

# ACTIVATED-HYDROGEN REACTOR FOR SYNTHESIS OF CARBON NANOTUBES

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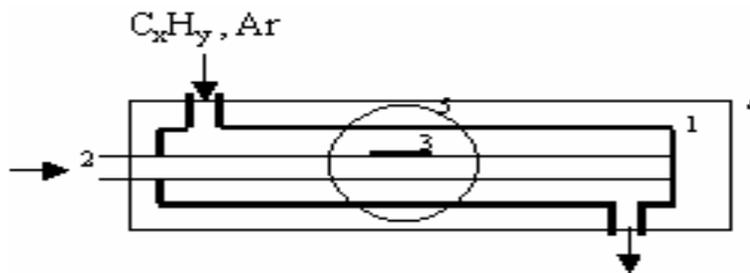
## Abstract

Activated-hydrogen reactor for synthesis of carbon nanostructures is proposed and implemented. Hydrogen activation is initiated by diffusion of molecular H<sub>2</sub> through the heated metallic Ni substrate. The conditions of pyrolysis deposition on Ni and some others substrates are investigated and some region for stable synthesis or production of multilayer carbon nanotubes and nanofibers is defined. The role of activated hydrogen in this reactor is analysed and discussed.

The development of reliable and low-cost methods for synthesizing of carbon nanotubes (CNTs) with desired properties is the main challenge making difficult their wide application. The structure of pyrolytic CNTs, i.e., those prepared by depositing the material from the gas phase via thermochemical decomposition, is known to substantially depend on a variety of process parameters, such as pressure, temperature, flow rate, buffer gas composition, carbon source, structure and parameters of catalysts, and so on. The special need for studying the role of hydrogen in such processes stems from the fact that it is one of pyrolysis products when CNTs are synthesized from hydrocarbons and is always present in the reactor. Moreover, hydrogen is often deliberately introduced into the reactor as an admixture to a buffer gas. Sometimes, hydrogen is used at various stages of synthesis for catalyst annealing and activation or applied directly as a buffer gas.

Although the effect of hydrogen on the end products of CNT synthesis has been extensively explored, this issue remains to be a subject of hot discussion. On the one hand, many argue that hydrogen suppresses amorphous carbon release during CNT growth and, thus, decreases the contamination of the end product. In particular, it has been noticed that the addition of hydrogen activates synthesis through the reduction of oxides and hydrogenation of amorphous carbon deposits on catalyst particles (Ivanov, 1994). On the other hand, some of the researchers assume that hydrogen introduced into the reactor limits the growth of single-wall nanotubes, e.g., saturating dangling carbon bonds (which favors the growth of open structures, such as carbon fibers or fragments of graphite planes, Nolar, 1995), or facilitates the growth of coarser structures, slowing down the synthesis (Resasco, 2004). Hydrogen present in the reactor may sometimes result in the formation of *sp*<sup>3</sup>-hybridized carbon atoms (like in diamond, Sun, 2004), while *sp*<sup>2</sup>-hybridized atoms are necessary for CNT synthesis. Actually, whether or not its addition is appropriate to a great extent depends on the way of its introduction into the reactor and on synthesis parameters. This issue is of undeniable interest, especially when we deal with activated atomic hydrogen.

In this work, we propose a pyrolytic reactor for CNT synthesis with external submission of hydrogen that is based on the unique ability of molecular hydrogen to readily penetrate through an incandescent metallic wall, dissociate into atoms, and then diffuse from a region where its pressure is high to a low-pressure region (diffusing through metallic wall, or DMW-hydrogen). In this reactor, the hydrogen concentration may be controlled over a wide range by varying the partition temperature and/or pressure drop. Under these conditions, the DMW-hydrogen concentration becomes an "independent" parameter of pyrolysis, since, as hydrogen is delivered or evacuated through the partition, other CNT synthesis parameters and the concentration of other reagents remain the same. Using this specific feature, one can study the "pure" effect of hydrogen on the growth of carbon nanostructures under various conditions by varying carbon sources, buffer gases and catalysts, and temperature-related and other parameters.



**Figure. I.** Schematic of the reactor for pyrolytic deposition of carbon nanostructures with DMW-hydrogen.

Figure I shows the schematic of the reactor used for pyrolytic CNT synthesis. Quartz tube 1 contained thin-walled resistively heated nickel tube 2, to which hydrogen is delivered under an excess pressure. A carbon source

$C_xH_y$  hydrocarbon mixed with a buffer gas (Ar), was delivered to tube 1 at a controllable flow rate and pressure. Substrates 3 were fixed on the surface of tube 2. In experiments, precursors of various catalysts were applied onto substrates 3. The entire system was placed in cooled metallic sheath 4 with round window 5, through which the nickel tube and substrate could be observed. Tube 2 heated to 700-1000°C (the temperature of the tube was controlled by changing the current passing through it) served to deliver (evacuate) the hydrogen, which leaks through the incandescent tube wall. The heat released by the nickel tube could be used for heating the substrate, hydrocarbon, and buffer gas. The temperatures of the tube and substrate surface were monitored through window 5 with an optical pyrometer. Note that, unlike in the standard CVD technique, in our experiments, the outer sheath of the steel-made reactor is cooled by water. Accordingly, the reactor had "cool" walls and so the temperature of tube 1 depended on the temperature of the inner nickel tube.

In common with the standard hot-wall CVD reactor, our reactor makes it possible to simulate various approaches to and conditions for synthesis of carbon nanostructures by varying the composition, pressure, and leakage rate of entering gases; substrate materials; catalysts; and temperature conditions. One can both apply catalysts on the substrate and deliver catalyst precursors in the gaseous phase (e.g., in a mixture with a hydrocarbon). If a substrate is used, carbon nanostructures are, as a rule, synthesized on its surface facing the nickel tube placed in the immediate vicinity. In such a scheme, the tube heats the substrate and also serves as a source of activated hydrogen, which can migrate from the incandescent wall of the tube toward the substrate and to the carbon structures being synthesized on it.<sup>1</sup>

Importantly, nickel tube 1 can be used both for supplying hydrogen (by producing an excess pressure in it) and for removing it (when the tube is evacuated). In the latter case, we are dealing with the reverse effect: the hydrogen being released as a synthesis product is removed from the reaction zone, which shifts the dynamic equilibrium of the pyrolysis reaction toward carbon deposition.

Below, we demonstrate the scope of our reactor. Acetylene was used as a carbon source, and synthesis was performed both on the surface of the nickel tube and on various substrates covered by catalyst precursors, which were fixed on the tube surface prior to the experiment. As substrates, we used pure polycrystalline carbon, fused silica plates, sapphire plates, and fragments of silicon wafers; as catalyst precursors, cobalt acetate and ferrocene.

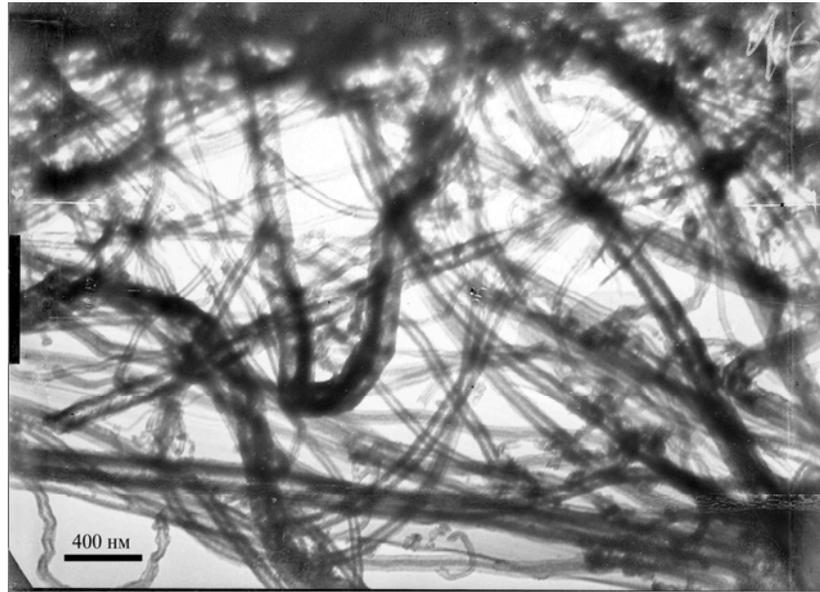
Analysis of the reaction products synthesized at a tube temperature of 700-1000°C showed that the basic ones are nanocarbon fibers 50-200 nm in diameter and several tens of microns long. These fibers have the form of curved rods without signs of a hollow inside, as is clearly seen under a transmission electron microscope (TEM). Such fibers were formed in the absence of catalysts and substrates: they were synthesized directly on the nickel tube. Sometimes, the synthesis products also contain a minor amount of multiwall nanotubes (MWNTs) 50-100 nm in diameter and several microns long. The optimization of the CNT synthesis conditions, which generally is a challenge, allowed us to increase the yield of MWNTs to 50-70%. Below, we describe one of the most successful processes.

The substrate used was a fused silica plate with several drops of a 0.4% water solution of cobalt acetate on its surface. After the plate has been dried in air, it was placed in a furnace, where it was annealed in air at 400°C for 10 min, and then fixed to the outer surface of the tube heated to 700°C in argon. Next, hydrogen was delivered to the nickel tube at a pressure of 4 atm and leaked through the incandescent tube wall. The hydrogen pressure inside the quartz tube was increased at a rate of about 0.01 atm/min. A catalyst precursor was applied on the surface adjacent to the nickel tube, so that the hydrogen leaving this tube hit the catalyst surface. After the plate had been annealed in argon and hydrogen for 10 min, an argon-acetylene (Ar :  $C_2H_2$  = 10 : 1) mixture at a pressure of 0.2 atm entered into the quartz tube and the nickel tube temperature was simultaneously raised to 900°C. The synthesis lasted 3 min; then, the gas was pumped out of the quartz tube and the nickel tube temperature was decreased to room temperature.

The deposits on the inner (facing the nickel tube) side of the substrate were studied by Raman spectroscopy and also under scanning and transmission electron microscopes. The Raman spectra did not reveal SWNTs; however, whether MWNTs are present in the deposits remained unclear. The resolution of the scanning electron microscope at hand was also too low to unambiguously characterize these nanostructures: we distinctly observed only large-scale features, such as nanofibers more than 50 nm in diameter, and failed to look into their fine structure. However, we succeeded in detecting MWNTs with the TEM (Fig. 2).

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<sup>1</sup> The use of activated hydrogen has been considered in some recent works (Lueking, 2004; Zacharia, 2005), where the effect of hydrogen spillover on filling of carbon nanotubes with hydrogen was studied.



**Figure. 2.** TEM micrograph of a sample with carbon nanotubes.

The sample shown in Fig. 2 was synthesized on that surface of the substrate facing the nickel tube. It represents of a tangle of rods and tubes. The rods are seen to be heavily twisted and curved. The tubes are both curved and straight. The latter are more than 10  $\mu\text{m}$  long and 9-100 nm in diameter. The amount of tubes 9 nm in diameter reaches 1% at most: the majority of the CNTs have a diameter of 30-60 nm.

As in the example shown in Fig. 2, the products of pyrolysis carried out under optimal conditions on substrates with traces of cobalt acetate contain MWNTs in an amount from 50 to 70%. Under off-optimum conditions, the content of nanofibers and amorphous carbon in the pyrolysis products increased. At low temperatures, the fibers grew thick and were heavily contaminated by amorphous carbon islands and soot particles.

Thus, we developed an appropriate method for an efficient pyrolysis reactor with DMW-hydrogen and found conditions providing reproducible and stable synthesis of multiwall carbon nanotubes with a fairly high yield. It is expected that the yield of single-wall nanotubes will also be substantially improved in the immediate future by adequately choosing catalysts consisting of metallic nanoparticles, as well as by modifying the gas phase composition and conditions of gas phase delivery. With this reactor, one can perform detailed study of the effect hydrogen has on the CNT growth parameters and estimate the feasibility of filling nanotubes with hydrogen using the spillover effect.

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