Fig. 4. STM image of helically-arranged fullerenes on the nanotube outer wall (scanned area =10 nm x 10 nm).

growth. It is known that both metal and carbon atoms are crucial for tube production [2]. In the usual arc-discharge method tube growth is initiated by submicron-sized catalytic metal particles [16] and, in the catalytic method, free carbon atoms aggregate around metal particles and start to grow with a neddlelike structure [4]. In our experiment, metal and free carbon atoms could be provided as follows: on its way to the substrate, sublimated $Nd@C_{82}$ has to pass through the filament coils whose temperature is up to $1500^{\circ}C$ during evaporation. Some molecules of $Nd@C_{82}$ have a chance to collide with the hot filament and may be broken up to produce metal and free carbon atoms for the tube growth. This interpretation is supported by the absence of nanotubes when the hot filament coils were shielded.

Unlike transmission electron microscopy (TEM), STM cannot reveal the inner structure of nanotubes. It is not clear whether the tube we measured is a single-layer tube or a multi-layer tube, or whether it is a hollow tube or there are metal atoms caged inside. These

uncertainties prevent us from identifying which parts contribute to the metallic nature of the tube.

In summary, we have successfully grown isolated nanotubes for STM study whose surface structure and electronic properties have been analyzed. The tube surface was found to be identical to that of graphite but with a chiral angle of $6.4 \pm 0.5^{\circ}$. The index of helical structure of the tube has been deduced and the tube has been found to be metallic. Also, we have observed a helical arrangement of fullerenes on the outer wall of the nanotube.

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Production of activated carbons: use of CO₂ versus H₂O as activating agent

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Activated carbons have important commercial uses for the removal of organic molecules from air and water streams. Removal is accomplished as a result of attractive interaction of the molecules with walls of micropores having dimensions comparable to those of the molecules. The extent of interaction depends upon the volume of micropores and their size distribution between about 0.4 and 2.0 nm.

An activated carbon is usually produced by the partial gasification of a microporous char in CO_2 and/or

H_2O. This gasification, resulting in the removal of carbon atoms, initially increases the number of open micropores and their size. At some point in the gasification process, pore walls begin to be broken through. The number of pores and the micropore surface area go through maxima.
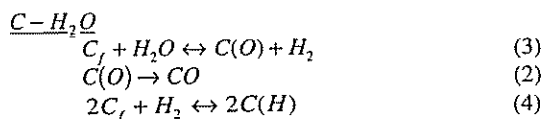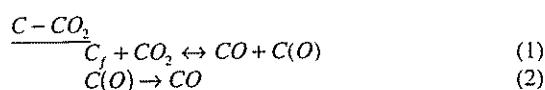
The volume of micropores and their size distribution produced as a result of activation to a particular carbon burn-off will depend upon a number of variables including: character of starting carbonaceous

precursor, activating gas, rate of gasification, rate of diffusion of activating gas(es) into and product gas(es) out of carbon sample, extent of product inhibition of the gasification rate, amount and nature of inorganic impurities in char, and amount and nature of oxygen surface complexes present following gasification.

The Spanish school at Alicante has been particularly interested in comparing the virtues of CO_2 and H_2O as activating agents [1, 2]. In their first paper, petroleum pitch-based activated carbon fibers were prepared by their gasification in either 0.1 MPa CO_2 or 0.05 MPa H_2O at 1160 K. The gasification rate in H_2O (up to 50% carbon burn-off) was about two times faster than that in CO_2. Activated carbons prepared by CO_2 gasification exhibited a larger micropore volume and a narrower micropore size distribution than those prepared from H_2O activation [1]. Also, CO_2 activation led to a smaller decrease in fiber diameter than that found following H_2O activation [1]. Similar experimental results were found in reference [2] for development of microporosity upon activation of olive stones. Alcañiz-Monge, et al. [1] attribute the enhanced development of microporosity when using CO_2 to its more uniform gasification rate in the radial direction of the carbon fiber than that found when using H_2O. They consider two possible explanations for differences in the uniformity of reaction in the carbon fiber: (i) differences in the extent of product inhibition in the C-CO_2 and C-H_2O reactions and (ii) differences in diffusion coefficients of H_2O and CO_2 within the carbon fibers. They discard the first explanation, saying that even though the C-H_2O and C-CO_2 reactions are severely limited by product H_2 and CO, respectively, differences in the inhibiting effect would not justify the differences noted. Rather they accept the second explanation for the greater uniformity of gasification in CO_2, that is a much greater diffusion coefficient for CO_2 than for H_2O.

We do not agree that the findings of Alcañiz-Monge, et al. [1] can be attributed to CO_2 having a much greater diffusion coefficient than H_2O. To the contrary, Koresh and Soffer, from their studies on diffusion in molecular sieve carbons, conclude that H_2O has a smaller critical molecular dimension than does CO_2 [3]. Thus, activated (or configurational) diffusion of H_2O would be larger than that for CO_2. As activation (gasification) proceeds, resulting in pore enlargement, and diffusion changes from activated to Knudsen, again H_2O is expected to have a higher diffusion coefficient because of its lower molecular weight compared to CO_2 [4].

We attribute differences in activation results for CO_2 and H_2O primarily to two explanations. The simplest, and most direct explanation, is that activation (gasification) in CO_2 proceeded at a less rapid rate than that in H_2O (see Figure 1 in reference [1] and reference [5]). The second explanation is explanation (i) above. Consider it in more detail. The C-CO_2 and C-H_2O reactions can be described as follows [5]:

$C - CO_2$
$$C_f + CO_2 \leftrightarrow CO + C(O) \tag{1}$$
$$C(O) \rightarrow CO \tag{2}$$

$C - H_2O$
$$C_f + H_2O \leftrightarrow C(O) + H_2 \tag{3}$$
$$C(O) \rightarrow CO \tag{2}$$
$$2C_f + H_2 \leftrightarrow 2C(H) \tag{4}$$

where C_f is a carbon-free active site, $C(O)$ is oxygen surface complex, and $C(H)$ is chemisorbed hydrogen. Carbon monoxide inhibits the C-CO_2 reaction by removal of oxygen complex from the carbon surface (described by reverse eqn. (1)). Hydrogen inhibits the C-H_2O reaction both by removal of oxygen complex from the carbon surface (reverse eqn. (3)) and by dissociative chemisorption of H_2 on the carbon surface (forward eqn. (4)).

Austin and Walker [6] have shown, both experimentally and theoretically, that the build-up of small concentrations of CO can lead to non-uniformity of carbon gasification in CO_2 at gasification rates where the assumption that the reaction is of integer order (negligible retardation by CO) would lead to uniform gasification. Using Langmuir-Hinshelwood kinetics, the steady state rate of the C-CO_2 reaction is given by

$$Rate_{C-CO_2} = \frac{k_1 p_{CO_2}}{1 + k_2 p_{CO} + k_3 p_{CO_2}}$$

if the reaction is described by eqns. (1) and (2) above [5, 7].

For the C-H_2O reaction, workers find that inhibition by H_2 is caused overwhelmingly by dissociative chemisorption of H_2 onto carbon-free active sites and not by the reverse of eqn. (3) above [8-10]. Under these conditions, the rate of gasification in H_2O is given by

$$Rate_{C-H_2O} = \frac{k_1 p_{H_2O}}{1 + k_2 p_{H_2}^{1/2} + k_3 p_{H_2O}}$$

To compare the extent of inhibition by CO for the C-CO_2 reaction with that by H_2 for the C-H_2O reaction, k_2's for the two reactions need to be compared. This was done by Biederman, et al. in our laboratory as follows [11]. The gasification of a high purity natural graphite was studied at temperatures between 1233 K and 1393 K at CO_2 pressures below 108 millitorr. For CO_2 depletion up to at least 90%, in a batch reactor, gasification rates were first order in CO_2 pressure with no inhibition by product CO observed. Now, consider a run at 1373 K in which a pressure of H_2 was injected into the gaseous mix following depletion of about 50% of the CO_2 (Figure 1). At the time of injection of about 32 millitorr H_2, the CO_2 pressure had fallen from about 65 to 31 millitorr; and the CO pressure had built up to about 68 millitorr. The reaction rate abruptly decreased, with a first order reaction again observed. The rate constant decreased from a starting value of about 670 units to about 54 units. That is H_2 is a much stronger inhibitor than is CO, or $k_{2,H_2} \gg k_{2,CO}$.

If inhibition by H_2 is attributed to its dissociative chemisorption onto carbon-free active sites, the rate constant, k_{2,H_2}, will equal the equilibrium constant, K, for eqn. (4) above. Biederman, et al. [11] confirmed this to be the case. The adsorption isotherm of H_2 on their graphite sample was measured at 1373 K, from which K was determined. The equilibrium constant was also calculated from the equation

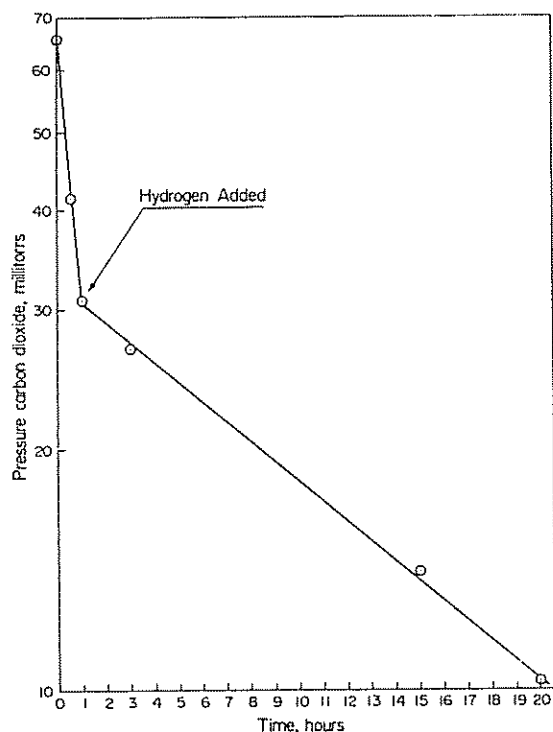$$Rate_{C-CO_2} = \frac{k_1 p_{CO_2}}{1 + K p_{H_2}^{1/2}}$$

Fig. 1. Effect of addition of 32 millitorr of H_2 on the rate of the C-CO_2 reaction at 1373 K [11].

Close agreement of equilibrium constant values was found [11].

In conclusion, H_2 is a much stronger inhibitor of the C-H_2O reaction than is CO for the C-CO_2 reaction. Therefore, H_2 is expected to cause greater non-uniformity of gasification in the C-H_2O reaction than is CO in the C-CO_2 reaction. To achieve greater uniformity of carbon gasification in the particle or fiber radial direction, it is clear that sufficient inhibitor, CO or H_2, needs to be added to the original reaction mixture to swamp out the effect of inhibitor concentration produced during carbon gasification. This would be expected to lead to improved uniformity of carbon gasification and superior development of microporosity.

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Liquid fluidized bed coating process

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A new type of fluidized bed, chemical vapor deposition (CVD) coating process is proposed. Instead of using conventional gaseous reagents, the articles to be coated are immersed in a liquid reagent and, unlike current liquid CVD coating processes, are fluidized. The substrate articles are heated inductively and become coated since they are surrounded by a region of vaporized reagent. The process should be applicable to the coating of particles, chopped fibers or whiskers, or larger articles such as components for mechanical heart valves or other prostheses.

Previously, gaseous fluidized bed coating processes have been used extensively to coat nuclear fuel microspheres [1], nuclear waste [2], and larger articles such as heart valve components [3]. Typically, a particulate fluidized bed is established inside a CVD coating furnace by the upward flow of a gas stream containing the CVD reagent and perhaps hydrogen or an inert gas such as helium or argon. The gas stream serves to fluidize and mix the particle bed. The desired product may be the coated particles or larger parts contained within the particle bed. A disadvantage of the process is that it is not easily scaled to large sizes since particle circulation and coating uniformity are not as good for

large size reactors. Other disadvantages are that the reagents must be metered accurately and the walls of the reactor become coated and require frequent cleaning and replacement.

The new liquid reagent process offers the promise of overcoming these disadvantages. Non-fluidized-bed liquid reagent CVD coating processes have been used previously. Basche and Fanti [4] coated continuous fibers of carbon, tungsten, tantalum, and stainless steel with crystalline SiC by heating them to 900-1500°C while immersed in liquid methyldichlorosilane. Very high coating rates of up to 1000 μm/min were achieved. They suggested that other silanes including methyltrichlorosilane could be used as the liquid reagent. Houdayer et al. [5] and Thurston et al. [6] have performed chemical vapor infiltration (CVI) of carbon using liquid cyclohexane as the reagent. Mixtures of cyclohexane and methyltrichlorosilane have been used to deposit a matrix consisting of a two phase mixture of carbon and SiC.

The proposed new fluidized bed process is shown schematically in Figure 1. The articles to be coated are immersed in the liquid reagent which is contained by the reactor vessel. Depending on whether the vessel is an electrical insulator or conductor, an induction coil is located outside or inside the vessel. The articles to be coated must have a sufficiently high electrical conductivity to permit their being heated inductively. Alternatively, it might be possible to use microwave or other heating methods. The heated articles vaporize the immediately adjacent liquid reagent resulting in deposition of a coating via CVD. The liquid reagent might be circulated, as shown in the figure, to permit cooling, addition of reagent, removal of any particulate coating debris, and to provide a liquid stream to effect fluidization and mixing of the bed. Cooling of the

reactor vessel and a reflux condenser could be used to minimize global heating of the reagent and loss of reagent vapor.

If the desired product is particles, chopped fibers, or whiskers, these materials, and perhaps some other "mixing" articles, would be immersed in the liquid reagent. When it is desired to coat larger articles they would be immersed in the liquid, either alone or with particles or other mixing articles. The fluidization of particles in a liquid is a well developed technology [7]. If the particles and mixing articles were made of a material that is an electrical insulator they would not be heated and therefore would not become coated. Therefore they could be reused. A mechanical agitator or auger could also be used since, if made of an insulator, it would not overheat or become coated.

Mechanical heart valves are typically made by coating graphite substrates with a mixture of carbon and SiC by immersing them in a particulate, gaseous, fluidized bed. The particles become coated and their purchase and disposal contribute to the manufacturing cost. This cost should be avoided with the new process since particles may not be needed and, if they are required, they will not become coated if they are made of glass, Al_2O_3, or other insulators.

Fluidization and circulation of larger parts may be simplified by use of a liquid rather than a gaseous bed because of the added buoyancy provided by the liquid. This may permit the coating of larger parts and more parts per reactor than currently possible with conventional fluidized bed coating processes. Use of more parts per reactor will also likely be possible if it can be shown that it is not necessary to add particles to the bed, i.e., use of only the large parts. A further advantage of the liquid process when coating very small particles or fibers is that they should be less likely to become lost by entrainment in the exhaust gas stream. Higher coating rates might also be possible compared to the conventional gaseous fluidized bed process since an abundance of reagent is in close proximity to the substrate.
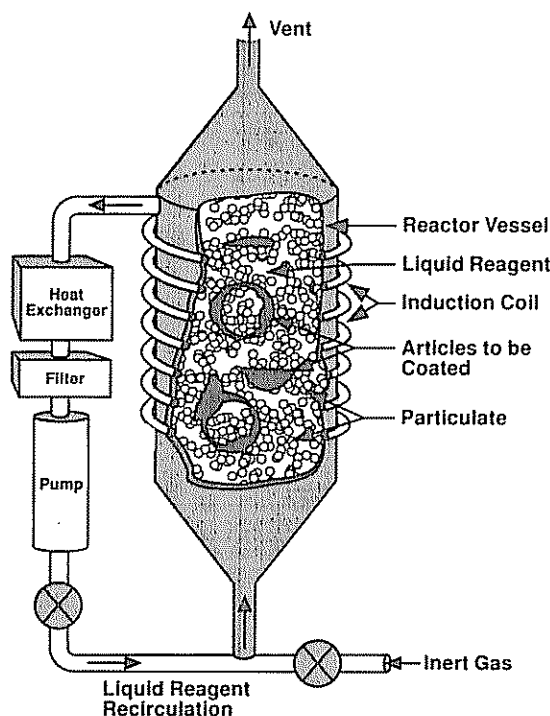

Fig.1. Schematic of the liquid reagent fluidized bed coating process.

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