

A scalable process for production of single-walled carbon nanotubes (SWNTs) by catalytic disproportionation of CO on a solid catalyst

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Abstract

Existing single-walled carbon nanotube synthesis methods are not easily scalable, operate under severe conditions, and involve high capital and operating costs. The current cost of SWNT is exceedingly high. A catalytic method of synthesis has been developed that has shown potential advantages over the existing methods. This method is based on a catalyst formulation that inhibits the formation of undesired forms of carbon; it can be scaled-up and may result in lower production costs.

Introduction

Single-wall carbon nanotubes (SWNTs) can be considered as one of the building blocks for nanoscale science and nanotechnology. They have shown unmatched electrical properties (Dresselhaus et al., 1996; Tans et al., 1998; Kwon et al., 1999), which depend on the symmetry of their honeycomb lattice and have been proposed to be the perfect electron emitters, being good candidates for the manufacture of flat panel displays. They would play an important role in nanoscale devices such as quantum wires, transistors, and molecular memory devices. At the same time, their mechanical strength would make SWNT useful in reinforcing fibers for applications in structural materials (Yakobson & Smalley, 1997; Andrews et al., 1999). SWNT-reinforced composites are being investigated using organic and inorganic matrices. At the same time, the rapid progress that has taken place in the theoretical understanding of the electronic and Raman spectra of SWNT has made it possible to get a fairly good characterization of the structure and type of SWNT that can be produced by a given method. However, the advances in the synthesis methods have not moved at a comparable pace and there is today little control in the production of

a given type of SWNT. Application as reinforcing materials or as emitters for flat panel displays would certainly require a large availability of SWNT at low cost. However, the production of SWNTs by the most common synthesis methods, laser ablation (Rinzler et al., 1998) and arc discharge (Journet et al., 1997), is still in the gram scale. The first serious attempt of developing a scalable process, able to produce sizeable amounts of SWNT, was started at Rice University a couple of years ago (Nikolaev et al., 1999), which resulted in the so-called HiPCO[®] process. In that process, SWNT are grown by thermal decomposition of iron pentacarbonyl in a flow of CO at high pressures and temperatures.

Another method that is widely recognized as being more easily scalable (Hafner et al., 1998) is the catalytic decomposition of a carbon-containing molecule on a solid catalyst (sometimes incorrectly called 'CVD method'). This method would be amenable to the development of continuous processes and truly large-scale operations, perhaps involving fluidized bed reactors, similar to a typical polymerization reactor. However, although the catalytic decomposition on solid catalysts has been investigated by several groups, in most cases, the resulting product has exhibited low selectivity to SWNT with a high density of imperfect multi-walled

tubes and fibers. As a result, the catalytic decomposition method has not been regarded as a viable alternative due to the low quality of the tubes that it produces. The reason for this poor performance is that, in most studies, the catalyst has not been tailored for the selective production of SWNT. As in every catalytic process, the design of the catalyst requires a detailed characterization of the different phases present in the solid during the various stages in the catalyst life.

The CoMoCAT process

We have developed a catalytic method (CoMoCAT[®]) that produces SWNT of high quality at very high selectivity, and with a remarkably narrow distribution of tube diameters. In this method, SWNT are grown by CO disproportionation (decomposition into C and CO₂)

at 700–950°C in flow of pure CO at a total pressure that typically ranges from 1 to 10 atm. In a two-year research program, which included characterization and testing of a large number of catalyst formulations and operating conditions, we developed a process that is able to grow a significant amount of SWNT (about 0.25 g SWNT/g catalyst) in a couple of hours, keeping a selectivity towards SWNT better than 80%. We discovered a synergistic effect between Co and Mo that is essential for the performance of the catalyst. We found that the catalyst is only effective when both metals are simultaneously present on a silica support with low Co:Mo. Separated, they are either inactive (Mo alone) or unselective (Co alone). Through a variety of characterization techniques such as EXAFS, XANES, UV/Vis-DRS, XPS, and DRIFTS of adsorbed NO, we were able to explain the reasons for the high selectivity of these catalysts. We established that the

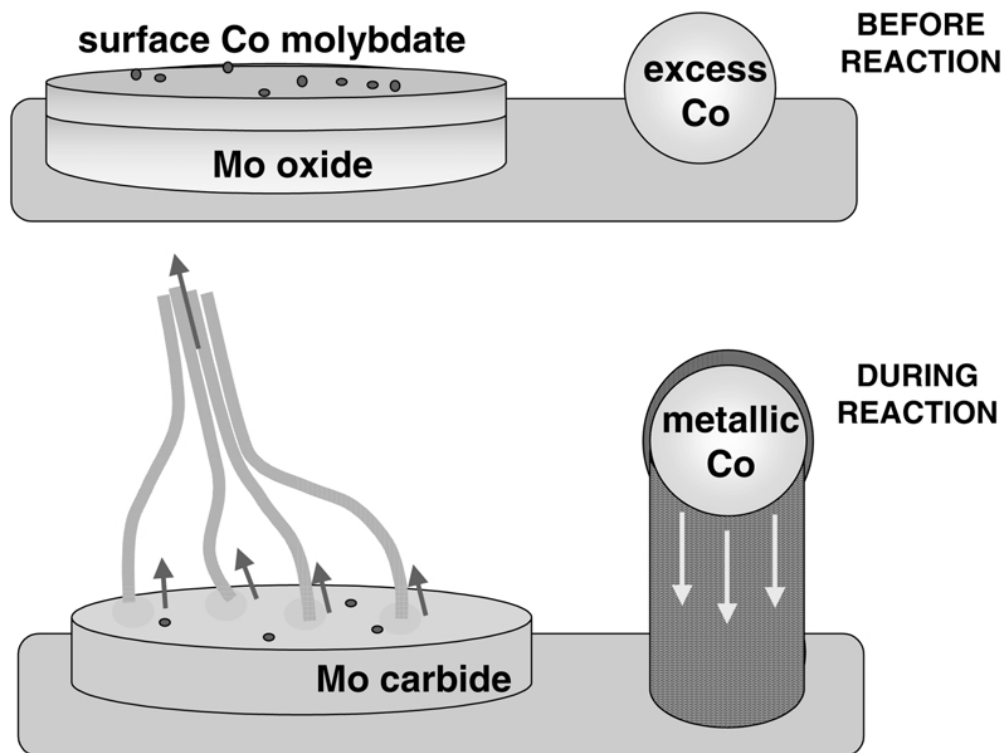


Figure 1. Schematic representation of the state of the catalyst components before and during the production of SWNT. The Co species stabilized by Mo resist reduction and sintering before the reaction. Under CO, Mo becomes carbide while Co becomes metallic and generates the SWNT. The excess Co, not stabilized by Mo, produces MWNT and fibers.

selectivity of the Co–Mo catalysts towards SWNT production by CO disproportionation strongly depended on the stabilization of Co^{2+} species by Mo oxide species (Resasco et al., 2000, 2001).

We found that the extent of the Co–Mo interaction is a function of the Co:Mo ratio in the catalyst and has different forms during the different stages of the catalyst life. We found that in the calcined state, Mo is in the form of a well-dispersed $\text{Mo}(6+)$ oxide. The state of Co strongly depends on the Co:Mo ratio. At low Co:Mo ratios, it interacts with Mo in a superficial Co molybdate-like structure. At high Co:Mo ratios, it forms a non-interacting Co_3O_4 phase. During the subsequent reduction treatment in hydrogen, the non-interacting Co phase is reduced to metallic Co, while the Co molybdate-like species remain as well-dispersed Co^{2+} ions. Figure 1 illustrates the action of a working catalyst before and during the production of nanotubes by indicating the role of the two different forms of Co, i.e., the selective Co species (interacting with Mo) and the unselective one (non-interacting). The important aspect to emphasize here is that the Co–Mo interaction inhibits the Co sintering that typically occurs at the high temperatures required for the

formation of carbon nanotubes. When large Co particles are present less desirable forms of carbon (MWNT, fibers, and graphite) are produced. By contrast, when the Co clusters are so small that they are only composed by a few atoms only SWNT are formed.

The effect of having Co stabilized in the Co-molybdate environment is dramatic. First of all, it avoids the formation of large metallic aggregates. The importance of preventing the reduction of Co is evident when the selective catalyst is compared with a non-selective one (Co:Mo ratio greater than 1:1). In the non-selective catalysts, most of the Co after calcination is Co_3O_4 , which is converted into large metallic Co clusters upon reduction. By contrast, on the selective catalyst, a concerted mechanism must take place during the reaction. As the CO disproportionation starts, Mo oxide is converted into Mo carbide. This transformation breaks up the Co molybdate-like structure, allowing for the reduction of Co by CO. However, the nascent metallic Co clusters are now highly dispersed and in the presence of high concentration of CO in the gas phase.

When metal atoms begin to agglomerate in the presence of gaseous CO, there is a nucleation period over

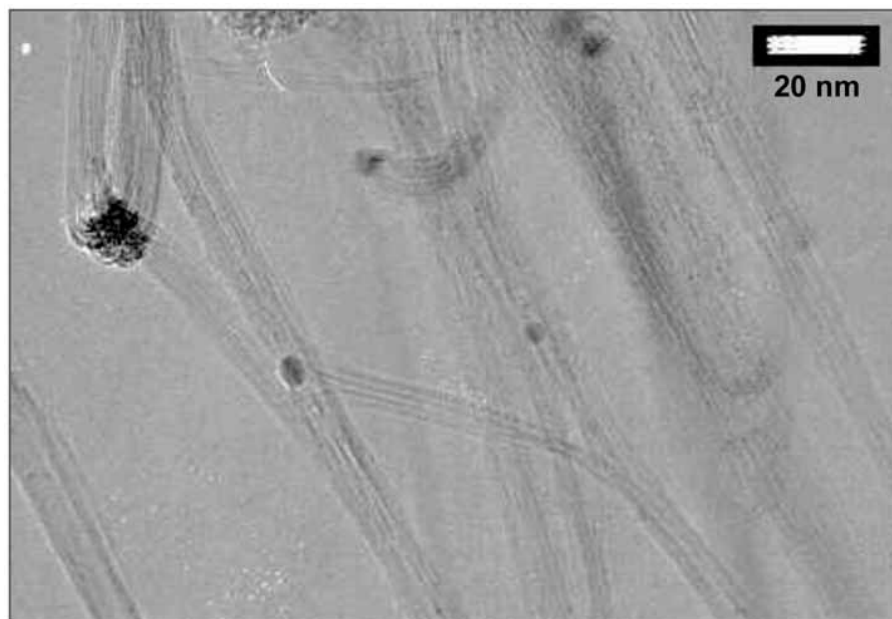


Figure 2. TEM photograph of SWNT produced by the CoMoCAT[®] process. Note the thin bundles that are produced by this method.

which there is no growth of nanotubes. This *in situ* nucleation involves the disruption of Co atoms from its interaction with Mo oxide when the latter becomes carbide. This disruption is followed by surface migration leading to agglomeration into mobile clusters that continue to grow under the bombardment of CO molecules. Some of these molecules decompose and begin to rearrange (nucleate) until a given configuration and carbon surface concentration are reached, which favor the formation of the tube. We propose to call this configuration *embryo*. When this embryo is formed, the subsequent incorporation of carbon and SWNT formation would proceed at a fast rate, perhaps controlled only by mass transfer. As a result, one may conclude that the growth of each tube is limited by nucleation, and after nucleation is completed, it is controlled by mass transfer. For this reason, we observe that the deposition of carbon on a solid catalyst continues for hours, although the growth of a single tube only takes milliseconds. The diameter of the tube is determined by the size of the embryo.

The investigation of different catalyst formulations was done in parallel with investigation of the optimal operating conditions. For example, since the CO disproportionation reaction is the exothermic Boudouard reaction: $2\text{CO}(\text{g}) \rightleftharpoons \text{C}(\text{SWNT})(\text{s}) + \text{CO}_2(\text{g})$, at the high temperatures needed to activate CO on the catalyst, it can be limited by equilibrium. Therefore, we found that high CO pressures are needed in order to counteract the effect of the temperature and drive the reaction in the forward direction. We demonstrated that, unless a high space velocity is used, the reaction can be inhibited in the catalyst bed by the CO_2 produced upstream in the reactor. High flow rates are also needed to avoid external diffusional effects in the catalyst particle. Both effects are more important during the first moments of the reaction when the catalyst is more active and the reaction rate is faster. By adjusting the space velocity, CO pressure, and temperature, we were able to produce SWNT at high yields.

The SWNTs grown by the CoMoCAT method remain mixed with the spent catalyst, which is composed of the silica support, and the Co and Mo species. We have developed an effective sequence of treatments that remove most of these impurities. The sequence starts with a basic attack in 2 M NaOH solution, which eliminates 99% of the SiO_2 , most of the Mo (>90%), and a significant fraction of Co (about 40%). After this treatment, the sample is further oxidized in air at

200–250°C, and finally attacked with an acid solution (nitric or HCl). The total removal of metals is about 95–99%.

Characteristics of SWNT produced by the CoMoCAT process

The SWNT were investigated by a number of techniques that included TEM, SEM, AFM, Raman spectroscopy, and temperature programmed oxidation (TPO). As illustrated in the TEM micrograph of Figure 2, the SWNTs produced by this method are very homogeneous and appear in bundles of only about 10–20 tubes each. This result was corroborated by AFM, which showed bundles with diameters significantly smaller than those from other SWNT products (Carboxlex, Rice, MER). The lower number of tubes per bundle produced in our catalytic method should have an advantage in dispersing the individual tubes. This dispersion may be a critical step in a number of applications, such as SWNT-reinforced composites, electronic nanoscale circuits, nanodevices, etc.

Raman spectroscopy is a powerful technique for the characterization of the structure of carbon nanotubes. It can provide information about the distribution of tube diameters from the analysis of the radial A_{1g} breathing mode frequency range (RBM) (Bandow et al., 1998). The RBM region can be used to analyze the diameter and helicity of SWNT, based on the relationship that exists between tube diameter and band position (Rao et al., 1997). For example, in Figure 3 we compare the RBM region of two Raman spectra that we have obtained on SWNTs produced by the HiPCO[®] and CoMoCAT[®] processes, respectively, using an excitation of 2.33 eV (532 nm). The material produced by the HiPCO[®] process yields a much larger number of bands, which indicate a greater variety of diameters than the material produced by our process. The distribution of diameters produced by the HiPCO process reported in the literature is also significantly broader than that of the product obtained from the CoMoCAT[®] process. The difference in diameter size distribution in the two methods can be rationalized in terms of the better control of metal cluster size that can be achieved when working with the catalyst in the solid state. Raman spectroscopy can also provide an indication of the level of disordered carbon in the sample. The size of the D-band relative to the tangential

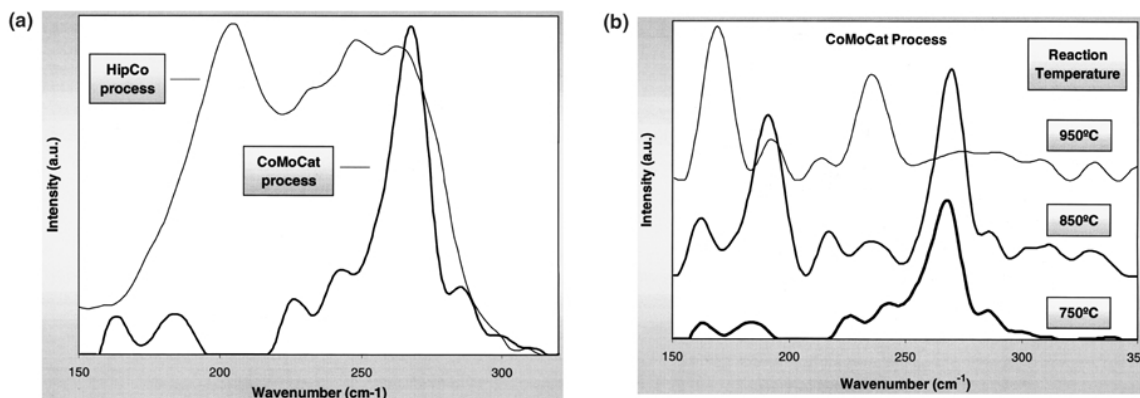


Figure 3. Comparison of Raman spectra obtained with an excitation laser of 532 nm. (a) SWNT produced by CoMoCAT process at 750°C (heavier line) and SWNT produced by HiPCO process (lighter line). (b) Comparison of spectra of SWNT produced by the CoMoCAT process at various reaction temperatures. Upper 950°C, Middle 850°C, Lower 750°C.

mode band is a qualitative measurement for the formation of undesired forms of carbon. We have made this analysis more quantitative by combining TEM, Raman, and TPO. TPO is a simple method to quantify the amount of SWNT because they burn in a relatively narrow temperature range, which lies below the temperature at which MWNT, graphite, and carbon fibers are burned and above the temperature at which amorphous and chemically impure carbon species are burned.

We have observed that when the catalytic synthesis of SWNT is conducted at higher temperature, that is 850°C or 950°C instead of 750°C, the distribution of diameters becomes broader. As illustrated in Figure 3, at higher temperatures the appearance new bands at lower frequencies correspond to the appearance of nanotubes of larger diameter. One possible explanation for this increase could be that as the temperature increases the rate of metal sintering increases, and as a result, there is a higher density of larger metal clusters on the catalyst surface. These larger clusters are in turn responsible for the formation of tubes of larger diameter.

Concluding remarks

The proposed catalytic process for production of SWNT can be scaled up, it operates at less severe conditions than other known processes, and exhibits

a promising control in the structural characteristics of the nanotubes. Because of the simplicity of the process and its similarity with standard catalytic processes employed in the chemical industry, the CoMoCAT process has the potential for production of SWNT at low cost.

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