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Cone-End Functionalization of Carbon Nanohorns

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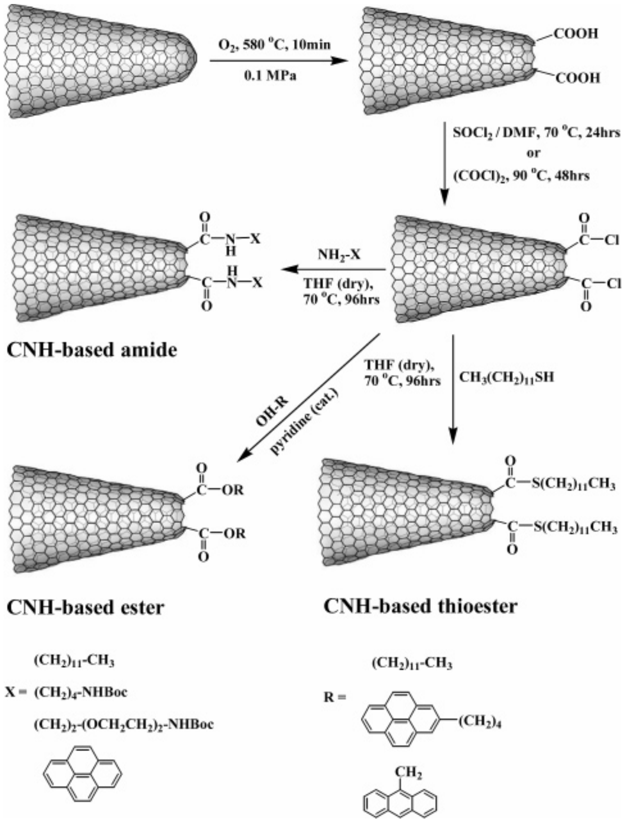
Carbon nanohorns (CNH) represent a largely unexplored carbon allotrope, within the family of fullerenes and nanotubes. CNH are produced in high yields upon laser ablation of graphite.[1,2] In addition, CNH similar to carbon nanotubes (CNT) are completely insoluble in all organic solvents as well as in aqueous media. However, CNH are completely free from metal nanoparticles and carbonaceous and other amorphous material impurities,[3] contrary to carbon nanotubes (CNT), whose purification[4−9] carries extra disadvantages such as degradation, defects, loss of electronic and mechanical properties, and significant decrease in the absolute mass of the material. Furthermore, the structural surface inhomogenicity of CNH, as compared to the symmetrical elongated CNT, is responsible for an unbalanced excess amount of strain located at the conical end site.

Therefore, it is absolutely timely and desirable to explore the chemistry and reactivity of CNH in the search for solubility enhancement. This will aid not only the performance of solution spectroscopic studies on these materials but also the generation of functional CNH-based hybrid materials suitable for nanotechnological applications.

Recently, we reported on the covalent functionalization of CNH upon the 1,3-dipolar cycloaddition of azomethine ylides which resulted on the decoration of the skeleton of CNH with numerous fused pyrrolidine rings.[10]

Scheme 1. Oxidative Removal of the Cone-Shaped Tip of CNH and Covalent Functionalization with Amines, Alcohols, and Thiols for the Generation of CNH-Based Amide, Ester, and Thioester Materials, Respectively



In this communication, we report for the first time on a functionalization procedure of CNH that is based on the opening of their conical and highly strained end and the attachement of various organic amines, alcohols, and thiols. In such a way, soluble CNH-based amide, ester, and thioester materials are easily produced.

CNH were synthesized from pure graphite targets by CO_2 laser ablation. To effectively remove the cone-shaped tip, treatment of CNH aggregates with molecular oxygen (0.1 MPa for 10 min) at 580 °C was conducted. This mild and short in time but very powerful oxidative treatment introduces carboxylic units at the cone end of the dahlia-type aggregates avoiding shortening of CNH and formation of any type of impurities, thus, retaining the CNH high purity. This step greatly differentiates the whole functionalization procedure from the original one applied for the tip opening of CNT (i.e., treatment under harsh conditions, e.g., strong acids, reflux, ultrasonication, and long times) which in addition cut the original long nanotubes in short pieces.[4]

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Table 1. Solubility of Cone-End Functionalized CNH in Various Organic Solvents

groups[a]	solubility[b]			
	methanol	toluene	CH_2Cl_2	THF
saturated alkyl chain	−	+	−	−
oligoethylene chain	+	+	+	+
aromatic chromophore	+	−	+	+

[a] Organic addend introduced. [b] Soluble material is identified with a + symbol while insoluble material is idendtified with − symbol.

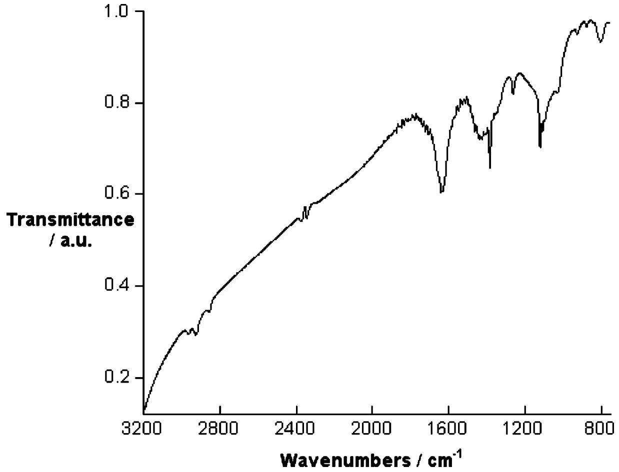

Figure 1. FT-IR absorption spectrum of soluble cone-end functionalized CNH-based amide.

The as-generated carboxylic acid terminated nanohorns converted to the corresponding acyl chlorides (CNH−COCl) upon treatment either with thionyl chloride, in the presence of a catalytic amount of dimethylformamide, or simply in refluxing oxalyl chloride. As it is shown in Scheme 1, treatment of CNH−COCl, in completely anaerobic and dry conditions, with a variety of amines, alcohols, and thiols, possessing short or long hydrophobic alkyl chains, polar oligoethylenic units, aromatic chromophores such as pyrene or anthracene groups, or even masked active groups suitable for further organic exploitations, gave the corresponding CNH-based amides, esters, and thioesters, respectively.

Different solubilities of the cone-end functionalized CNH were observed depending on the nature of the organic addend introduced. Thus, functionalized material possessing polar oligoethylene chains was readily solubilized in tetrahydrofuran (THF), dichloromethane, chloroform, acetone, and toluene (ca. < 1 mg/mL). However, the presence of apolar alkyl chains induced solubility only in toluene. A summary of the observed solubilities is presented in Table 1.

Very diluted solutions of modified CNH are gray colored while concentrated deep-black solutions are visually nonscattering. In addition, the soluble functionalized material was found to be stable over several weeks under ambient conditions without observing any precipitation.

Fourier transform infrared (FT-IR) spectroscopy indicates the covalent cone-end modification of CNH. In this context, in functionalized CNH-based amides the absorptions corresponding to the C=O (1655 cm^{-1} and 1634 cm^{-1}) of the amide as well as the C−H stretching and bending active vibrations (2962 cm^{-1}, 2925 cm^{-1}, and 2854 cm^{-1}) of the alkyl chain are easily observed (Figure 1).[11]

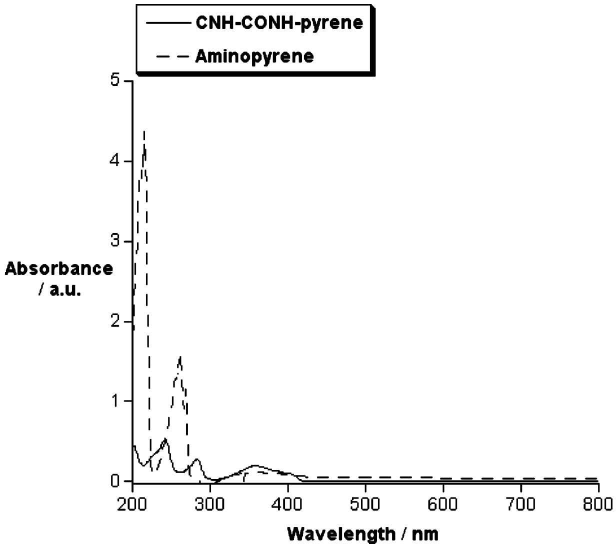

Figure 2. Electronic absorption spectra of aminopyrene (solid line) and cone-end functionalized CNH pyrene amide (dotted line).

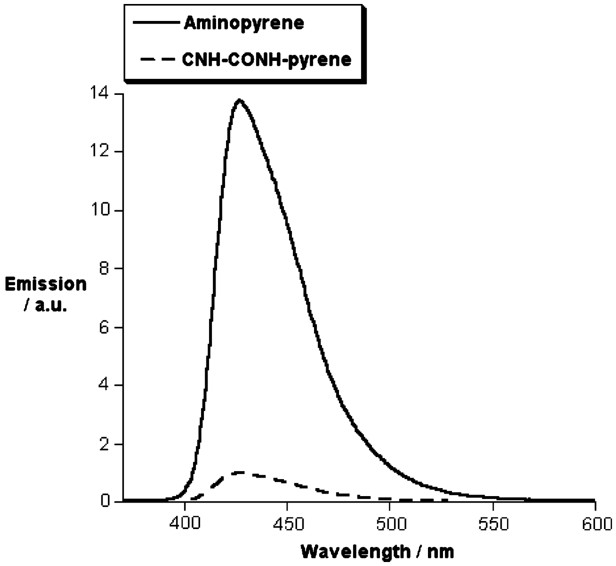

Figure 3. Steady-state fluorescence spectra of aminopyrene (solid line) and cone-end functionalized CNH pyrene amide (dotted line), with matching absorptions at the 310 nm excitation wavelength.

The functionalized CNH exhibit a featureless absorption UV−vis spectrum unless a chromophore is present. Thus, the UV−vis electronic absorption spectrum of CNH-based pyrene amide shows characteristic $\pi-\pi$ transitions at 405, 352, 287, 268, 261, and 253 nm due to the covalently attached pyrene. Some of these transitions are red-shifted while others are collapsed as compared with the ones derived from free aminopyrene (Figure 2), suggesting evidence for electronic intramolecular communication betweeen the two components, namely, the pyrene and the nanohorn units. Similarly, in the UV−vis absorption spectrum of CNH-based pyrene ester the characteristic absorptions due to pyrene are identified at 344, 328, 314, 277, 266, 256, 244, and 235 nm.

Steady-state fluorescence studies on the functionalized CNH-based pyrene amide material confirm and verify the intramolecular electronic interactions identified in the absorption spectrum. Namely, more than 90% quenching of the strong pyrene emission at 425 nm was observed upon 310 nm excitation (Figure 3). At this point, it is important

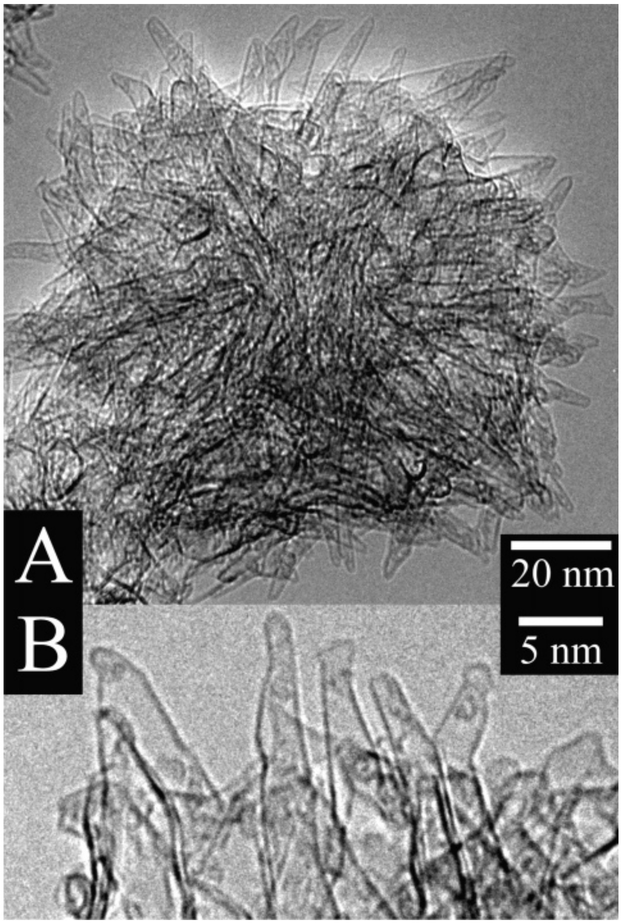

Figure 4. Representative HR-TEM images of soluble cone-end functionalized CNH at low (panel A) and high magnification (panel B), respectively.

to mention that we have already shown the occurrence of intramolecular fluorescence quenching in CNH *possessing an intact cone-end* while being covalently decorated with pyrene units derived upon the 1,3-dipolar cycloaddition reaction.[10] The significant decrease in emission intensity of the modified CNH-based pyrene amide is caused by quenching of the energy derived from the pyrene single excited state through a charge-transfer mechanism to the covalently bound nanohorns aggregate.

Unfortunately solubility values of cone-end functionalized CNH are not sufficiently high to allow proper NMR studies. In addition, the inhomogeneous magnetic environment of the π system of CNH, shielding effects, and the restricted mobility of the aggregated nanohorn system handicapped our attempts for obtaining suitable spectra.

High-resolution transmission electron microscopy (HR-TEM) was used to prove the presence of cone-end functionalized CNH in solution. A drop of a THF or toluene solution of cone-end functionalized CNH was cast on a holey-carbon TEM grid and examined at 120 kV. As Figure 4 shows, the characteristic morphology is retained on the cone-end modified CNH. The unit core of CNH remained intact, and nanohorn structures with diameters in the range of 2−5 nm were identified. Careful examination of the micrographs reveals that the opened tips and the so-generated holes on the cone-end functionalized CNH are not seen, contrary to their visualization on the non-functionalized but oxidized CNH. We believe that the chemical attachment of organic units decreases the contrast of the hole edges and thus makes their observation difficult. Instead, in some cases, soft material, which is attributed to the added organic molecules, attached to the conical tips and side-walls is visible. Evidently, the modification process does not cause any other significant changes in the morphology of nanohorns, and interestingly the aggregated superstructure is highly retained; namely, the solubility enhancement achieved is not enough to bring out isolated single nanohorns from the supramolecular nanohorn aggregation.

In conclusion, the ability to remove the cone-shaped end and then chemically modify the carboxylic acid terminated CNH without significantly disrupting their unique structure while retaining their high purity opens new avenues for the synthesis of a plethora of nanohorn-based hybrid materials potentially suitable for nanotechnological applications. Particularly in the context of solar energy conversion and mimicking natural photosynthesis CNH can indeed play a central role as efficient electron acceptors similarly to other carbon-based nanomaterials such as fullerenes and nanotubes.[12−15]

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Supporting Information Available: Infrared spectrum of pristine CNH, electronic absorption and fluorescence spectra and HR-TEM images of oxidized CNH as well as CNH-based pyrene butyl ester (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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