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Synthesis of single-walled carbon nanotubes in vibrationally non-equilibrium carbon monoxide

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Abstract

Single-walled carbon nanotubes (SWNTs) are synthesized in a gas-phase non-equilibrium plasma process. The carbon producing CO disproportionation reaction is driven very efficiently in a flow reactor, in which extreme disequilibrium between the vibrational and translational mode of the carbon monoxide gas is maintained even at low translational temperatures by using a powerful and efficient carbon monoxide gas laser. In the presence of metal catalysts, the vibrationally excited CO reacts to form CO_2 and structured carbon molecules, notably SWNTs. The individual tubes form ropes or flat ribbons and these are aligned parallel to each other into larger structures of SWNT material without any post-synthesis treatment. © 2002 Published by Elsevier Science B.V.

1. Introduction

Since their discovery in the early 1990s [1,2], single-walled carbon nanotubes (SWNTs) have been a very active topic of study and many exciting new applications in nanotechnology and material science have been proposed. Controlled synthesis of SWNTs can contribute to the fundamental understanding of macromolecules and their organization. At present, several methods of producing SWNTs are being actively pursued in laboratories worldwide. Most of them are variations of three principal techniques: arc vaporization [2,3], laser vaporization [4], and chemical vapor deposition [5–8]. While each of these techniques can provide high-purity material, scaling to efficient, industrial quantity production of the pure material required for applications appears problematical. In this Letter, we present a novel method for the synthesis of SWNTs, which uses a thermally non-equilibrium flow reactor with extreme molecular vibrational mode disequilibrium of the primary feedstock, carbon monoxide (CO) gas. The vibrationally excited CO reacts in the presence of metal catalysts to form CO_2 and structured carbon molecules, notably SWNTs. This method is found

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to produce SWNTs in a continuous (non-batch) process.

Vibrationally non-equilibrium carbon monoxide is produced by initial resonance absorption of radiation from a continuous wave CO molecular gas laser into the lowest CO vibrational quantum states (v = 1 to $v \sim 10$). The vibrational mode energy is subsequently redistributed into higher vibrational levels by inelastic collisions among the CO molecules, so-called anharmonic vibration-tovibration (V–V) up-pumping, or 'Treanor pumping' [9]

$$\frac{\operatorname{CO}(v) + \operatorname{CO}(w) \to \operatorname{CO}(v-1) + \operatorname{CO}(w+1)}{v < w}$$
(1)

In Eq. (1) CO(v) and CO(w) represent carbon monoxide molecules in vibrational quantum states v and w. This approach produces, in the steady state, strong vibrational disequilibrium, resulting in population of high-vibrational states (up to v = 40), at high-gas densities and low translational temperatures. Optical pumping by a CO laser has been previously achieved in gas-phase carbon monoxide [10-16] at pressures of up to 20 atm [10], in gas-phase nitric oxide [17,18], in liquid-phase CO [19,20], and in solid CO and NO matrices [21,22]. Recently, optical pumping has also been demonstrated in mixtures of a few percent CO diluted by infrared inactive gases, such as nitrogen and air, at atmospheric pressure [23,24]. The reactor conditions, such as gas temperature, pressure, and composition, can be varied extensively while still maintaining a strong vibrational nonequilibrium.

The vibrationally excited CO created by the above process produces atomic carbon by the Boudouard disproportionation reaction:

$$CO(v) + CO(w) \rightarrow CO_2 + C$$

$$E_v + E_w \ge 5.5 \text{ eV}$$
(2)

Since the activation energy for this reaction is provided by the vibrational energy mode, the gas kinetic temperature does not determine the carbon production rate. Therefore, the temperature can be kept at a value most suitable for the formation of SWNTs from the carbon produced. Iron pentacarbonyl, $Fe(CO)_5$, and nickel tetracarbonyl, $Ni(CO)_4$, which decompose in the reactor and form small metal clusters, are used to nucleate the SWNT formation.

2. Experimental

The experimental setup is shown in Fig. 1. Initial excitation of the vibrational mode of carbon monoxide at room temperature is achieved with a CO laser operating on the lowest vibrational transitions of CO, at a wavelength of about 5 µm. The laser, designed and fabricated at Ohio State in collaboration with the University of Bonn [25], has a c.w. power output of 18 W with a multiline spectrum containing vibrational transitions $1 \rightarrow 0$ (\sim 300 mW) to 10 \rightarrow 9. The laser is focused into the reaction cell with a beam diameter of ~ 1 mm. The reaction cell is fabricated from Pyrex and equipped with ports providing access for various optical diagnostics and sampling assemblies. Windows at the tube ends, which are purged with argon to prevent build-up of carbonaceous deposits, provide the laser optical access into the apparatus. Carbon monoxide gas is introduced into the cell flowing at velocities of about .05 m/s. The total gas pressure is 100 Torr with equal amounts of CO and Ar. At these conditions, two thirds of the laser power is absorbed into the vibrational mode of CO.



Fig. 1. Experimental setup.

Gaseous metal carbonyls, $Fe(CO)_5$ and $Ni(CO)_4$, a few ppm of which are always present in commercial CO in steel cylinders [26] and nickelcontaining gas regulators, are used as catalyst precursors. Iron pentacarbonyl and nickel tetracarbonyl rapidly decompose at temperatures above 250 °C; in addition, several of the CO laser transitions present in the multiline laser spectrum are absorbed by the metal carbonyls, and therefore the decomposition of the carbonyls is enhanced by photodissociation. Organometallic catalyst precursors have been successfully used previously for the synthesis of SWNTs in gas-phase continuousflow techniques. Typically, a mixture of a carbon source gas, such as hydrocarbons [5,6], and an organometallic compound is reacted in a heated furnace, where the organometallics decompose and subsequently form metal clusters, on which the carbon nanotubes grow. Most closely related to this work, the Rice University Center for Nanoscale Science and Technology has demonstrated a high-pressure gas-phase synthesis of SWNTs in a thermal equilibrium reactor using CO feedstock and $Fe(CO)_5$ as the catalyst precursor [7].

A Bruker IFS66 Fourier transform spectrometer is employed to measure the spontaneous infrared emission from the laser excited CO, which is used to determine the non-equilibrium vibrational distribution function (VDF) present in the CO and to measure the rotational mode temperature [16]. At the reactor operating pressures, rotational and translational modes are equilibrated. The relative concentrations of the metal carbonyls were monitored in the exhaust line using FT-IR absorption spectroscopy. However, a calibration of the FT-IR absorption measurements for determination of absolute carbonyl concentrations has not been performed at this time.

3. Results and discussion

Fig. 2 shows the measured distribution of populations among the CO vibrational quantum levels, when the reactant is prepared in the manner described above. The measured VDF is compared with a thermal equilibrium distribution at 4100 K.



Fig. 2. Relative population distribution of vibrationally excited carbon monoxide: (•) denotes the measured non-equilibrium vibrational distribution; (_____) denotes a calculated Boltzmann distribution at 4100 K. The translational temperature is 1200 K.

The extreme departure from a thermal equilibrium (Boltzmann) distribution of vibrational level populations is evident. Vibrational levels extending as high as v = 30 are substantially populated; the energy of such levels is ~ 6.5 eV. The gas-phase activation energy of the CO disproportionation reaction is around 5.5 eV. Providing comparable population of these highly energetic states using thermal equilibrium excitation would require temperatures of about 10000 K. Since vibrational mode activation substantially contributes to establishing the reactive complex in the disproportionation, the vibrational excitation process strongly enhances the disproportionation reaction. The enhancement is large even for lower activation energies, such as the reported $\sim 4 \text{ eV}$ activation energy required to drive the reaction on an FeO catalytic surface [27], or on other catalytic surfaces.

In our synthesis reactor, the translational/rotational molecular modes remain in equilibrium at a relatively low temperature, 1200 K under the present conditions. The translational temperature in the excited CO can be controlled in steady state by conductive and flow-convective cooling of the reactor gases, as well as, in some cases, by adding a non-reactive diluent species (such as argon) to increase the heat capacity of the mixture.

For analysis by transmission electron microscopy (TEM), the carbonaceous products are collected on substrate surfaces, such as TEM grids or silicon wafers, at different locations in the reaction cell during runs of, typically, 10–90 min duration. High-resolution TEM has been performed using a Philips/FEI CM300 FEG STEM. Figs. 3–5 show transmission electron microscope images of the carbonaceous deposits produced using the nonequilibrium synthesis technique. The images are obtained from raw material that has been analyzed without any post-synthesis purification. Under these conditions, the products appear to be either



Fig. 3. High-resolution TEM image of a rope of SWNTs. Scale bar 10 nm. Note that the individual nanotubes have a diameter of 1.04 nm and align parallel into a cylindrical rope or flat ribbon.



Fig. 4. High-resolution TEM image of several ropes of SWNTs. Scale bar 10 nm. Note that the individual nanotubes end at a common edge.



Fig. 5. High-resolution TEM image of several ropes or ribbons of SWNTs aligned parallel to each other. Scale bar 10 nm.

flat ribbons or cylindrical ropes approximately 7– 15 nm wide consisting of closely packed SWNTs. The individual tubes within one rope appear to have the same diameter with diameters varying between 0.7 and 1.2 nm in different bundles. Remarkably, the individual tubes in these structures appear to cut off at a common edge (Figs. 3 and 4). This could be caused by either a fracture of a longer SWNT structure or it could be a feature of the SWNT formation mechanism in the nonequilibrium plasma. Typically, the ropes or ribbons appear to be in a length range of up to 0.5-1 µm. In some of the material samples, also the bundles are oriented in a preferred direction and line up parallel to each other (Fig. 5). This orientation of the ropes or ribbons as well as the alignment of the individual SWNTs into bundles with a common cut-off is possibly due to the interaction of the strongly polarizable SWNTs with the linearly polarized CO laser field during the growth process. This may present a relatively simple means for forming larger structures of aligned SWNT materials. Other methods for producing aligned arrays of SWNTs involve many steps for the production of suitable catalyst templates [28,29].

For the deposited material shown in Figs. 3-5, the purity of the SWNT material was estimated from TEM images to be on the order of 70%. However, purity levels were found to vary, and this is attributed to changes in the metal carbonyl concentrations in the CO feedstock. The natural abundance of $Fe(CO)_5$ in CO steel cylinders is known to vary significantly with cylinder gas pressure and temperature [26]. The same is true for $Ni(CO)_4$, which forms to some extent in nickel containing gas regulators. The results from Figs. 3–5 were obtained with a mixture of $Ni(CO)_4$ and $Fe(CO)_5$. Similar results were obtained with only nickel carbonyl precursor. From the currently available data we cannot conclude whether a mixture of $Ni(CO)_4$ and $Fe(CO)_5$ has any advantages over a pure $Ni(CO)_4$ catalyst precursor. Iron pentacarbonyl alone did not produce aligned SWNTs, instead only very few individual singlewalled nanotubes of about 1 nm diameter have been observed together with large amounts of amorphous carbon. These results are in contrast to the Rice University high-pressure gas-phase CO (HiPCO) process [7], which produces pure carbon nanotube material using Fe as the catalyst. However, other synthesis methods, particularly those relying on the presence of free carbon, such as laser ablation, have yielded best results using Ni or mixtures of Ni and other metals [30]. Multi-walled carbon nanotubes have yet to be detected in our experiments.

The material deposited in a two-hour run by a laser excited volume of about 1 cm³ was collected and weighed. This measurement gives a total deposition rate of 10-20 mg/h. It must be emphasized that the results shown in Figs. 3-5 were obtained with a CO partial pressure of 50 Torr. Nevertheless, the non-equilibrium vibrational up-pumping necessary to drive the nanotube synthesis process also has been demonstrated to occur at CO pressures in excess of one atmosphere [10]. Both the rate of the gas-phase CO disproportionation reaction and the laser power required to sustain the same level of vibrational non-equilibrium scale quadratically with CO pressure. Therefore, the vield of the disproportionation reaction scales linearly with the available laser power so that much higher throughputs can be achieved using a higher power laser to excite CO at high pressures. Highpower CO lasers have been demonstrated with c.w. powers of several hundred kW and efficiencies of 30% [31-33]. Consequently, the non-equilibrium CO disproportionation method should be scalable to large quantity production of SWNTs.

The overall energy efficiency of the laser-induced non-equilibrium SWNT synthesis process based on the CO disproportionation reaction critically depends on the fraction of energy going into carbon production by this reaction that subsequently forms carbon nanotubes in the presence of metal catalyst. This fraction may well depend on a number of process parameters such as temperature, pressure, catalyst partial pressure, etc. Further studies of the SWNT synthesis process in optically pumped CO plasmas are needed to provide insight into this critical issue. The non-equilibrium SWNT synthesis technique reported here enables mechanistic studies of the processes involved in nanotube formation, since the synthesis reactor is equipped with optical access ports into the reaction volume and process parameters, most notably the gas temperature, can be varied over a wide range. This technique for the synthesis of SWNTs represents a new type of laser induced mode selective chemistry in collision-dominated environments.

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