Electronic Supplementary Information

Microwave-assisted functionalization of carbon nanohorns
via [2+1] nitrenes cycloaddition

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**General**

All solvents and reagents were purchased from Aldrich and used without further purification unless otherwise stated. Pristine CNHs were produced by CO$_2$ laser ablation of graphite in the absence of any metal catalyst under an inert Ar atmosphere (760 Torr) at room temperature. For the microwave synthesis, a CEM Discover microwave reactor (frequency = 2.45 GHz, $P_{\text{max}} = 300$ W) with internal infra-red pyrometer and pressure control system was used. The microwave reactions were carried out in a 10 mL capacity glass vessel with self-sealing septa, specially designed for operation in the microwave apparatus. Magnetic stirring was provided to assure complete mixing of the reactants, which irradiated under appropriate power and time. All measurements were performed at room temperature unless otherwise stated. HR-TEM measurements were carried out using a Topcon EM002B operated at an accelerating voltage of 120 kV for imaging. EDX analysis was performed on a scanning transmission electron microscope (HITACHI HD-2300) equipped with an energy dispersive X-ray spectroscopy measurement system. Dynamic light scattering measurements were performed in the angular range of 20–150° by a ALV/CGS-3 Compact Goniometer System (ALV GmbH, Germany), using a JDS Uniphase 22mW He–Ne laser, operating at 632.8 nm, interfaced with a ALV-5000/EPP multi-tau digital correlator with 288 channels and a ALV/LSE-5003 light scattering electronics unit for stepper motor drive and limit switch control. Autocorrelation functions were collected five times at each observation angle for each solution and they were analyzed by the cumulants method and the CONTIN routine using the software provided by the manufacturers. Hydrodynamic radii were calculated through the Stokes–Einstein relationship. Steady-state UV-Vis electronic absorption spectra were recorded on a Perkin Elmer (Lambda 19) UV-VIS-NIR spectrophotometer. Mid-infrared spectra in the region 550–4000 cm$^{-1}$ were obtained on a Fourier Transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). Micro-Raman scattering measurements were performed at room temperature in the backscattering geometry using a RENISHAW inVia Raman microscope equipped with a CCD camera and a Leica microscope. A 2400 lines mm$^{-1}$ grating was used for all measurements, providing a spectral resolution of ± 1 cm$^{-1}$. As an excitation source the Ar$^+$ laser (514 nm with less than 0.5 mW laser power) was used. Measurements were taken with 60 seconds of exposure times at varying numbers of accumulations. The laser spot was focused on the sample surface using a long working distance 50x objective. Raman spectra were collected on numerous spots on the sample and recorded with Peltier cooled CCD camera. The intensity ratio $I_D/I_G$ was obtained by taking the peak intensities following any baseline corrections. The data were collected and analyzed with Renishaw Wire and Origin software. The thermogravimetric analysis was performed using a TGA Q500 V20.2 Build 27
instrument by TA in an inert atmosphere of nitrogen. In a typical experiment, 1 mg of the material was placed in the sample pan and the temperature was equilibrated at 60 °C. Subsequently, the temperature was increased to 900 °C at a rate of 10 °C min⁻¹ and the weight changes were recorded as a function of temperature.

Microwave-assisted synthesis of aziridine-functionalized CNHs – hybrid materials 1 and 2. In a typical experiment, 10 mg CNHs, 0.5 mol of 1-dodecyl azide (72 mg) or 6-azido-1-hexanol (105 mg) and 3 mL of \( N \)-methyl-2-pyrolidone were placed in a microwave glass vessel, dissolved with the aid of sonication and flushed with nitrogen. The vessel was tapped with sealing septum and placed in the microwave reactor. The initial power was 100 W, the preselected temperature was set at 220 °C and the reaction time at 60 min. Under these conditions, the temperature raised up to 220 °C within 2 min and the pressure in the tubes up to 52 psi. After completion of the reaction time, the crude material was suspended in DMF, filtered on a PTFE membrane filter (0.2 μm), washed with DMF, methanol and dichloromethane and dried.

Preparation of functionalized CNHs – hybrid material 3. The hydroxy-functionalized CNHs 2 (5 mg) and thioctic acid (0.39 mmol, 80 mg) were dispersed in 9 mL dry CH₂Cl₂ via sonication and the mixture was stirred for 15 min at 0 °C (ice/water bath) under \( N_2 \). Then 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (0.8 mmol, 153 mg) and 4-(dimethylamino)-pyridine (0.08 mmol, 10 mg) in 5 mL of CH₂Cl₂ were added, and the mixture was stirred for another 15 min at 0 °C. Subsequently, the cooling bath was removed and the reaction mixture allowed warming to room temperature and stirred for another 72 h under \( N_2 \). Then, the reaction mixture filtered on a PTFE membrane filter (0.2 μm), washed with N,N-dimethylformamide, methanol and dichloromethane and dried.

Stabilization of Au nanoparticles onto functionalized CNHs – hybrid material 4. With the aid of sonication, 5 mg of HAuCl₄·3H₂O dissolved in 5 mL of methanol. A dispersion of thioctic-aziridine-functionalized CNHs 3 (5 mg) in 5 methanol and 0.07 mL of acetic acid were added to the above gold salt solution under stirring. After 5 min, a freshly prepared solution of NaBH₄ in water (0.5 mg in 0.5 mL) was added to the mixture under vigorous stirring at room temperature. The reaction was quenched after 1 h by adding 2 mL of 1 M aqueous hydrochloric acid solution. After the partial removal of the solvent under reduced pressure and at maximum 40 °C, the precipitate was filtered on a PTFE membrane filter (0.2 μm), and washed thoroughly with 0.01 N HCl, water, methanol and dichloromethane.
**Fig. S1.** a) Microwave power applied, b) temperature in the vial as measured by infra-red pyrometer and c) pressure observed in the glass vessel over the period of the reaction (60 min) in the microwave reactor. The bold green and red lines denote the threshold for microwave irradiation power intensity (100W) and temperature (220 °C).
Fig. S2. ATR-IR spectra of a) alkyl-functionalized CNHs 1 (black) and b) hydroxy-functionalized CNHs 2 (black) and thioctic-functionalized CNHs 3 (blue).
**Fig. S3.** Raman spectra of pristine CNHs (black, D/G = 1.09) and a) functionalized CNHs 1 (red, D/G = 1.27) and b) functionalized CNHs 2 (red, D/G = 1.35), with 514 nm laser excitation.
Fig. S4. Dynamic light scattering curve of functionalized CNHs 3, obtained in DMF (average diameter is 125 nm).