

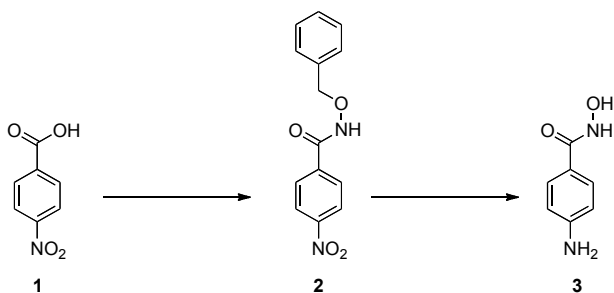
Surface Selective One-step Fabrication of Carbon Nanotube Thin Films with High Density

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Supporting Info

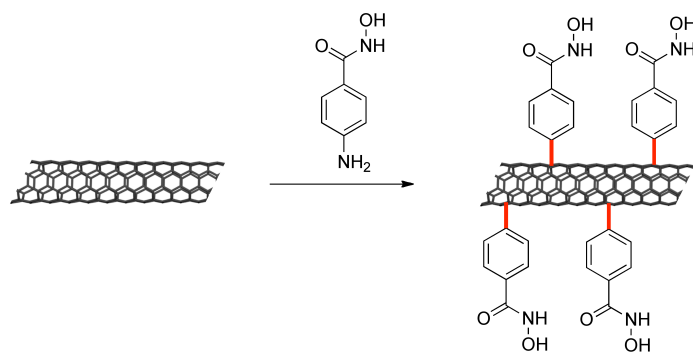
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CNT Functionalization



4-amino-N-hydroxybenzamide (3). CNT functionalization reagent **3** was synthesized in two steps from 4-nitrobenzoic acid (**1**)¹. In a dried and nitrogen evacuated Schlenk flask connected to a Schlenk line, 2g of 4-nitrobenzoic acid were suspended in 25ml of dry dichloromethane (DCM), to which 2 eq of oxalyl chloride were added. After addition of a 0.15 ml of dimethylformamide (DMF), the reaction mixture bubbled vigorously and was stirred at room temperature for 3 hours, after which the volatiles were removed in a roatavap. The resulting white dried solid was redissolved in 6 ml of anhydrous DCM and added onto a mixture of 1.91 g benzylhydroxylammonium hydrochloride in 15 ml of anhydrous DCM and 3.3 ml triethylamine. The mixture was quenched with diluted aqueous HCl and the volatiles were removed. The resulting white solid was washed with water and used without further purification. The structure of the resulting benzamide, **2** (2.6g 85% yield) was confirmed by ¹H-NMR (CDCl₃, ppm): 5.03 (s, 2H), 7.4-7.6 (m, 5H), 7.92 (d, *J*= 7 Hz, 2H), 8.30 (d, *J*=7 Hz, 2H).

Benzamide **2** (2.2 g) was dissolved in 80ml anhydrous methanol in a flask evacuated with nitrogen and equipped with a reflux condenser. Ammonium formate (3 g) was added, followed by Pd/C (400 mg) under a stream of nitrogen. The mixture was refluxed for 8 hours, filtered while hot and the filtrate was evaporated under vacuum to obtain a light brown solid, which was reprecipitated from isopropanol to yield product **3** as a white solid (0.91 g, 70% yield). ¹H-NMR (d⁶-DMSO, ppm): 5.6 (s, 2H), 6.6 (d, *J*=6 Hz, 2H), 7.5 (d, *J*=6 Hz, 2H), 8.65 (s, 1H).



Functionalized CNTs. CNTs decorated with hydroxamic acids on their surface were synthesized following one of the following routes using either organic solvents or water, mixed or separated SWCNTs. No difference was observed in the assembly capabilities.

*Functionalization from an organic solvent.*² 3 mg of SWCNTs were sonicated with a probe sonicator in 10 ml orthodichlorobenzene for 10 min. 4-amino-N-hydroxybenzamide **3** (50 mg) previously dispersed in 5 ml acetonitrile were added to the CNT solution and the mixture was sparged with nitrogen for 10 min. Isoamyl nitrite (0.15 ml) was added dropwise and the mixture was heated to 60°C over night while connected to a vacuum line (caution: overpressure can develop over the course of the reaction).

*Functionalization from an aqueous solution.*³ 4-amino-N-hydroxybenzamide **3** (50 mg) was dissolved in 5 ml dry acetonitrile in a flask that was previously dried and evacuated with nitrogen. Nitrosyl tetrafluoroborate (70 mg) was added and the mixture was stirred at room temperature for 30 min. The resulting mixture was added onto an aqueous solution (10 ml water, 1% sodium dodecylsulfate -SDS) containing 3 mg of SWCNTs which had been previously sonicated for 10 min. The mixture was stirred at room temperature over night.

CNT purification. CNTs obtained by either method were purified by reprecipitation from an excess of acetone followed by centrifugation at 3.5K for 30 min. This process was repeated twice and the resulting CNT residue was dried and resonicated in water with a probe sonicator. The solution was filtered with a Millipore filtration system using cellulose acetate filters (0.2 μm pore size) and washed with an excess amount of water. The CNTs trapped in the filter were resonicated into water and centrifuged at 3.5K for 30 min to remove bundles. The resulting solution was submitted to two more purification cycles of filtration, washing, resonication and centrifugation to result in an aqueous solution of functionalized CNTs.

Contact Angle measurement

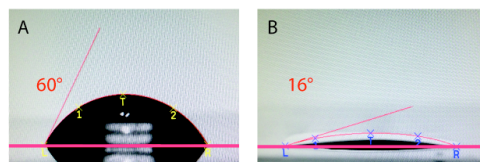


Figure S1 – Contact angle measurements on substrates containing HfO₂ features on SiO₂. The surface wetting increases when transitioning from water (A) to ethanol (B) as indicated by a decreased contact angle for the same volume of solvent.

SEM Images

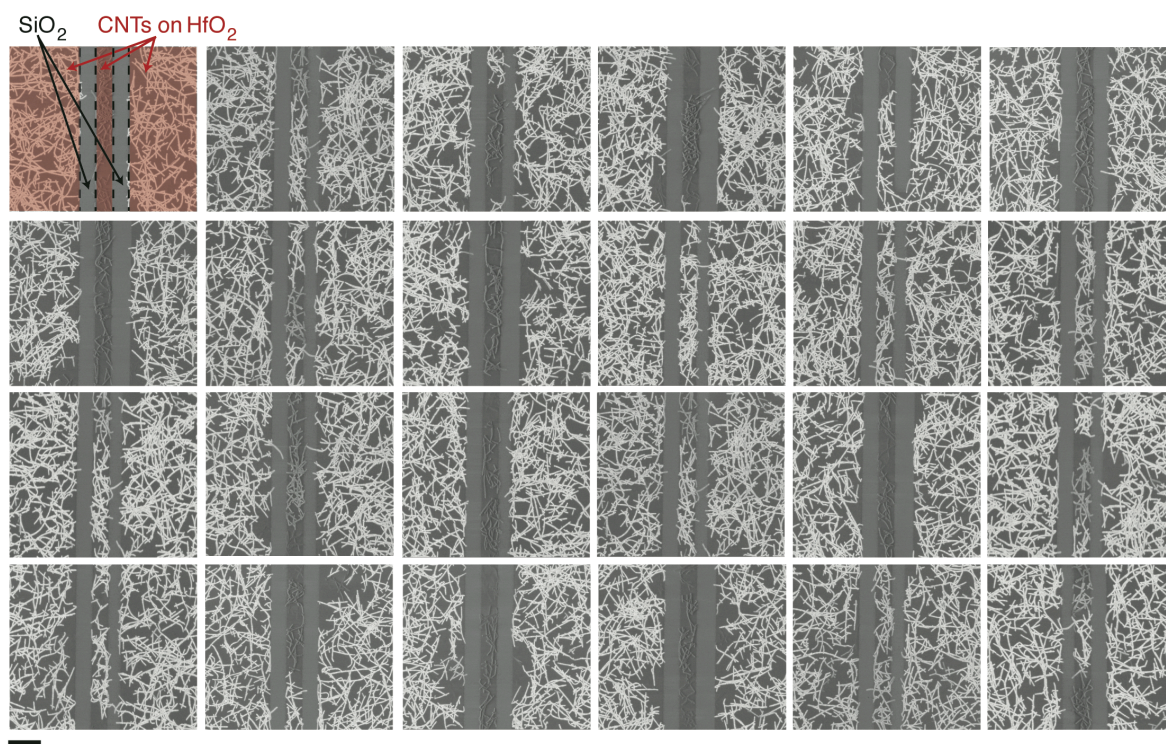


Figure S2. SEM images of CNT assembly on different parts of a substrate with HfO₂/SiO₂ features. HfO₂ areas and rigs are completely covered in CNTs and highlighted in red, while SiO₂ trenches are defining the numbers. Scale bar: 1 micron.

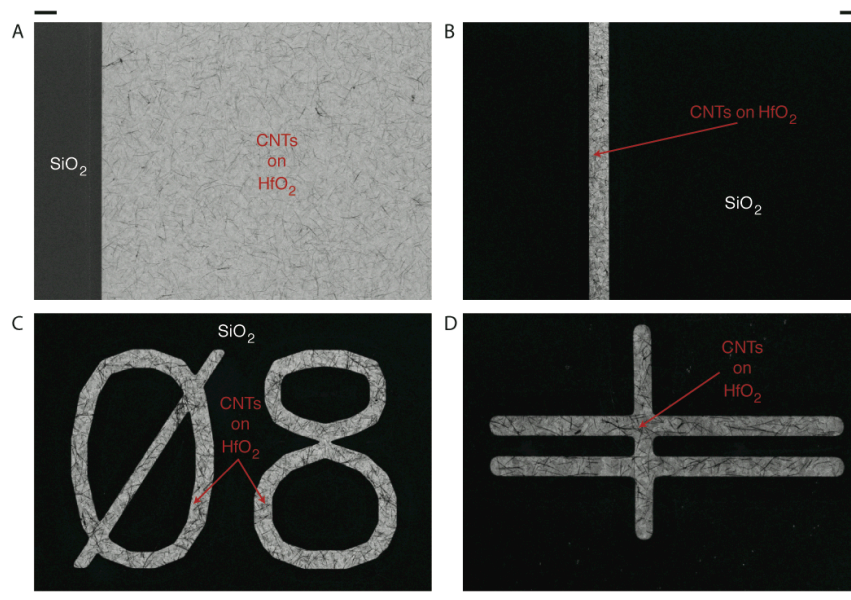


Figure S3. SEM images of CNT assembly on HfO₂/SiO₂ substrates with HfO₂ trenches. HfO₂ is the underlying layer for these substrates, while the upper layer (showing darker contrast in these images) is SiO₂. Good CNT densities can be observed over large areas (A), as well as in narrower trench features (B, C, D). Scale bars: 1 micron.

Raman Spectra

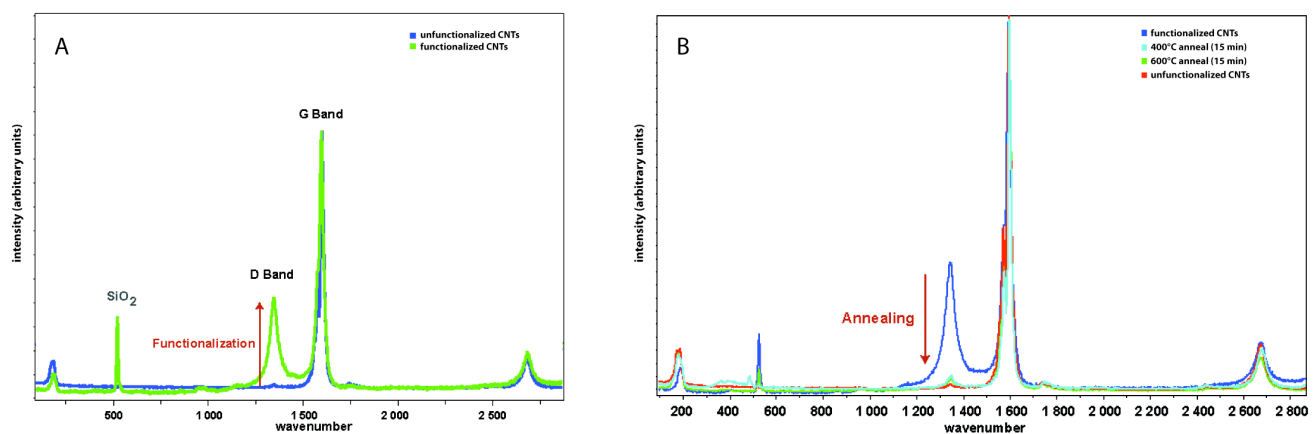


Figure S4 – Raman spectra of CNT films (A) after functionalization and (B) after annealing. The relative intensity of the D band increases when compared with a normalized G band, which is an indication of covalent functionalization. Annealing at 400°C or 600°C allows for recovery of the CNT conjugated backbone as indicated by a decrease in the intensity of the D band.

References

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- ² Bahr, J. L.; Tour, J. M. Highly Functionalized Carbon Nanotubes Using *in situ* Generated Diazonium Compounds. *Chem. Mater.* **2001**, *13*, 3823–3824.
- ³ Dyke, C. D.; Tour, J. M. Unbundled and Highly Functionalized Carbon Nanotubes from Aqueous Reactions. *Nano Lett.* **2003**, *3*, 1215-1218.