

Rational Design of Amphiphilic Polymers to Make Carbon Nanotubes Water-Dispersible, Anti-Biofouling, and Functionalizable

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Materials. Dodecyl methacrylate (dodecylMA), benzyl methacrylate (benzylMA), methacrylic acid, poly(ethylene glycol) methyl ether methacrylate (PEGMA, average $M_n = ca. 475$), and 2,2'-azobisisobutyronitrile were purchased from Aldrich Chemical Co. (Milwaukee, WI). Pluronic F-127 was purchased from BASF Corp. (Parsippany, NJ). Hipco[®] derived single walled carbon nanotubes were purchased from Carbon Nanotechnologies, Inc. (Houston, TX). (+)-Biotinyl-3,6,9-trioxaundecanediamine (biotin-amine) and streptavidin were purchased from Pierce (Rockford, IL). All organic solvents were used as received without further purification.

Measurements. ¹H NMR (300 MHz) spectra was recorded on a JEOL JNM-LA300WB FT-NMR (Tokyo, Japan). Organic phase gel permeation chromatography (GPC) was performed using a Waters 1515 series isocratic pump, a Rheodyne model 7725 injector with a 100 μ L injection loop at a flow rate of 0.4 mL min⁻¹. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Kratos AXIS Ultra Imaging X-ray Photoelectron Spectrometer with a monochromatized Al K X-ray source. The size and dispersion quality of polymer coated CNTs was examined by TEM using a TECNAI F20 electron microscope (Philips Electronic Instruments Corp., Mahwah, NJ) operated at 200 kV. For the TEM sample preparation, each polymer coated CNT was diluted and deposited on a copper grid and allowed to air-dry. AFM measurements were performed on a Digital Instruments Multimode AFM, controlled by a Nanoscope IIIa scanning

probe microscope controller. The AFM was equipped with Quadrex for phase imaging and was stabilized by Micro 40 active anti-vibration unit (Halcyonics). Tapping mode etched silicon probes (RTESP) (Veeco probe) were used. Raman spectra were acquired from dispersion of free CNTs and poly-1 coated CNTs. Dispersions were dispensed directly onto slide glass and analyzed. All Raman spectra were acquired using an inVia reflex Raman Microscope (Renishaw, England) equipped with a 50X, N/A = 0.85 objective lens. The laser excitation wavelength, spectral resolution, and typical excitation intensity were 633 nm, $\sim 1\text{-}2\text{ cm}^{-1}$, 1.7 mW, respectively. The 632.8 nm laser excitation was provided by a He-Ne laser operated at 17 mW.

Synthesis of amphiphilic polymers. The synthetic procedure of poly-1 was briefly described as follows. DodecylMA (4 mmol, 1.016 g, 2 equiv), PEGMA (4 mmol, 1.9 g, 2 equiv), and methacrylic acid (2 mmol, 0.172 g, 1 equiv) were dissolved in 10 mL of THF (anhydrous, 99.9%, inhibitor-free). This mixture was degassed for 15 min by bubbling with stream of N₂ gas. After adding 0.1 mmol of 2,2'-azobisisobutyronitrile (16.4 mg, 0.05 equiv) as a radical initiator, the vial was sealed with a Teflon-lined screw cap. The polymerization reaction was carried out at 70 °C for 24 h. The final product solution cooled to room temperature and stored at 4°C until use. BenzylMA were substituted for dodecylMA for the synthesis of poly-2 and others were the same as described above. Each polymer was characterized by ¹H NMR and gel permeation chromatography. ¹H NMR (300.40 MHz, DMSO-d⁶): poly-1 δ = 4.05 (br, 2H, CO₂-CH₂ of PEGMA), 3.82 (br, 2H, CO₂-CH₂ of dodecylMA), 3.66 (s, 30H), 3.40 (s, 3H), 2.0-1.71 (br, 10H), 1.5-1.1 (br, 20H), 0.87 (br, 3H); poly-2 δ = 7.30 (s, 5H), 4.93 (br, 2H,

CO₂-CH₂ of benzylMA), 4.05 (br, 2H, CO₂-CH₂ of PEGMA), 3.66 (s, 30H), 3.40 (s, 3H), 2.0-1.71 (br, 10H), 0.87 (br, 3H), 0.72 (br, 4H).

GPC: poly-**1** ($M_n = 19581$ with $M_w/M_n = 1.88$), poly-**2** ($M_n = 21831$ with $M_w/M_n = 1.97$).

Dispersion experiments of CNTs. In a typical dispersion experiment, CNTs were suspended in 1 ml polymer solution (1 wt%, 10 mg ml⁻¹). The mixture was kept in an ice-water bath and sonicated for 20 min using a VCX-500 Ultrasonic Processor (Sonics & Materials, Inc., Newtown, CT) at a power level of 80W. After sonication, the mixture was centrifuged for 10 min at 1500 g to remove aggregated materials.

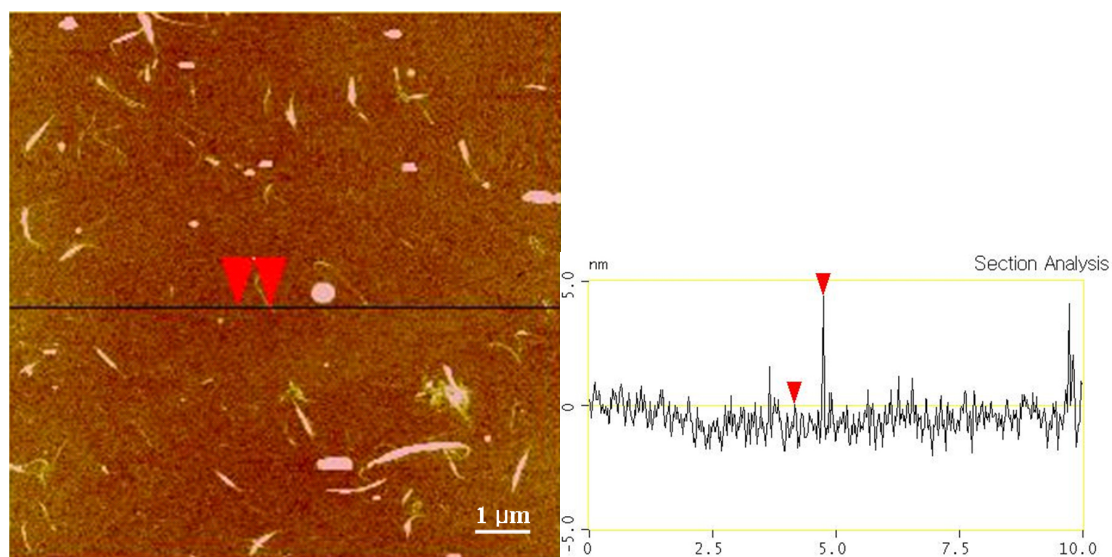


Fig. S1. A height contrast AFM image of the poly-**1** coated CNTs.

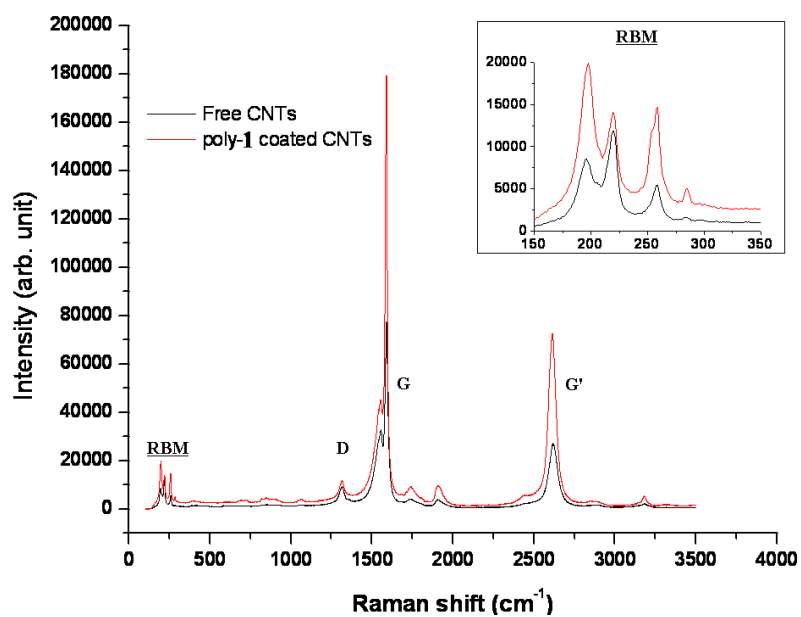


Fig. S2. Raman spectra of bare CNTs (black line) and poly-1 coated (red line) CNTs using 632.8 nm excitation.



Fig. S3. A photograph of Pluronic F-127 coated CNTs after incubation in 10% serum-containing medium for 3 days.

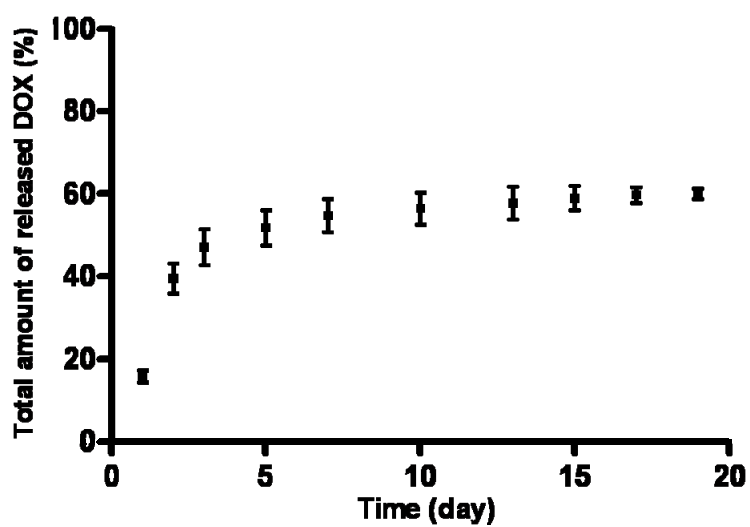


Fig. S4. The drug release profile from the Dox-loaded CNTs measured upon incubation in phosphate buffered saline (pH 7.4) at 37 °C.