## Low-Temperature Plasma Functionalization of Carbon Nanotubes

## This process is dry, clean, and relatively simple.

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A low-temperature plasma process has been devised for attaching specified molecular groups to carbon nanotubes in order to impart desired chemical and/or physical properties to the nanotubes for specific applications. Unlike carbon-nanotube-functionalization processes reported heretofore, this process does not involve the use of wet chemicals, does not involve exposure of the nanotubes to high temperatures, and generates very little chemical residue. In addition, this process can be carried out in a relatively simple apparatus and can readily be scaled up to mass production.

The apparatus used in this process includes two vacuum chambers, denoted the target chamber and the precursor chamber. A plasma of the chemical precursor of the molecular groups to be deposited is generated in the precursor chamber. The plasma flows from the precursor chamber to the target chamber, wherein the carbon nanotubes to be functionalized are mounted on a substrate.

The process is best described by use of an example of functionalizing carbon nanotubes with hydrogen atoms. The precursor chamber is backfilled with high-purity (99.9999 percent or greater) H<sub>2</sub> gas, optionally mixed with an inert carrier gas (N<sub>2</sub>, Ne, or Ar), to a total gas pressure between 0.1 and 1 mm of Hg (between about 13 and about 130 Pa). The gas is irradiated with microwaves, thereby generating free electrons and a partially ionized gas that includes free radicals (in particular, monatomic hydrogen). Instead of a microwave source, a DC, non-microwave-radio-frequency, inductive-discharge, or electron-cyclotron-resonance source can also be used to generate the plasma. The tem-



A **Hydrogen Plasma** is generated in the precursor chamber and flows into the target chamber, where hydrogen atoms become chemically bonded to the carbon nanotubes.

perature of the free electrons is typically of the order of a few electron volts (1 eV = 11,604 K). The temperature of the partially ionized gas typically lies in the approximate range from 350 to 1,000 K.

The two chambers are connected by a curved tube or plug made of polytetrafluoroethylene or other suitable material. Typically, the tube or plug has an inner diameter of about 1 mm, an outer diameter of between 5 and 25 mm, and a length between 5 and 25 mm. The substrate holding the carbon nanotubes is positioned to face directly into the plasma flowing into the target chamber through the hole in the tube or plug.

The tube or plug is curved to eliminate a direct line of sight between the interiors of the chambers in order to prevent ultraviolet light originating in the precursor chamber from reaching the carbon nanotubes. This is necessary for the following reasons: Some ultraviolet radiation is generated in the undesired but unavoidable recombination of some of the monatomic hydrogen into  $H_2$ molecules. This radiation is capable of breaking the C–H bonds in hydrogenated materials, including hydrogenated carbon nanotubes. Other ultraviolet radiation generated in the precursor chamber may be capable of breaking C–C bonds in the nanotubes.

There is no need to maintain the temperature in the target chamber at any particular value in order to achieve functionalization. Experiments have shown that carbon nanotubes can be functionalized with hydrogen to the point of saturation in a process time of about 30 seconds, at or below room temperature. It is also possible to functionalize carbon nanotubes with molecular groups other than hydrogen. For example, by choosing a suitable precursor, one could attach halogen or alkali metal atoms or low-molecular weight hydrocarbons.

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