Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Preparation and Characterization of Soluble Carbon Nano-Onions by Covalent Functionalization Employing a Na/K alloy

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Experimental Section

Reagents were used as purchased. Commercially available nanodiamond was purchased from Carbodeon with a crystal size between 4-7 nm. Raman measurements were performed using a SmartRaman spectrometer equipped with a 180 degree sampling holder from Thermo Scientific using an excitation wavelength of 532 nm. FTIR spectra were recorded using a Perkin Elmer 100 spectrometer with neat samples. Absorption studies were perfomed using a Cary 5000 UV-NIR spectrometer from Varian using fused Quartz glass cuvettes with a 1 cm optical path. For TGA analysis a TGA/DSC analyzer from Mettler Toledo was used. A heating rate of 10 °C/min was employed until 1000 °C. All samples were measured in Alumina crucibles with a volume of 0.7 μl. NMR spectra were measured using a 600 MHz JEOL spectrometer. The films were imaged by secondary electron SEM using an S-3000N scanning electron microscope from FEI (Tokyo, Japan). The accelerating voltage of the electron beam was either 15 or 20 keV and the working distance was 10 mm. For HR-TEM measurements, the samples were deposited on Cu grid holey carbon supports and the solvent was evaporated. Transmission Electron Microscope images were recorded using an FEI Tecnai™ transmission electron microscope. The accelerating voltage of the electron beam was 200 keV.

Reduction and functionalization of CNOs

Solvent purification was conducted via vapor transfer of 1,2-DME though a vacuum manifold in three stages; one containing CaH_2, a second with dried silica and a third one containing a sodium/potassium alloy (see Figure S1a-b). Finally, the solvent (40 mL) was vapor transferred into a three necked flask containing 0.1 mL of a Na/K (1.77 mmol K/ 0.83 mmol Na) alloy and the solution was vigorously stirred until a deep blue color was obtained (see Figure S1c). At this point, 22 mg of CNOs (1.83 mmol carbon) were added and the solution was stirred for 3 days, then an excess of 1-bromohexadecane was added to the solution while stirring for 3 additional days. The solution was washed with hexane, ethanol, THF and water. The sample was dried in a vacuum oven at 45 ^{o}C overnight, resulting in 38 mg of functionalized CNOs. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ 1.24 (br, 22H), 0.87 (t, J = 7.0 Hz, 3H).

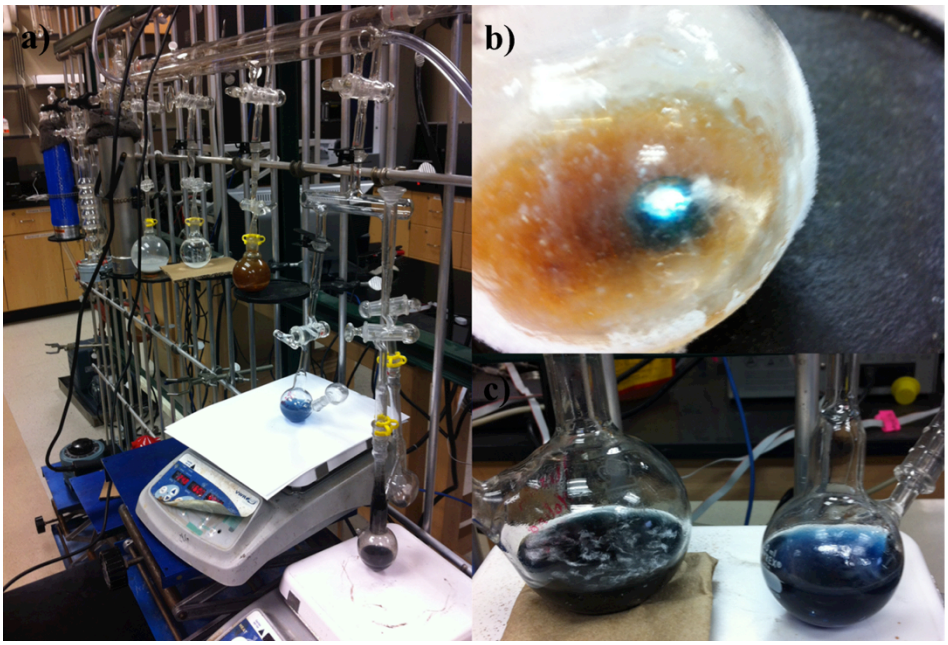

Figure S1. (**a,b**) Vacuum manifold for the purification of 1,2-DME and (**c**) formation of the deep blue between the Na/K alloy and solvent molecules.

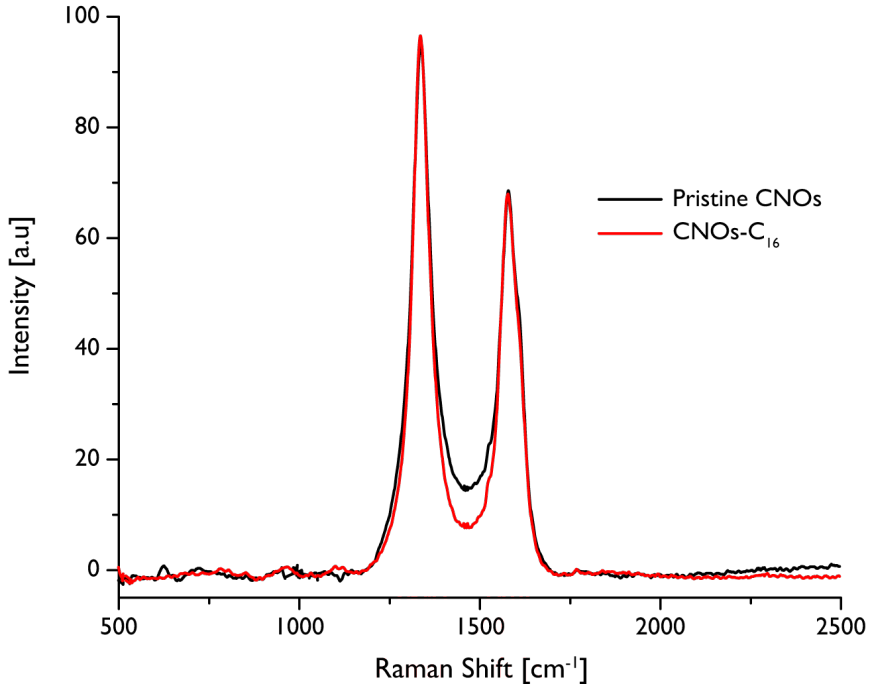

Figure S2. Raman spectrum (λ_{exc}=532 nm) of pristine CNOs and functionalize CNOs-C_{16} after TGA at 430 ºC.

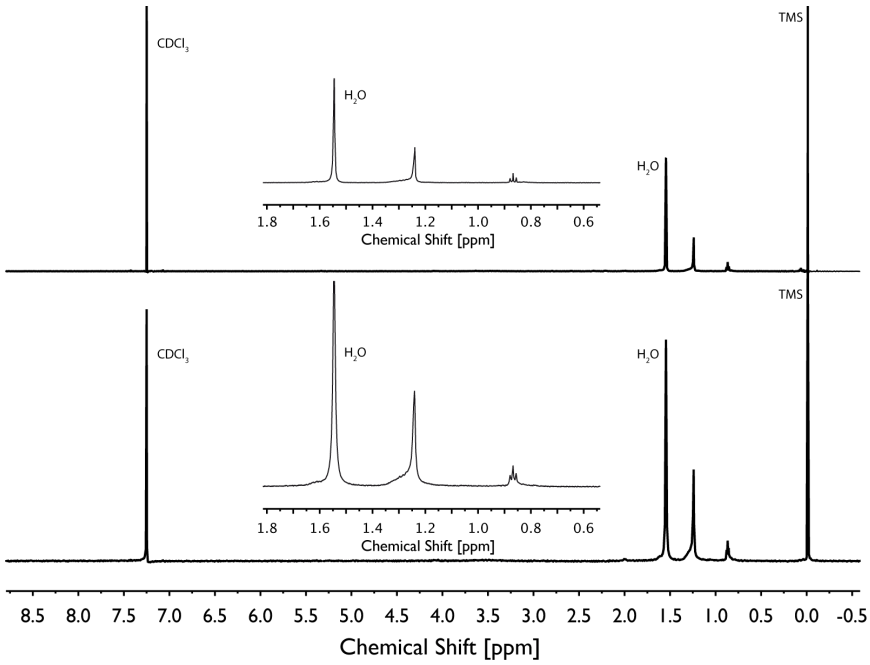

Figure S3. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) spectra of CNO-C_{16} before (bottom) and after filtration (top) in $CDCl_3$ at 25 ºC.

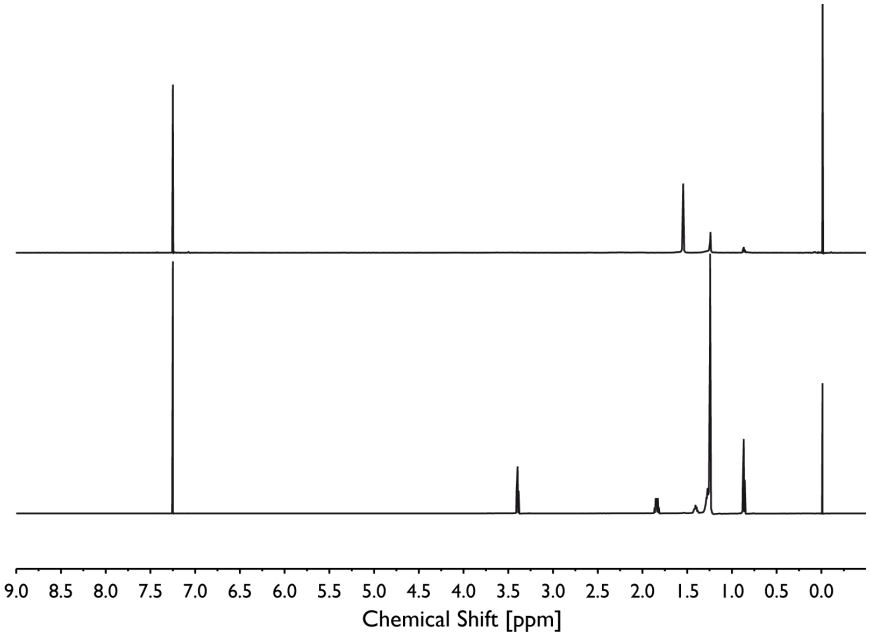

Figure S4. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) spectra of 1-bromohexadecane (bottom) and functionalize CNOs-C_{16} (top).

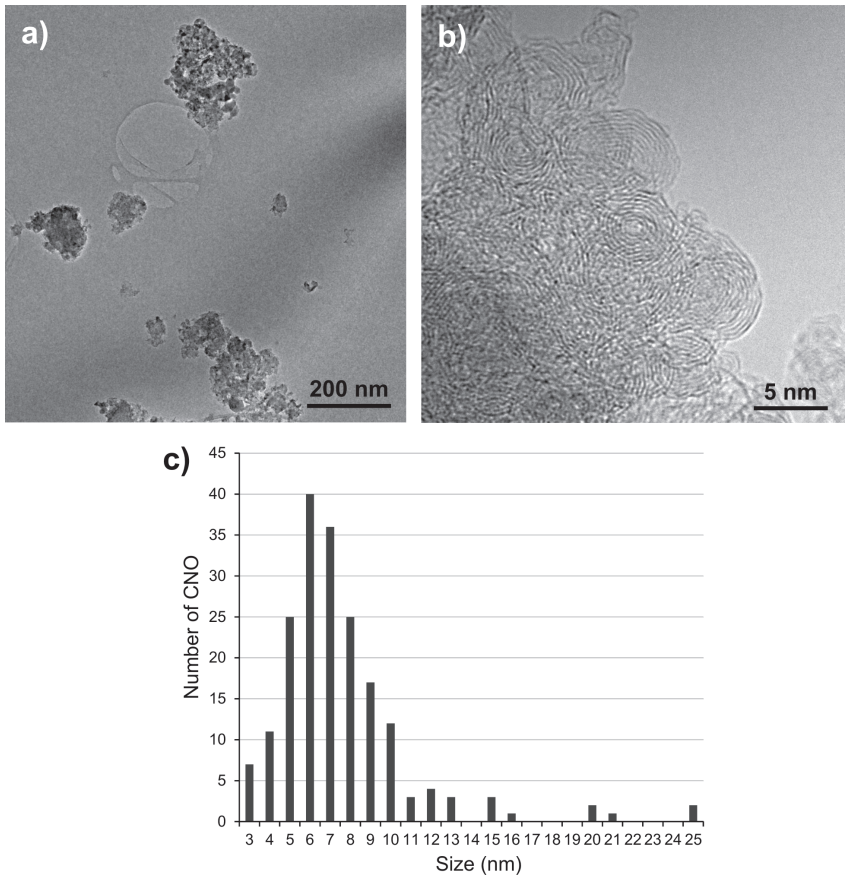

Figure S5. TEM images of the Cu holey carbon covered with CNOs-C_{16} in NMP/$CHCl_3$ (1:1, v/v) (a) and (b) after filtration through a 0.1 µm PVDF filter, (c) stadistycal study over 250 TEM pictures.

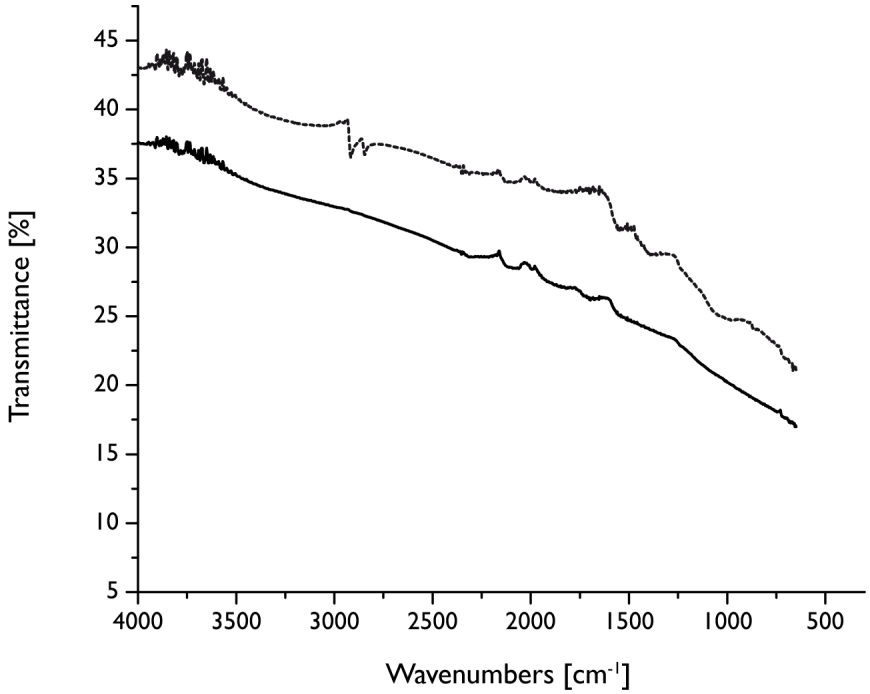

Figure S6. FTIR spectra of pristine CNOs (solid line) and functionalize CNOs-C16 (dotted line).

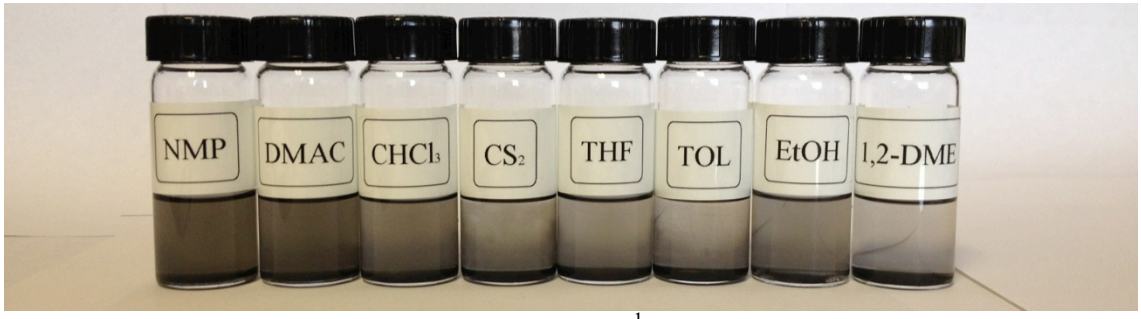

Figure S7. Stable dispersions of CNOs-C_{16} (0.1 mg mL^{-1}) in differents solvents after 1 hour sonication 10 and 30 minutes centrifugation at 1000 rpm.

Figure S8. Solution of functionalize CNOs-C_{16} filtered through a 0.2 μm PVDF filter.

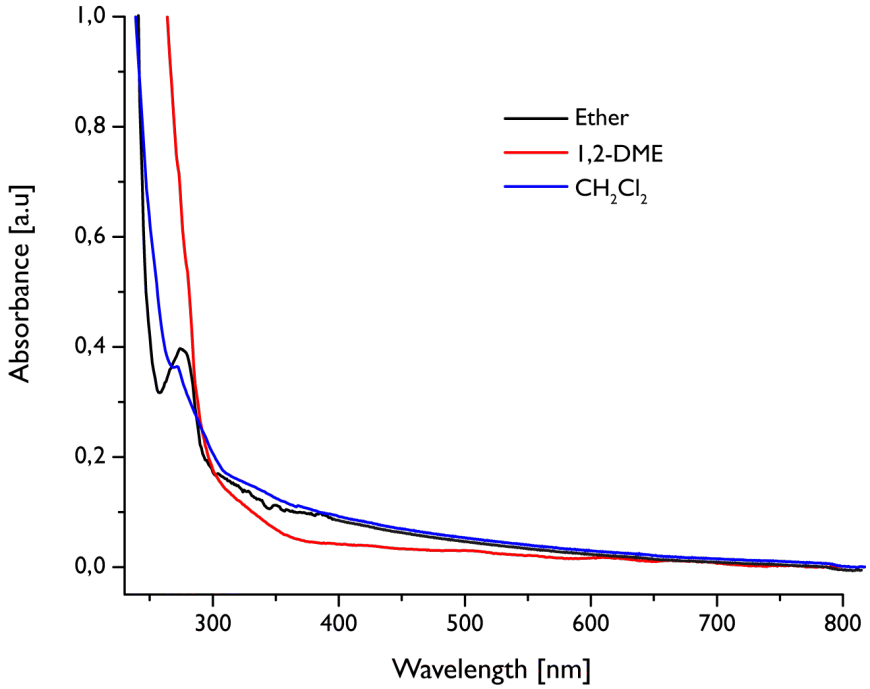

Figure S9. UV-vis spectra of functionalize CNOs-C_{16} in differents solvents at 0.1 mg mL^{-1} concentration.

5