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High-yield synthesis of carbon nanotubes using a water-soluble catalyst support in catalytic chemical vapor deposition

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Carbon nanotubes have been the subject of a recurrent interest for long. As a result, various types of carbon nanotubes are now widely available on the market. A recent survey of classical literature by Monthioux [1] reflects history of carbon nanotubes, which have been known for about 40 years. The last peak of interest started in the nineties [2], and considerable efforts have been made since then to synthesize them via various methods including conventional ones [3–5]. In the present communication, we would like to report a useful approach to enhance conventional synthesis of carbon nanotubes by means of catalytic chemical vapor deposition (CCVD), which is a common method for synthesis of carbon nanotubes [6]. This is of interest for fundamental understanding, and improvement of commercial synthesis of carbon nanotubes.

Catalyst supports are an essential ingredient for the synthesis of carbon nanotubes via CCVD. Common examples are MgO, Al_2O_3, SiO_2, etc., providing high surface area for CCVD reaction. Although it is practical and common in commercial synthesis of carbon nanotubes, subsequent post-treatments such as washing with acid make problems (cost, environment, . . .). Here, we suggest using a catalyst support which can be easily removed with water. The basic idea returns to Steigerwalt and Lukehart [7] who employed silicate or carbonate as catalyst support. Chloride such as NaCl was also used [8,9]. However, little attention has been paid to these pioneering works, since the results were not satisfactory, and such synthesis routes tend to form other forms of nanostructured carbon materials [9] rather than carbon nanotubes. We report here a case of water washable catalyst support with high-yield. In addition to the ease of using washable catalyst support, this synthesis route is even more efficient than conventional and commercial ones employing metal oxide catalyst supports.

In a typical experiment, a catalyst was prepared by dissolving 0.25 g $Co(NO_3)_2$, 5 g $CaCl_2$, and 5 g citric acid in water. Then, it was slowly dried to form a low-density foam. Since the internal part of the foam is not easily accessible in CCVD process, the foam was ground to form fine particles. In this case, the catalyst is uniformly distributed within the matrix of catalyst support. As the result of the subsequent thermal decomposition of the foaming agent (citric acid) that takes place before the main CCVD reaction, the previous porous structure within the whole powder is maintained yet modified. Such features can be easily verified from SEM images (not shown). The CCVD reaction was performed in a horizontal quartz tube furnace by passing a mixture of 1:1:10 C_2H_2:H_2:N_2 for 30 min at 700 °C. Electron microscopy investigations were made using a Philips XL30 scanning electron microscope and a Philips transmission electron microscope.

Fig. 1 displays typical scanning and transmission electron microscopy (SEM and TEM) images of the carbon nanotubes synthesized. The carbon nanotubes have

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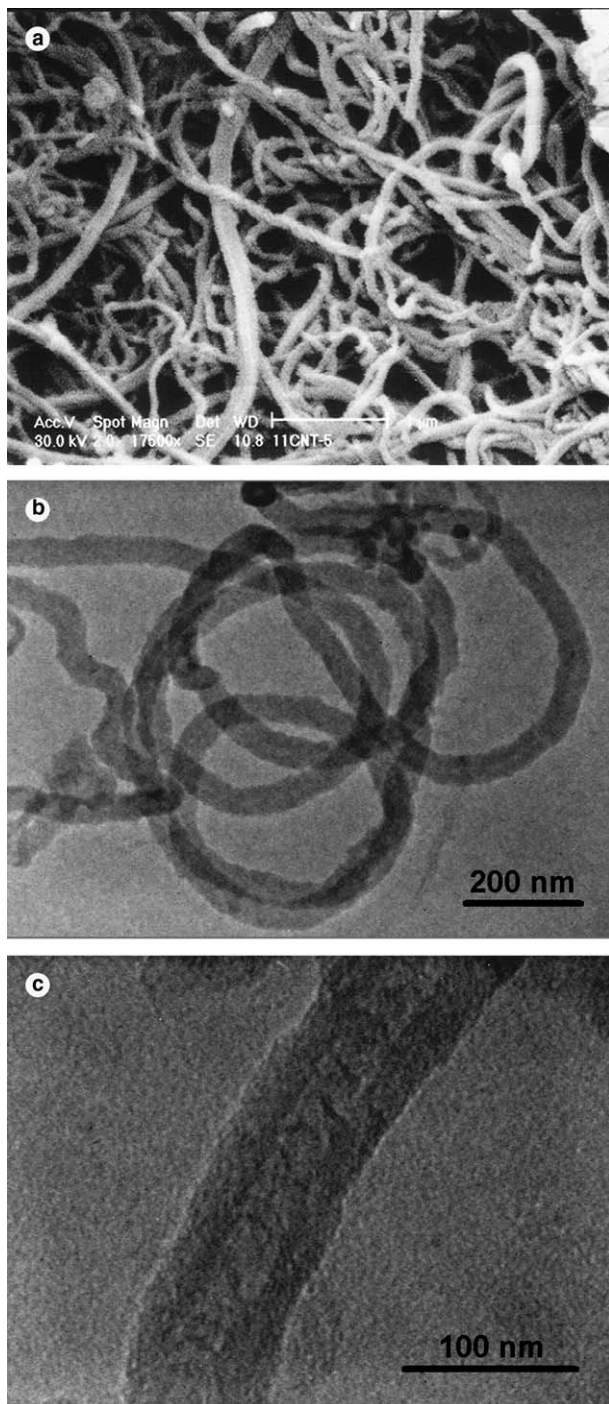*E-mail address:* eftekhari@merc.ac.ir (A. Eftekhari).

Fig. 1. (a) SEM, (b) and (c) TEM images of the carbon nanotubes synthesized by means of calcium chloride as catalyst support and citric acid as foaming agent. Despite the low resolution of the micrographs, the tubular texture can be ascertained along with the bamboo texture from (c), thereby indicating that MWNTs are herringbone-type.

diameters ranging from 30 to 150 nm. In general, it is obvious that ideal multi-wall carbon nanotubes (MWNTs) are formed as well as those prepared with conventional methods. In other words, water washable catalyst support did not affect the structure of MWNTs, and it is applicable as well as known porous catalysts supports made from

metal oxides. The main problem associated with the absence of high surface area catalyst supports (such as MgO, SiO$_2$, etc.) is a low-yield of products due to lower accessibility of the catalyst involved in the CCVD reaction. However, in spite of the low-porosity obstacle was even worse in the system under investigation (in comparison with common metal oxides), the water washable catalyst supports appeared to provide an appropriate accessibility for the CCVD reaction, as the resulting carbon was weighted (after washing the catalyst support with water) to be 4.7 g. This means that the synthesis yield was more than 1500% in with respect to the initial weight of catalyst. This is truly high, as the yield of optimized synthesis of carbon nanotubes via CCVD is lower than 700% [10,11]. To ascertain that the resulting product is actually carbon, thermogravimetric (TG) investigations were made (Fig. 2). It is obvious that 94% of the product is burned at 500 °C, presumably as a single species. This species was demonstrated to be carbon nanotubes by TEM (Fig. 1). Correspondingly, an extensive investigation of large amount of the sample by means of TEM did not show the existence of any non-filamentous carbon species. Thus, the high yield efficiency of this approach for the synthesis of MWNTs can be concluded, with a yield in the range of 94%. The remaining material is the catalyst, which was not dissolved in water.

Very interestingly, this high-yield synthesis makes unnecessary subsequent treatment for removing the remaining catalyst. In other words, the metallic impurity is about 5%, which is quite common even in commercial samples (at least low-cost samples). Anyway, for our experiment material, it is possible to remove a part of the metallic impurity by washing in HNO$_3$ to obtain carbon product with only 2% metallic impurity.

In addition, Raman spectra were recorded using an Almega Raman spectrometer with an Ar$^+$ laser at an excitation wavelength of 514.5 nm. The Raman spectrum of the resulting product indicates two peaks at 1586 and 1340 cm^{-1} (Fig. 3), corresponding to the vibration of sp^2-bonded carbon atoms in a 2D hexagonal lattice and the vibrations of carbon atoms with dangling bonds in the plane terminations of turbostatic and poorly ordered car-
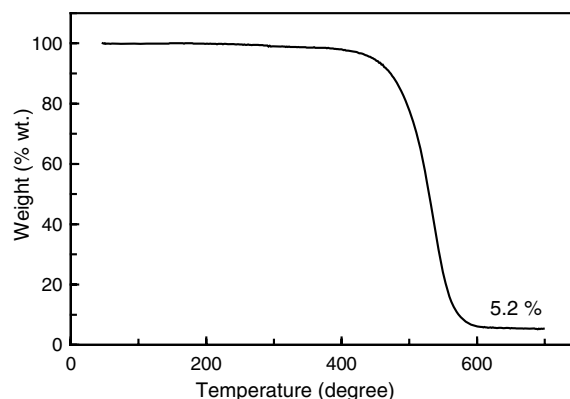

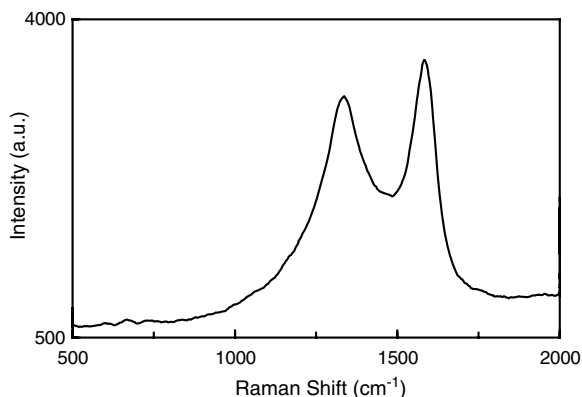Fig. 2. Thermogravimetric (TG) analysis of the carbon nanotubes.

Fig. 3. Raman spectrum of the carbon nanotubes.

bon, respectively. The ratio of these peaks, in the range of $G/D = 60/40$, indicates that the carbon nanotubes exhibit a rather defective structure, however in an extent which is quite common for CCVD-prepared nanotubes. This is quite consistent with what can be guessed from the TEM images, despite their low resolution.

The high-yield synthesis is related to the catalyst support employed. Similar water washable catalyst supports such as alkali metal chlorides result in yield lower than 200%, as it has also been reported by Szabo et al. [9]. However, the 2000% yield is not exclusively related to $CaCl_2$ and citric acid also plays an important role. A catalyst support made of pure $CaCl_2$ without foaming agent resulted in a yield of 154%. Surprisingly, the foaming agent by itself is not responsible for the high-yield synthesis either, as this is not applicable for other cases. For instance, NaCl plus citric acid as foaming agent leads to a yield of 300% only. In general, adding a foaming agent to alkali metal chloride catalyst supports increases the carbon nanotubes synthesis yield by a factor of 1.5. However, a peculiar behavior was observed for $BaCl_2$. When $BaCl_2$ is added with a foaming agent, the yield of carbon nanotubes synthesis is only 360%. Surprisingly, using a catalysis support of pure $BaCl_2$ is accompanied by a high-yield synthesis of 1500%. This indicates that catalyst supports of alkali-earth metal chlorides play a special role in the CCVD reaction, and it is strongly dependent on the final catalyst structure.

According to Liu et al. [8], NaCl catalyst support has an inhibiting effect on the growth of carbon nanotubes, and carbon-encapsulated cobalt nanoparticles will be formed instead. They attributed this behavior to low melting point of NaCl, and reported partial formation of carbon nanotubes when using NaF, whose the melting point is higher (993 °C). When the CCVD process (at 700 °C) occurs just 100 °C lower than the melting point of NaCl (801 °C), it

can swallow the catalyst particles, leading to the formation of carbon-encapsulated cobalt nanoparticles [8]. This is the reason why the yield of carbon nanotubes synthesis is higher for catalyst support of alkali-earth metal chlorides. High melting point of $BaCl_2$ (963 °C) overcomes this problem. In the case of $CaCl_2$ having a low melting point (782 °C), the thermal decomposition of the foaming agent avoids the aforementioned swallowing effect. However, these are just speculations based on the experimental results obtained. It is vivid that there are different factors affecting the carbon nanotubes synthesis. For instance, it is not clear why the foaming agent is not applicable for the case of $BaCl_2$. We repeated the experiments several times, but the results were completely reproducible.

It is obvious that the peculiar phenomena observed for alkali-earth metal chloride catalyst supports need extensive investigations to reveal the exact mechanisms involved. However, we aim to communicate such astonishing results without claiming an exact mechanism because a 2000% yield is no common in the available processes for carbon nanotubes synthesis, as it may introduce new strategy for designing catalysts for carbon nanotubes synthesis via CCVD in commercial processes.

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