Carbon Nanohorns Made Soluble through Covalent Chemical Modification

Laser ablation of graphite produces carbon nanohorns (CNHs) in high yield. CNHs not only differ from single-walled carbon nanotubes (CNTs) in their shape; CNHs are free from impurities and do not require purification that results in degradation and reduced mechanical and electronic properties. Like CNTs, however, CNHs are completely insoluble in organic solvents and in aqueous media. Recently, N. Tagmatarchis and graduate student G. Pagona at the National Hellenic Research Foundation in Athens, Greece, together with J. Fan and co-researchers from the Japan Science and Technology Agency and NEC Corp., both in Ibaraki, Japan, functionalized CNHs, making them soluble.

As reported in a communication published in the August 22 issue of *Chemistry of Materials* (p. 3918; DOI: 10.1021/ cm0604864), Tagmatarchis and coresearchers treated CNHs with O2 at 0.1 MPa and 580°C for 10 min to remove the strained hemispherical tip and introduce carboxylic acids at the cone ends. These mild conditions retain high purity and, unlike a previously published tipopening procedure for CNTs, do not substantially shorten the CNHs. The carboxylic acid-terminated CNHs were converted to acylchloride-terminated CNHs by treatment with thionyl chloride together with a dimethylformamide catalyst or by refluxing with oxalyl chloride. Subsequent functionalization with a variety of amines, alcohols, and thiols possessing long or short hydrophobic alkyl chains, polar oligoethylenes, aromatic chromophores, or masked active groups suitable for further functionalization, was performed in dry, anaerobic conditions.

The functionalized CNHs displayed expected solubilities; for example, polar derivatives are soluble in polar solvents while apolar derivatives are soluble in apolar solvents. The researchers used high-resolution transmission electron microscopy to show that functionalized CNHs in solution retain their characteristic
morphology. Fourier transform infrared spectroscopy was used to verify the covalent cone-end functionalization. UV–vis spectra of CNHs functionalized with chromophores were very similar to the spectra
of the chromophores themselves; red-shifted and somewhat collapsed transitions of the functionalized CNHs suggested to the researchers that electronic intramolecular communication occurs between the CNHs
and the chromophores. The researchers point to the quenching of the strong fluorescence emission of pyrene by more than 90% in the CNH–pyrene hybrid as verification of this intramolecular electronic
communication. The researchers said that their procedure "opens new avenues for the synthesis of a
plethora of nanohorn-based hybrid materials suitable for nanotechnology applications, particularly in the context of solar energy conversion, photovoltaics, and photosynthesis biomimetic systems where CNHs play a role as efficient electron acceptors."

STEVEN TROHALAKI