Cleaning Carbon Nanotubes by Use of Mild Oxygen Plasmas

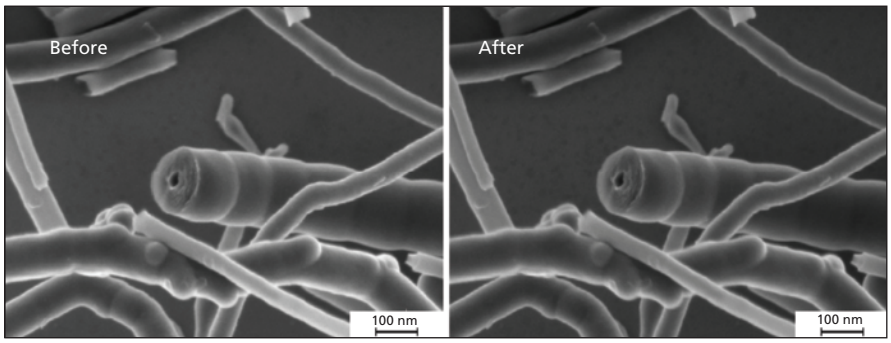
Mildness of the plasmas is the key to cleaning without destruction.

NASA's Jet Propulsion Laboratory, Pasadena, California

Experiments have shown that it is feasible to use oxygen radicals (specifically, monatomic oxygen) from mild oxygen plasmas to remove organic contaminants and chemical fabrication residues from the surfaces of carbon nanotubes (CNTs) and metal/CNT interfaces. A capability for such cleaning is essential to the manufacture of reproducible CNT-based electronic devices.

The use of oxygen radicals to clean surfaces of other materials is fairly well established. However, previously, cleaning of CNTs and of graphite by use of oxygen plasmas had not been attempted because both of these forms of carbon were known to be vulnerable to destruction by oxygen plasmas. The key to success of the present technique is, apparently, to ensure that the plasma is mild — that is to say, that the kinetic and internal energies of the oxygen radicals in the plasma are as low as possible.

The plasma oxygen-radical source used in the experiments was a commercial one marketed for use in removing hydrocarbons and other organic contaminants from vacuum systems and from electron microscopes and other objects placed inside vacuum systems. In use, the source is installed in a vacuum system and air is leaked into the system at such a rate as to maintain a background pressure of ≈0.56 torr (≈75 Pa). In the source, oxygen from the air is decomposed into monatomic oxygen by radio-frequency excitation of a resonance of the O_2 molecule (N_2 is not affected). Hence, what is produced is a mild (non-energetic) oxygen plasma. The oxygen radicals are transported along with the air molecules in the flow created by the vacuum pump.



These **SEM Images of CNTs** were taken before and after cleaning in a mild oxygen plasma. Unlike an oxygen plasma of the type used in dry etching, this plasma seems not to have damaged the CNTs.

In the experiments, exposure to the oxygen plasma in this system was shown to remove organic contaminants and chemical fabrication residues from several specimens. Many high-magnification scanning electron microscope (SEM) images of CNTs were taken before and after exposure to the oxygen plasma. As in the example shown in the figure, none of these images showed evidence of degradation of CNT structures.

This work was done by Mihail Petkov of Caltech for **NASA's Jet Propulsion Laboratory**. *Further information is contained in a TSP (see page 1).*

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Generating Aromatics From CO_2 on Mars or Natural Gas on Earth

The terrestrial version may make it economical to recover some natural-gas deposits.

John F. Kennedy Space Center, Florida

"Methane to aromatics on Mars" ("METAMARS") is the name of a process originally intended as a means of converting Martian atmospheric carbon dioxide to aromatic hydrocarbons and oxygen, which would be used as propellants for spacecraft to return to Earth. The process has been demonstrated on Earth on a laboratory scale. A truncated version of the process could be used on Earth to convert natural gas to aromatic hydrocarbon liquids. The greater (relative to natural gas) density of aromatic hydrocarbon liquids makes it more economically feasible to ship them to distant markets. Hence, this process makes it feasible to exploit some reserves of natural gas that, heretofore, have been considered as being "stranded" too far from markets to be of economic value.

In the full version of METAMARS, carbon dioxide is frozen out of the atmosphere and fed to a Sabatier reactor along with hydrogen (which, on Mars, would have been brought from Earth). In the Sabatier reactor, these feedstocks are converted to methane and water. The water is condensed and electrolyzed to oxygen (which is liquefied) and hydrogen (which is recycled to the Sabatier reactor). The methane is sent to an aromatization reactor, wherein, over a molybdenum-on-zeolite catalyst at a temperature 700 °C, it is partially converted

into aromatic hydrocarbons (specifically, benzene, toluene, and naphthalene) along with hydrogen.

The aromatics are collected by freezing, while unreacted methane and hydrogen are separated by a membrane. Most of the hydrogen is recycled to the Sabatier reactor, while the methane and a small portion of the hydrogen are recycled to the aromatization reactor. The partial recycle of hydrogen to the aromatization reactor greatly increases the catalyst lifetime and eases its regeneration by preventing the formation of graphitic carbon, which could damage the catalyst. (Moreover, if graphitic carbon were allowed to form, it would be necessary to use oxygen to remove it.) Because the aromatics contain only one hydrogen atom per carbon atom, METAMARS produces four times as much propellant from a given amount of hydrogen as does a related process that includes the Sabatier reaction and electrolysis but not aromatization.

In the terrestrial version of METAMARS, the Sabatier reactor and electrolyzer would be omitted, while the hydrogen/ methane membrane-separating membrane, the aromatization reactor, and the unreacted-gas-recycling subsystem would be retained. Natural gas would be fed directly to the aromatization reactor. Because natural gas consists of higher hydrocarbons in addition to methane, the aromatization subprocess should be more efficient than it is for methane alone.

This work was done by Anthony C. Muscatello, Robert Zubrin, and Mark Berggren of Pioneer Astronautics for **Kennedy Space Center**. *For further information, contact the Kennedy Innovative Partnerships Office at (321) 867-1463.*
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