Electronic Supplementary Material (ESI) for ChemComm.


**Supporting Information**

# Controlled cutting and hydroxyl functionalization of carbon nanotubes through autoclaving and sonication in hydrogen peroxide

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## Experimental

### Effect of autoclave time on CNT functionalization

Hydrogen peroxide (30%) was purchased from Avantor Performance Materials, Inc., (Phillipsburg, NJ). Multi-wall carbon nanotubes were provided by CTubes (CNT Co., LTD, Incheon, Korea). 20 mg of CNTs were measured and then added to 20 mL hydrogen peroxide (30%). The solution was equally divided into four separate vials. The solutions were autoclaved at 15 psi and 121°C for 0, 1, 3 and 5 h. Each solution underwent sonication at 4 W for 2 h in an ice bath using a tip sonicator (XL-2000, Misonix, Farmingdale, NY). The ice bath was included to prevent excessive CNT sidewall damage. Following drying in a drying oven and resuspension in deionized (DI) water, the average size of CNTs was determined by DLS (Zetasizer Nano ZS, Malvern Instruments, UK) equipped with a red laser at a wavelength of 633 nm and scattering angle of $90^{o}$ at 25°C. TEM imaging of CNTs was performed on a JEM-4000FX (JEOL, Tokyo, Japan) at 200 kV. The TEM samples were prepared by adding 10 μL of CNT solution onto a Formvar grid for 3 min. Control experiments were conducted by autoclaving CNTs in DI water alone for 3 h to verify hydrogen peroxide was responsible for functionalization.

### Effect of sonication duration on size reduction of CNTs

The effect of sonication duration on functionalization of CNTs was addressed by first adding 15 mg of CNTs to 15 mL of hydrogen peroxide (30%). The solution was then autoclaved at 15 psi and 121 °C for 3 h. The solution was evenly distributed into three vials, and each solution was sonicated separately at 4 W for 1, 2 and 4 h in an ice bath. After drying and resuspension in DI water, the particle size distribution was measured using DLS. Further characterization of the cutting process was performed with TEM analysis. Control experiments were conducted by

sonicating CNTs in DI water alone for 4 h to verify hydrogen peroxide was responsible for functionalization.

**Effect of sonication power on size reduction of CNTs**

Sonication power was studied by adding 15 mg of CNTs to 15 mL hydrogen peroxide (30%). The solution was autoclaved (15 psi, 121 °C) for 3 h. Next, the solution was equally divided into three vials. Each solution was sonicated for 2 h at powers of 4, 12 and 20 W in ice baths. Following sonication and resuspension in DI water, the size distribution was measured by DLS.

**Characterization of CNT functionalization**

To examine whether hydroxyl and carboxyl groups presented on the treated CNT surface or not, the dried CNT samples from previous experiments were loaded on an ATR/FTIR spectrometer (Spectrum One, Perkin Elmer, Waltham, MA). FTIR spectra were obtained accordingly. Here, the treated CNTs were prepared by having 15 mg of CNTs autoclaved in 15 mL of hydrogen peroxide for 3 h, and then sonicated at 4 W for 4 h.

To further confirm the presence of hydroxyl groups on the CNT surface, the treated CNTs were reacted with perfluoro-octanoyl chloride (Sigma Aldrich, St. Louis, MO) to examine if perfluoroalkyl groups were able to bind on CNT surface via esterification. 15 mg of dried and treated CNTs was resuspended in chloroform in a 3-neck round-bottom flask. Following the addition 0.26 g of $Na_2CO_3$, the solution was then purged in nitrogen and placed in an ice bath. 2.5 mmol (0.6 mL) of perfluoro-octanoyl chloride was added dropwise to the solution under agitation. The solution was allowed to react for 2 h. Excess solid $Na_2CO_3$ crystals were removed by centrifugation at 4,500 rpm for 20 min. The solution was then washed by centrifugation 6 times with FC-77 (3M, Minneapolis, MN) then twice with DI water at 19,000 g for 30 min. The final CNT pellet was dried in an oven. 5 mg of dried and fluorinated CNTs was resuspended in

0.7 mL of deuterium oxide ($D_2O$) and loaded into an NMR tube. 2 mg of sodium trifluoroacetate ($CF_3COONa$) used as the internal NMR standard was added to the aforementioned NMR tube containing fluorinated CNTs suspended in $D_2O$. The NMR tube was vortexed for 30 seconds and then sonicated in a sonication bath for 15 min. The $^{19}F$ NMR spectrum was obtained on a Varian Unity/Inova 400 MHz instrument (Sparta, NJ). Control experiments were conducted for pristine CNTs and CNTs treated with 3 h autoclave without sonication.

To further check for the existence of carboxyl groups, 15 mg of CNTs were autoclaved in 15 mL of hydrogen peroxide, then sonicated for 4 h at 4 W. After drying in an oven, 2 mg of the cut CNTs was added to 1 mL of DI water. The solution was briefly sonicated at 4 W to promote resuspension of the CNTs. Following addition of 1.5 mg of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (Sigma Aldrich, St. Louis, MO), the solution was agitated for 2 h at room temperature. 1 μg of Lucifer yellow (Sigma Aldrich, St. Louis, Missouri) was then added, and the solution was reacted for 12 h. After 5 washes with DI water by centrifugation at 19,000 g for 30 min, the solution was resuspended in 1 mL of DI water and briefly sonicated at 4 W. The absorbance of the solution was measured using a UV-Vis spectrophotometer (Du 730, Beckman Coulter, Brea, CA).

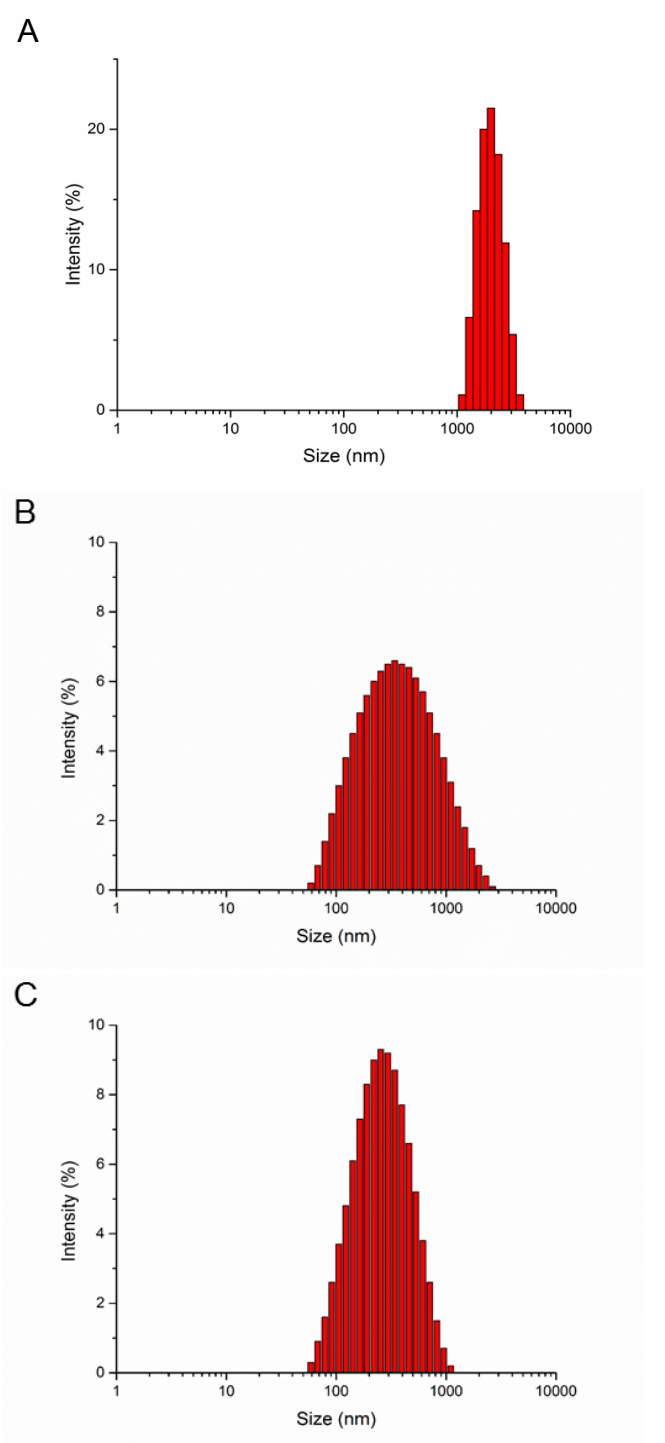


**Fig. S1** Particle size distribution when varying the autoclave time (A) 1 h, (B) 3 h and (C) 5 h. Sonication time and power were kept constant at 2 h and 4 W, respectively. The data represents one typical result of experiments performed in triplicate.

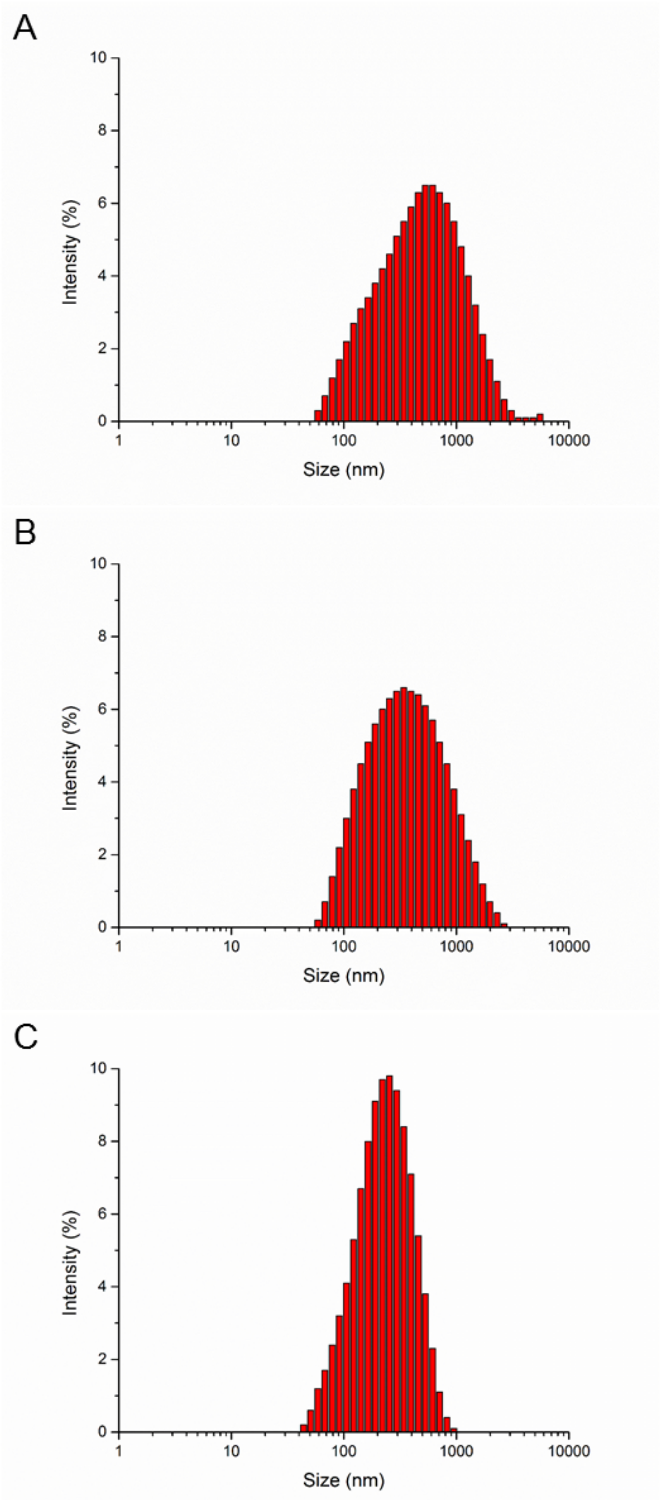


**Fig. S2.** Particle size distribution when varying the sonication duration (A) 1 h, (B) 2 h and (C) 4 h. Autoclave time and sonication power were kept constant at 3 h and 4 W, respectively. The data represents one typical result of experiments performed in triplicate.

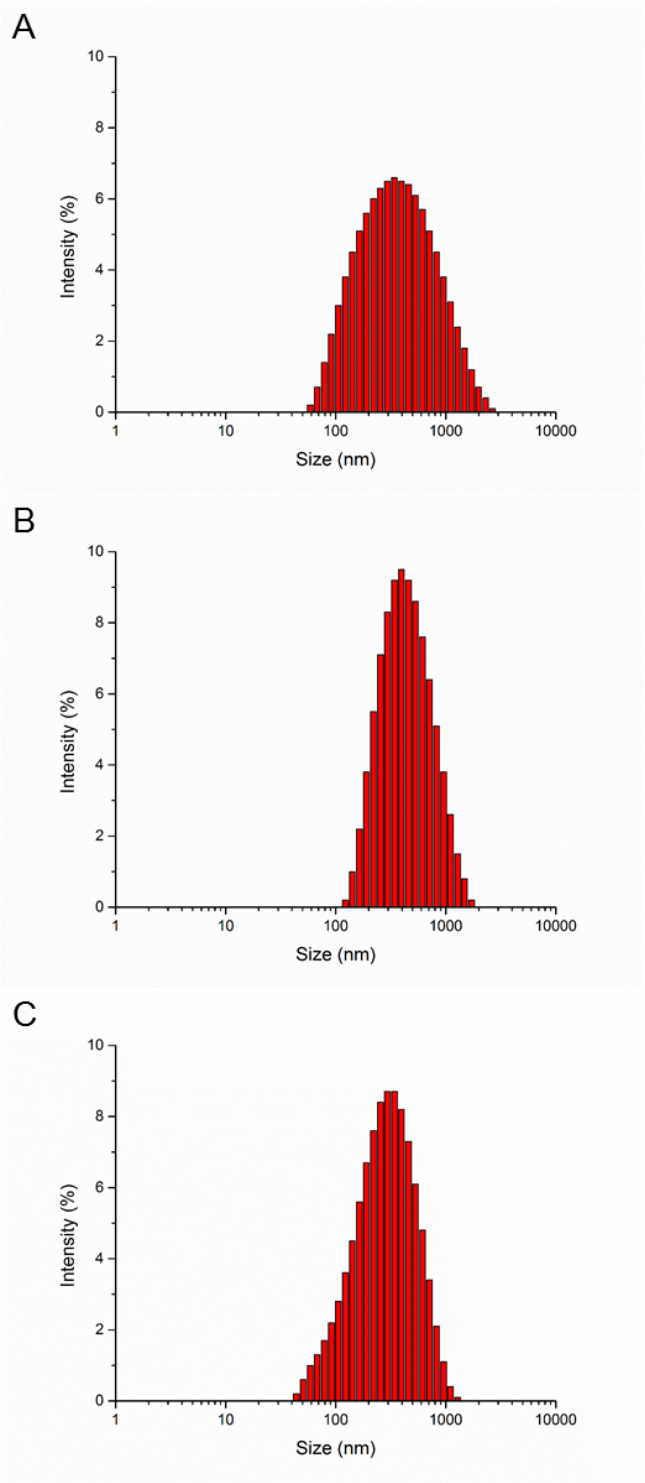


**Fig. S3.** Particle size distribution when varying the sonication power (A) 4 W, (B) 12 W and (C) 20 W. Autoclave time and sonication duration were kept constant at 3 h and 2 h, respectively. The data represents one typical result of experiments performed in triplicate.

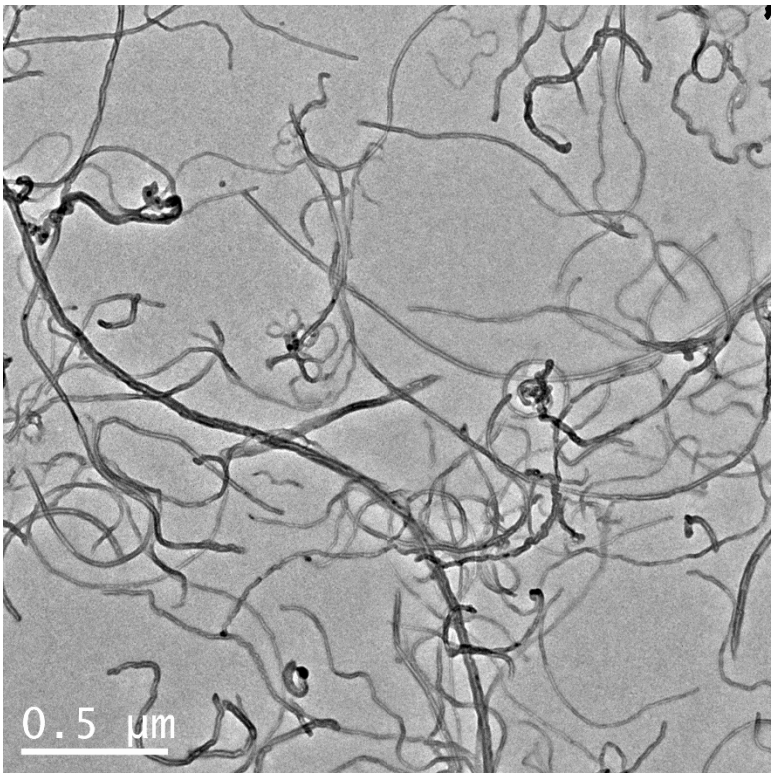


**Fig. S4.** TEM image of pristine CNTs.

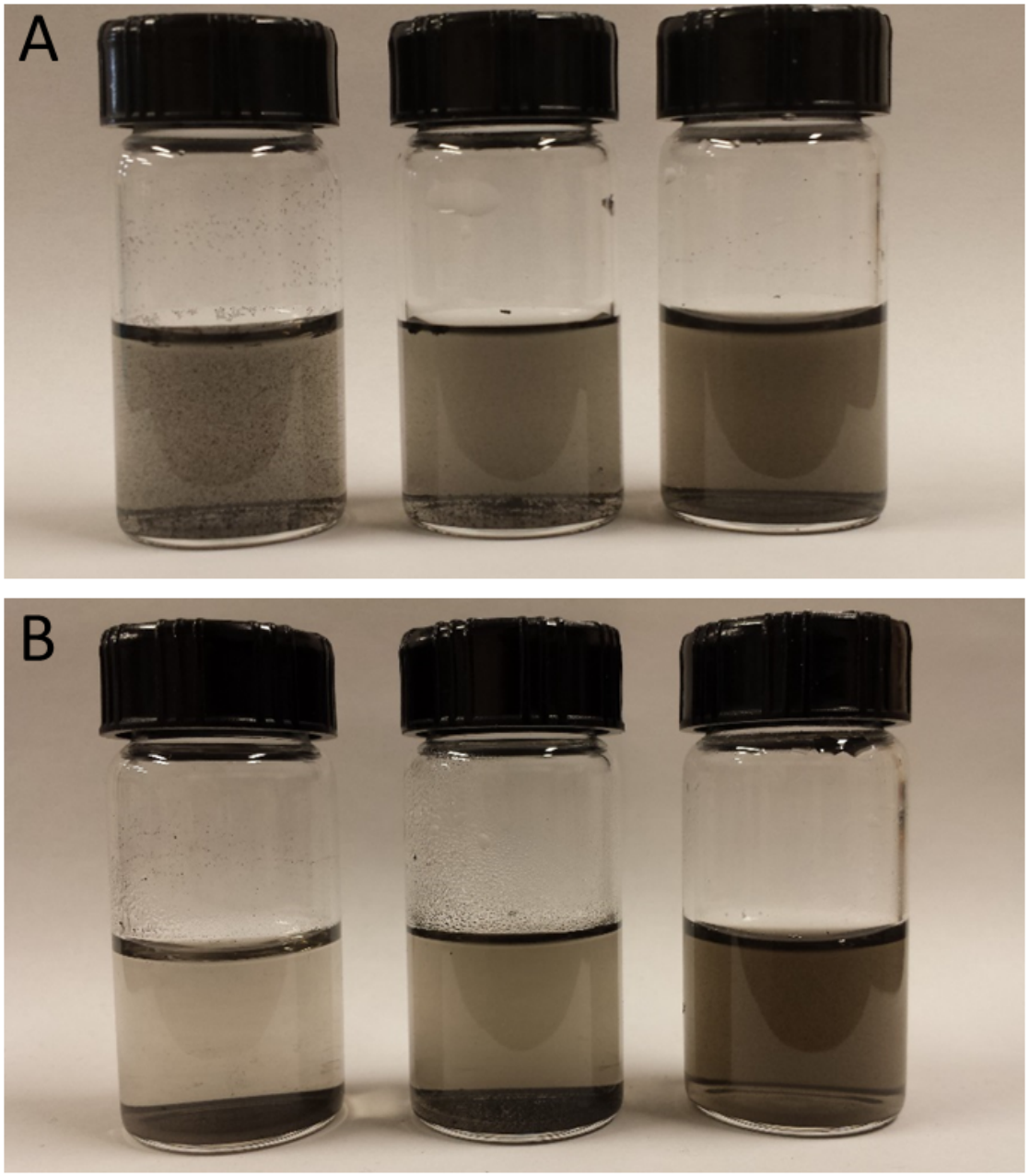


**Fig. S5.** Solubility of pristine CNTs (left), CNTs with 3 h autoclaving (middle), and CNTs with 3 h autoclaving and 4 h sonication (right) in water after 5 min of tip sonication (A) 0 h, and (B) 72 h. Note large amounts of CNT deposits were observed in the bottom of the vials after 72 h for pristine CNTs (B – left) and CNTs treated with autoclaving alone (B – middle).

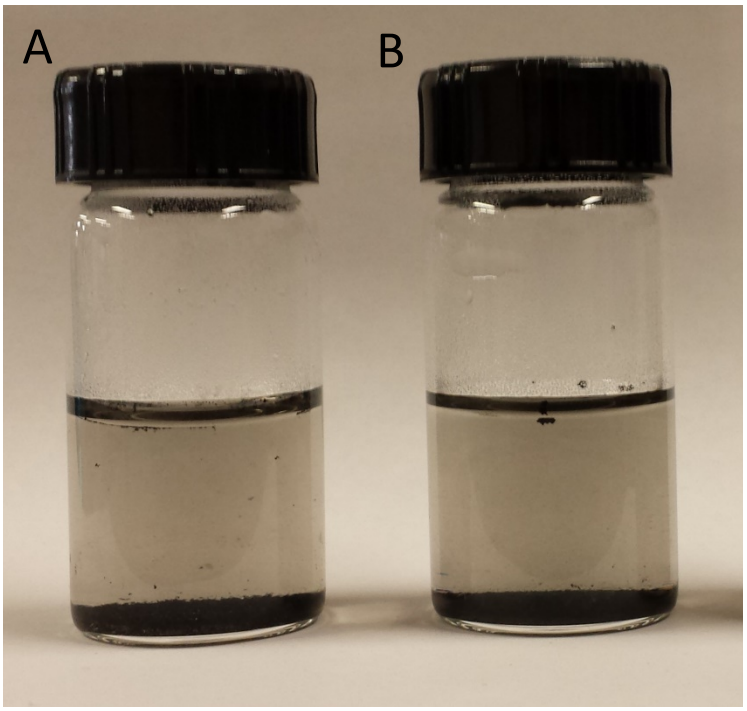


**Fig. S6.** Dispersibility of CNTs autoclaved or sonicated in DI water. (A) 3 h autoclaving, and (B) 4 h sonication.

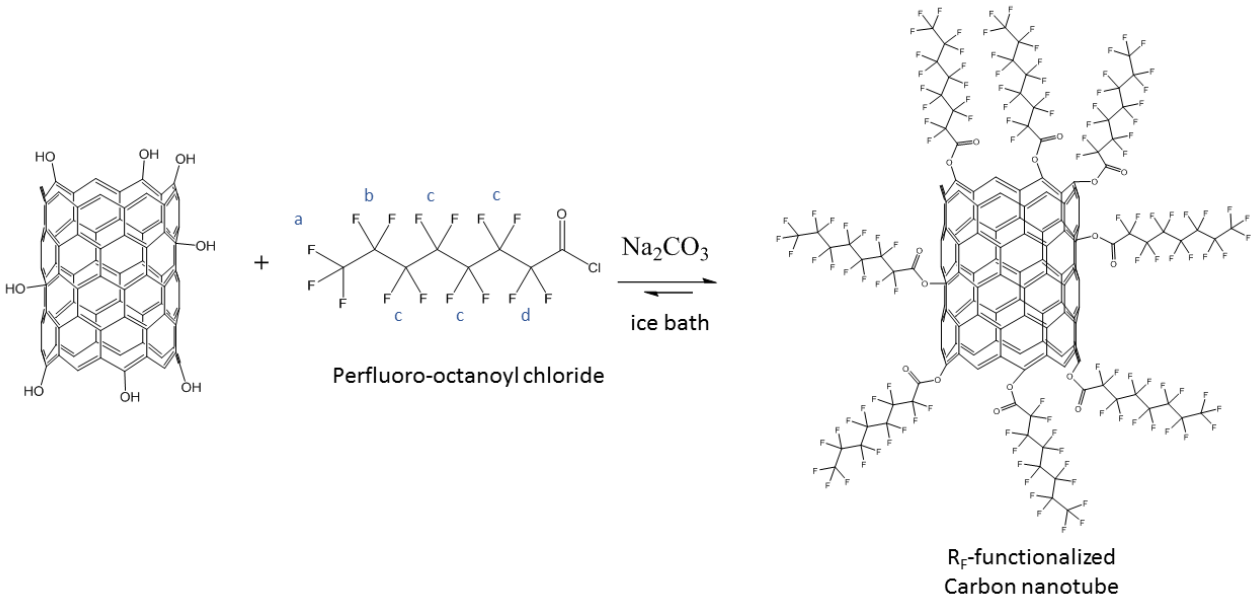


**Fig. S7.** Esterfication reaction of OH-Functionalized CNT with perfluoro-octanoyl chloride. CNT functionalized with perfluoroalkyl groups can be easily detected by $^{19}F$ NMR analysis.

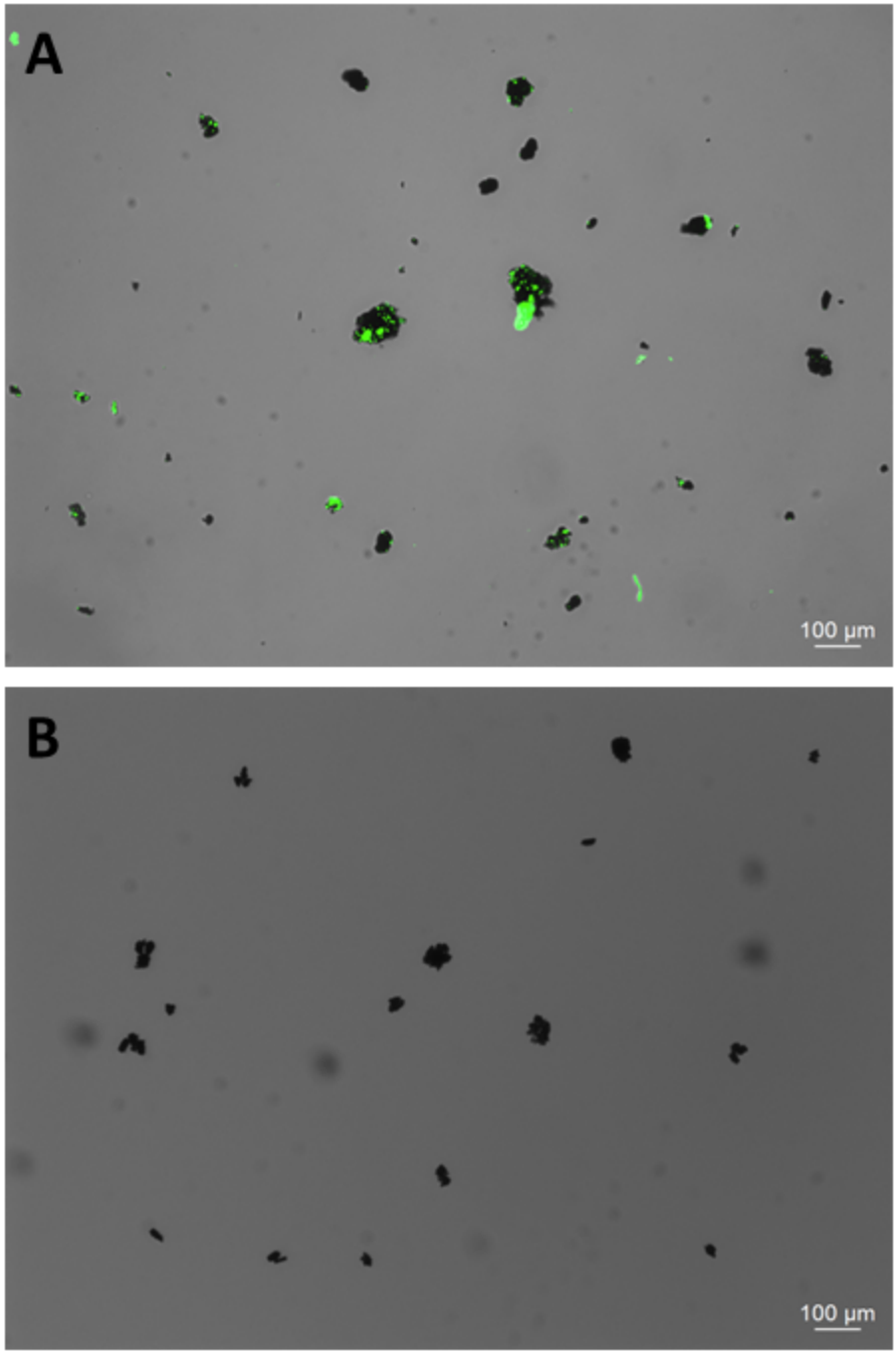


**Fig. S8.** Hydroxyl-functionalized CNTs were further derivatized and conjugated with streptavidin-FITC. (A) hydrogen peroxide treated CNTs and (B) control CNTs.