Electronic Supplementary Information

Reductive dismantling and functionalization of carbon nanohorns

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Experimental Section

Techniques. Reaction of reduction, functionalization and metal decoration were performed under inert atmosphere in an Innovative Technology Inc. glovebox. Dry THF and DMSO were obtained through an Innovative Technology Pure Solv system connected to specific taps within the glovebox. Raman spectroscopy measurements were done using a Jobin-Yvon Horiba Labram II micro-Raman system with excitation laser wavelength of 514 nm. The incident power was kept under 3mW to avoid any sample damage. The spot size was 2µm using a 100x objective. Steady-state UV-Vis electronic absorption spectra were recorded on a Perkin Elmer (Lambda 19) UV-VIS-NIR spectrophotometer. The thermogravimetric analysis were performed either using a TGA Q500 V20.2 Build 27 instrument by TA in an inert atmosphere of nitrogen or a Setaram TAG-16 apparatus. For TEM observations, one drop of reduced CNHs in DMSO or dispersed CNHs was deposited on carbon grid or graphene coated copper grids. Concentration measurements were performed by UV-vis spectroscopy on solution prepared in DMSO centrifuged at 4000 rpm during 1 hour. The solution was diluted enough to avoid any saturation of the spectrometer and calculations were performed based on the absorbance at 400 nm.

Materials. Solvent and reactants were purchased from Aldrich and Alfa Aesar. Solvent were dried and distilled before being used. Reactants were used as received. Raw CNHs were produced from pure graphite targets by CO_2 laser ablation.

Reduced CNHs 1. A potassium naphthalenide solution was prepared by adding 100 mg (2.56 mmol) of potassium chips to 136 mg (1.06 mmol) of naphthalene in 150 mL of dry THF under inert atmosphere. The mixture was refluxed 12 hours before being filtrated over a conical paper filter. Then, 100 mg (8.3 mmol) of raw CNHs are mixed with the fresh potassium naphthalenide solution and stirred at room temperature under inert atmosphere for 12 hours. The black suspension of reduced CNHs is filtered through a 0.22 µm nylon membrane and washed several times with dried THF until the color of the filtrate remained transparent.

Dissolution and individualization of reduced carbon nanohorns. CNHs salt **1** was solubilized in DMSO at 1 mg ml^{-1}. The solution was stirred for 12 hours before being centrifuged at 4000 rpm for 1 hour to remove any unsolubilized materials.

Re-oxidized CNHs 2. A solution of reduced CNHs **1** was oxidized by bubbling dried air in the solution. After 12 hours, CNHs are aggregated and filtrated thought a 0.45 µm PTFE membrane, washed several times with DMSO and methanol and then lyophilized overnight.

Functionalized CNHs 3a-c. A two-fold excess of the halide reactants were added into a DMSO solution of reduced CNHs **1**. Typically, 30 mg of **1** were dissolved in 30 mL of DMSO. After centrifugation at 4000 rpm for 1 hour, 2-fold excess of iodomethane (100 µL) in 1 mL of DMSO was added to the supernatant. Aggregates started to appear in the black solution few minutes after addition. The solution was stirred for 48 hours and the suspension was filtrated in 0.22 µm nylon membrane and washed with DMSO and methanol. The residual solid was washed with distilled water to remove KI and then ashed with methanol and CH_2Cl_2. The residual solid was lyophilized over night to obtain 26 mg of functionalized CNHs **3a**.

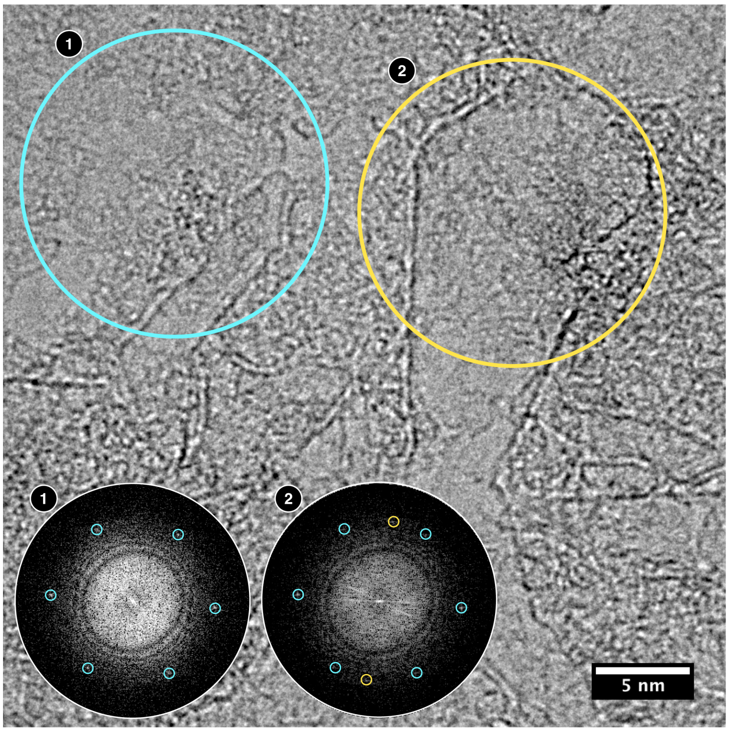

Figure S1. TEM micrograph of reduced CNHs **1** deposited on graphene membranes. The Fast-Fourier-Transform (FFT) of region (1) shows the six reflections (blue circles) at 0.213 nm from the honeycomb lattice of the graphene membrane. The FFT from the region of CNHs, in addition to the six reflections from the underlying graphene, shows a spot at 0.213 nm from the CNHs crystal lattice.

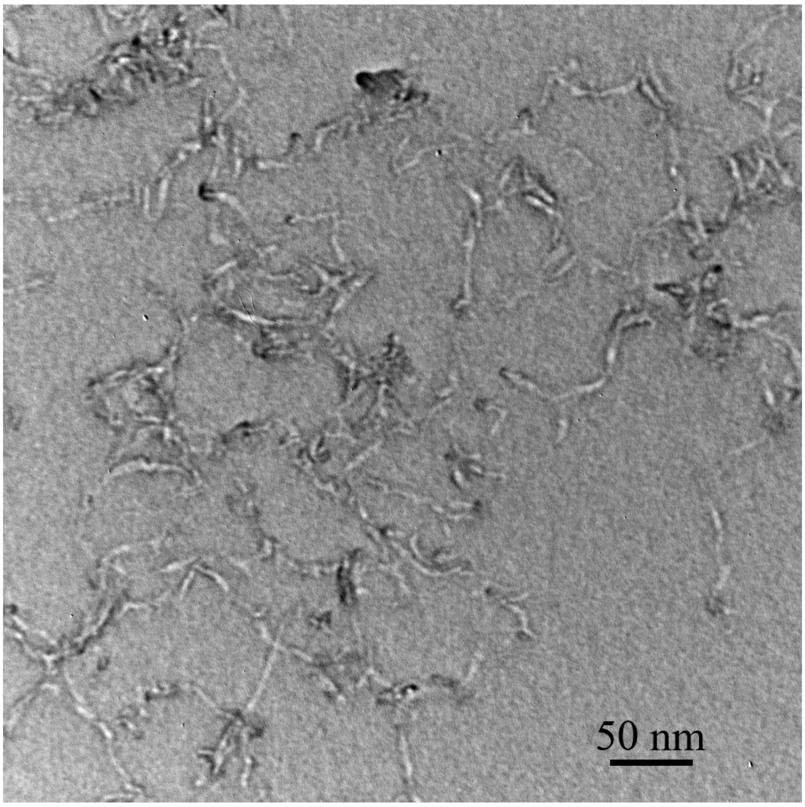

Figure S2. TEM image of functionalized CNHs **3c**.

Table S1. Summary of Raman and TGA results for pristine CNHs, re-oxized CNHs **2** and functionalized CNHs **3a-c**.

	D-band (cm^{-1})	G-band (cm^{-1})	2D-band (cm^{-1})	I_D/I_G ratio	Weight loss (%)	Functionalization degree (organic unit per C atoms)
Pristine CNHs	1334	1575	2670	1.14	0	-
2	1335	1587	2670	1.15	0	-
3a	1341	1596	2678	1.57	13	9
3b	1341	1594	2676	1.56	12	77
3c	1341	1595	2676	1.44	11	57

Table S2. Qualitative solubility of functionalized CNHs in a variety of solvents.

	MeOH	CH_2Cl_2	DMF	o-DCB	Toluene	CH_3CN	Acetone
Pristine CNHs	-	-	+	-	-	-	-
2	-	-	+	-	-	-	-
3a	-	+	+	+	-	+	+
3b	-	-	+	+	-	+	+
3c	-	-	+	+	-	+	+