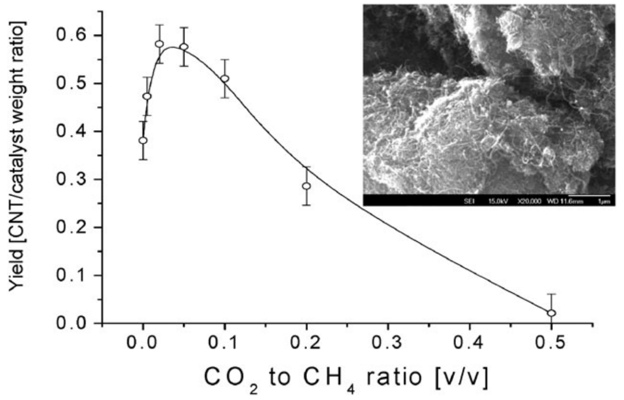

Fig. 1 The SWNT yield obtained from the pyrolysis of a mixture of CH_4 and CO_2 on the Fe–Mo/MgO catalyst as a function of the $CO_2 : CH_4$ ratio. The inset displays the SEM image of the SWNTs grown from the Fe–Mo/MgO catalyst.

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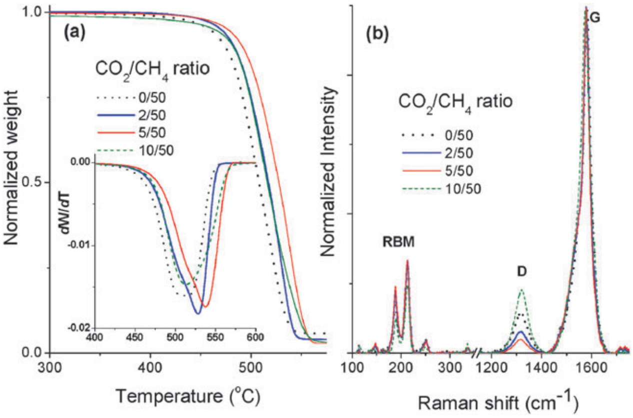

Fig. 2 (a) The TGA and the derivative TGA (dW/dT, inset) profiles of the SWNTs obtained under different CO_2 concentration in the feedstock. (b) The Raman scattering spectra of the carbon nanotubes produced from catalytic CVD of methane with CO_2 assistance.

change the diameter distribution of the CNTs, as indicated by the lack of changes in the RBM peak positions. It seems that the diameter of SWNTs in this study is only determined by the structure of the catalyst which is not altered by the CO_2 addition. Furthermore, the defects-associated D-band intensity decreases with an increase in the CO_2 concentration in the feed, but it increases for higher concentrations of CO_2. Therefore, we can efficiently reduce the defects in the final CNTs with CO_2 assistance.

To understand the role of CO_2 in the synthesis of SWNTs, we carried out mass spectral studies of the effluent gases from the CVD growth reaction at $CO_2 : CH_4 = 1 : 10$. As seen in Fig. 3(a), besides the carrier gas Ar, fragments of CH_4, and CO_2 coming from the feedstock, other intermediates such as CO and CH_3OH were also detected. The CO concentration is found to increase within the first 15 min (typical growth time for SWNTs) of the reaction and then decrease (Fig. 3(b)). One can suppose that CO_2 reacts with methane to produce carbon for the SWNTs *via* the following reactions:

$$CH_4 \rightarrow C + 2H_2 \qquad (1)$$

$$CH_4 + CO_2 \rightarrow 2C + 2H_2O \qquad (2)$$

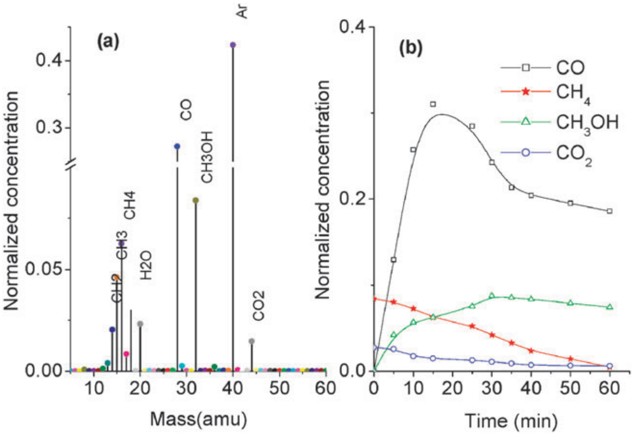

Fig. 3 (a) The mass spectrum of the effluent for the CO_2-assisted methane CVD system. (b) Time evolution of the effluent for the CO_2-assisted CVD system.

$$2CH_4 + CO_2 \rightarrow C + 2CO + 4H_2 \qquad (3)$$

$$CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O \qquad (4)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (5)$$

$$CH_4 + CO_2 \rightarrow CH_3OH + CO \qquad (6)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad (7)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (8)$$

$$CH_3OH \rightarrow C + H_2O + H_2 \qquad (9)$$

As these complex chemical processes suggest, carbon could directly be produced (reactions (1), (2) and (3)) or produced afterward as end products of reactions (4)–(9). Note that the byproduct CO is also a good carbon source for the SWNT growth *via* CO disproportionation ($2CO \rightarrow C + CO_2$).[9,10] Narrowly (*n*,*m*) distributed SWNTs can also be obtained from thermal CVD of CH_3OH similarly through reaction (9).[11,12] The trace amount of byproduct H_2O is beneficial for the amorphous carbon removal.[13] The intermediate product H_2 (from reactions (1), (3), (5), and (9)) might help to generate methane (reaction (8)) and methanol (reaction (7)), and its presence in the reaction also keeps the metallic catalyst particle from being oxidized. CO_2 is available from the feed, but it must also be generated from the products *via* the water–gas shift reaction: $H_2O + CO \leftrightarrow CO_2 + H_2$ and/or CO disproportionation: $2CO \leftrightarrow C + CO_2$. The yield of CO_2 regeneration was reported higher than 90%.[14] Moreover, the CH_4 regeneration could occur through the CO hydrogenation (reaction (8)).

Based upon the above chemical reactions, CO_2 plays at least two important roles in the SWNT synthesis. First, CO_2 acts as an oxygenate to remove the amorphous carbon, which would keep the catalyst active for a longer time and consequently increase the length and yield of tubes. The removal of amorphous carbon basically is through these two reactions: $C + CO_2 \rightarrow 2CO$ and $C + H_2O \rightarrow CO + H_2$. Secondly, CO_2 can be dissociated on the surface of the catalyst clusters and reacts with other molecules and radicals, resulting in intermediates that can be more effective for the SWNT growth. Additionally, CO_2 also can interact with the MgO support, which decreases its particle size and increases the specific surface area of the catalyst, accordingly increasing the yield, purity, and specific surface area of SWNTs.[15]

In the SWNT growth reaction, metallic Fe particles act as catalytic species to activate CH_4 and CO_2 for the SWNT growth. Density functional theory calculation[16] revealed that the adsorption strength of CO_2 is controlled by the d-band center of the metal surfaces and also affected by the charge transfer from the metal surfaces to the chemisorbed CO_2. The degree of C=O bond activation depends on the transferred charge. The Fe(110) surface can elongate the sum of the C–O bond lengths to 2.615 Å, and this is the most activated structure whereas it has moderate strengths on the (111) surfaces of Co, Ni, Rh and Pd with slightly positive binding energies. The element Mo probably plays two different roles in the CNT synthesis. First, Mo can act as a secondary support for the active metal like Fe here. The active metal particles docked on the relatively large Mo particles which were

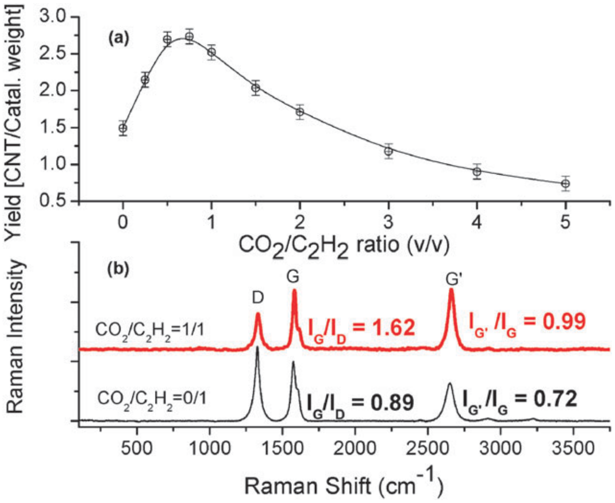

Fig. 4 (a) The MWNT yield as a function of $CO_2 : C_2H_2$ ratio. (b) The Raman scattering spectra from the MWNTs grown on Fe–Co (1 : 1 atomic ratio) with and without CO_2. The higher I_G/I_D and $I_{G'}/I_G$ values of the MWNTs grown with CO_2 indicate higher quality.

supported by the MgO powders.[17] Second, Mo can also participate in the breakup of the hydrocarbon molecules. It has been reported that the use of the conditioning catalyst Mo/Al_2O_3[18] caused more double wall carbon nanotubes than SWNTs to grow, possibly because of an increase in the amount of the active carbon species.[19] Carbon-containing radicals are much more active for the carbon tube formation, since they greatly reduce the reaction potential.

More importantly, it is worth mentioning that the enhancement effect of CO_2 is not limited to the SWNT growth from the hydrocarbon CVD; it is also valid for any type of CNT synthesis from pyrolysis of hydrocarbons. A more than 80% increase in the MWNT yield has been also observed with CO_2 assistance in pyrolytic acetylene CVD on a $Fe–Co/CaCO_3$ system (see ESI† and Fig. 4(a)). Similarly, a suitable concentration of CO_2 in the hydrocarbon feedstock acetylene can also reduce the amorphous carbon accumulation and improve the crystallinity of the resulting MWNTs (Fig. 4(b)).

In summary, we demonstrated the enhanced CNT synthesis from chemical vapor deposition of hydrocarbon with appropriate CO_2 assistance. In the CNT growth reaction, CO_2 can react with the hydrocarbon and form intermediates such as CO and CH_3OH, both of which are good carbon sources for the SWNT synthesis. CO_2 along with the intermediates such as CO, CH_3OH and H_2O can efficiently remove the amorphous carbon layer generated on the metal particle surfaces *via* various reactions. These findings provide a highly efficient method to increase the yield and quality of any type CNT growth from pyrolysis of hydrocarbons at low cost.

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