# ELECTRONIC SUPPLEMENTARY INFORMATION

## Robust Polyelectrolytes Microcapsules Reinforced with Carbon Nanotubes

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## EXPERIMENTAL DETAILS

### Materials

Poly(sodium styrenesulfonate) (PSS, $M_w \approx 70$ kDa), poly(diallydimethyl ammonium) chloride 35 wt. % in water (PDADMAC, very low molecular weight $M_w < 100$ kDa), branched polyethylenimine (PEI, $M_w = 25$ kDa), multi-walled carbon nanotubes (MWCNTs, >98% carbon basis, internal diameter: 4.5 nm, external diameter: 10 nm, length: 3-10 μm), dextrans labeled with fluorescein isothiocyanate (FITC-dextran, $M_w = 4$ kDa and 70 kDa), ethylenediaminetetraacetic acid (EDTA, p.a.) were all purchased from Aldrich. Sodium carbonate ($Na_2CO_3$), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), rhodamine B, were purchased from POCH (Gliwice, Poland) (all p.a.). All chemicals were used as received, without further purification unless stated otherwise. Deionized water was used in all the experiments.

### Procedures

***Preparation of $CaCO_3$ particles with embedded MWCNTs.*** Briefly, a mixture of 0.0175g of MWCNTs and 0.8g of PSS in 60 ml of water was sonicated using a Ultrasonic Homogenizer UP50H (the power of the instrument : 50 W, the mode of action: continuous) with titanium sonotrodes in an ice bath for 0.5h or 3h to provide a negative charge at the nanotubes surface and to shorten their length. The obtained suspensions were then mixed with 20 ml of 0.075 M $Na_2CO_3$ aqueous solution and the same volume of 0.075 M $Ca(NO_3)_2$ solution. The final concentration of PSS was 8 g/L. The mixture was then sonicated for 6 min. The precipitated $CaCO_3$ particles with embedded MWCNTs ($CaCO_3$-MWCNTs) were immediately washed with water and centrifuged at 4000 rpm for 10 min (at least three times).

***Preparation of $CaCO_3$ particles.*** $CaCO_3$ template microparticels were prepared following the method previously described.[1] Briefly, 50 ml of 0.03 M $Na_2CO_3$ aqueous solution was mixed with the same volume of 0.03 M $Ca(NO_3)_2$ solution containing PSS. The final PSS concentration was 2 g/L. The mixture was then sonicated for 6 min. The precipitated $CaCO_3$ particles were immediately washed with water and centrifuged at 4000 rpm for 10 min (at least three times).

***Preparation of hollow microcapsules.*** PEMs were deposited on $CaCO_3$ and $CaCO_3$-MWCNTs microparticles using layer-by-layer technique. PDADMAC and PSS (both at concentration 2 g/L) in 0.25M NaCl aqueous solutions were applied for that purpose. After each layer deposition, the excess of polyelectrolytes was removed by at least three cycles of centrifugation at 4000 rpm for 5 min, washing and redispersing the microparticles in water. The procedure was repeated until 5 bilayers were deposited. Then, the cores were removed by placing the microparticles in 0.1 M EDTA solution (pH=7, adjusted by NaOH) under stirring for 1 h. Such obtained hollow capsules were filtrated, washed three times with EDTA solution and three times with water.

**Apparatus**

***Scanning Electron Microscopy (SEM).*** SEM images were obtained using Hitachi S-4700 microscope with an operation voltage of 10 kV or 20 kV. Samples were prepared by applying a drop of particles or capsule suspension on to a silicon plate pre-coated with PEI, drying under argon and coating with sputtered gold layer before imaging.

***Scanning Transmission Electron Microscopy (STEM).*** STEM images with High Angle Annular Dark Field detector were obtained using FEI TecnaiOsiris with operation voltage 200kV. A drop of aqueous suspension of microcapsules was deposited onto Cu grid (lacey carbon, AGAR Scientific). Statistical analysis of the STEM images of MWCNTs-PSS were performed using ImageJ software.

***Transmission Electron Microscopy (TEM).*** TEM images were obtained using a Tecnai F20 TWIN microscope (FEI Company, USA) equipped with field emission gun, operating at an acceleration voltage of 200 kV. Images were recorded using Eagle 4k HS camera (FEI Company, USA) and processed with TIA software (FEI Company, USA). Specimen preparation was done by dropping of the solution on grids with holey carbon film (Quantifoil R 2/2; Quantifoil Micro Tools GmbH, Germany). Prior to use, the grids were activated for 30 seconds in oxygen plasma using a Femto plasma cleaner (Diener Electronic, Germany). The

sample was prepared by applying a droplet (5.0 μL) of the capsule's solution onto a grid and then blotting with filter paper.

***Confocal Laser Scanning Microscopy (CLSM).*** The permeability of the capsules was determined using CLSM. Images were acquired using an A1-Si Nikon (Japan) confocal laser scanning system built on a Nikon inverted microscope T*i*-E using a Plan Apo 100×/1.4 Oil DIC objective. Two diode lasers (488 and 561 nm) were used for excitation. Images were acquired at a resolution of 1024×1024 pixels. The capsules suspension was mixed with the fluorescent probe so that the final concentration of the used FITC-dextrans was 1 g/L. The measurements were taken after 10 min and 150 min of magnetic stirring. A droplet of the suspension was then placed on a glass slide, covered with a cover slip and sealed using nail lacquer. This ensured that evaporation of water did not occur and thus concentration of the fluorescence probe remained constant during the measurements.

***Dynamic Light Scattering (DLS).*** The DLS measurements were performed using a Malvern Nano ZS instrument working at 173° detection angle, at 22°C in water. The reported values of hydrodynamic radiuses and ζ-potentials were averaged from three parallel measurements (10-100 runs each).

***Atomic Force Microscopy (AFM)***. AFM images were obtained with Dimension Icon AFM (Bruker, Santa Barbara, CA) working in the PeakForce Tapping® (PFT) mode with standard silicon cantilevers for measurements in air (nominal spring constant of 0.4 N/m). The capsule wall thickness was determined from the cross-section profiles of the captured images, using method introduced previously and commonly used elsewhere.[2] Measurements of the height difference between the surface of silicon substrate and the dried hollow capsules were taken from the regions free of folds with minimum height. Measurements of 10 capsules in several spots on each capsule were averaged. The measured values were regarded as twice the wall thickness.

***Thermogravimetric analysis (TGA).*** TGA was performed using SDT Q600 Simultaneous Thermal Analyzer. First, water was evaporated from the suspension of capsules. Then as prepared sample was heated in air flow from room temperature to 900 °C with a ramp rate of 5°C/min.

**RESULTS**

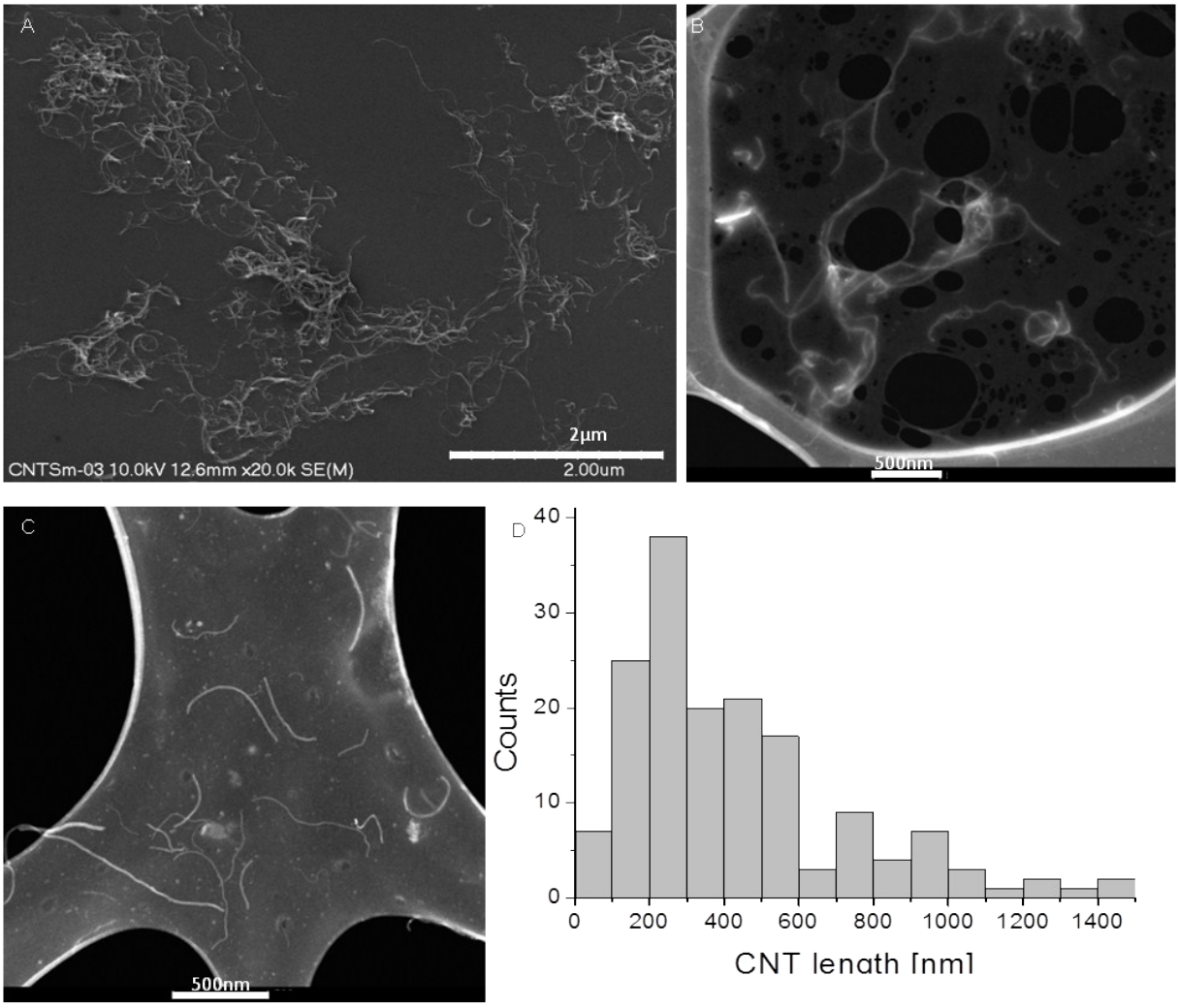


Figure S1. (A) SEM images of non-treated MWCNTs; (B) STEM images of MWCNTs wrapped by PSS after 0.5 h of soniction and (C) after 3h of sonication; (D) histogram of the lengths of wrapped MWCNTs after 3h of sonication.

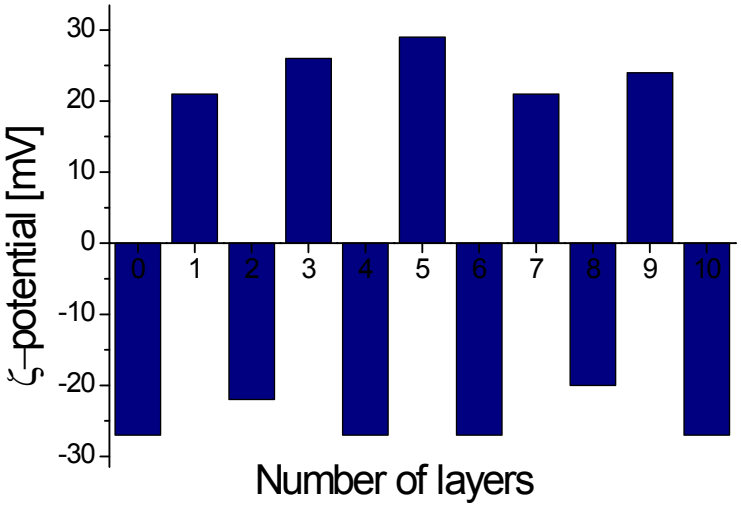


Figure S2. ζ-potential changes as a function of number of PDADMAC and PSS polyelectrolyte layers deposited on $CaCO_3$-MWCNTs cores.

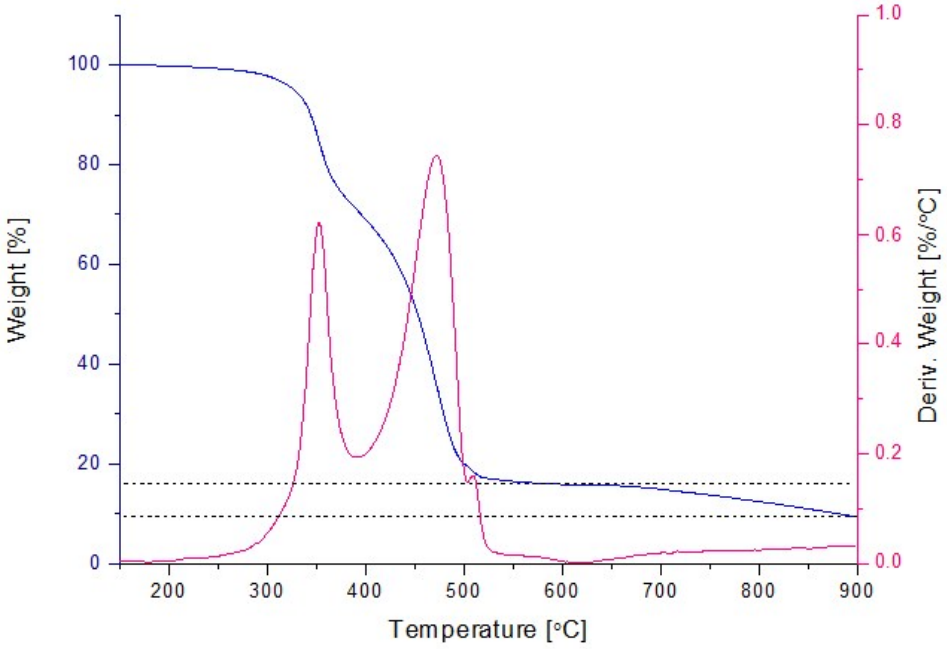


Figure S3. Thermograwimetric analysis (TGA) of MWCNTs-$(PDADMAC/PSS)_5$ capsules. The horizontal dotted lines indicate the difference in mass related to decomposition of MWCNTs.

TGA plot presented in Fig. S3 is typical for PEMs up to ca. 580°C when it flattens. Above this temperature MWCNTs start to decompose and continue up to ca. 900 °C.[3] Thus, based on Fig. S3 one can determine the content of MWCNTs in MWCNTs-$(PDADMAC/PSS)_5$ capsules to be ca. 7% (distance between the two dotted lines in Fig. S3).

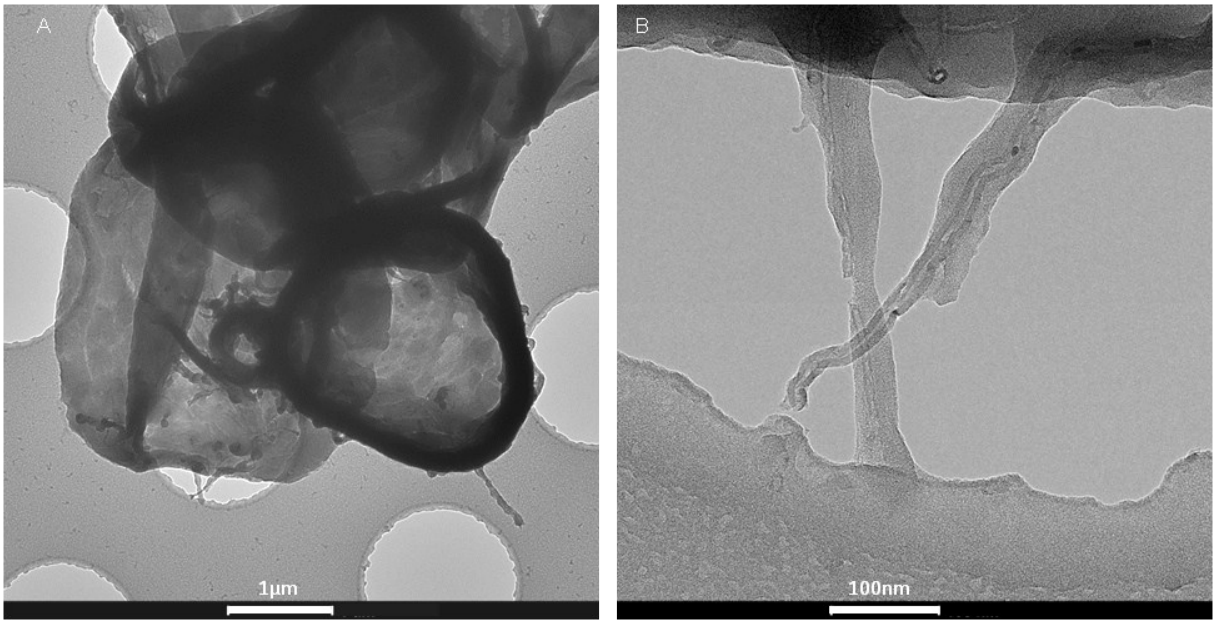


Figure S4. TEM images of (A) hollow MWCNTs-$(PDADMAC/PSS)_5$ capsules; (B) magnification of (A).

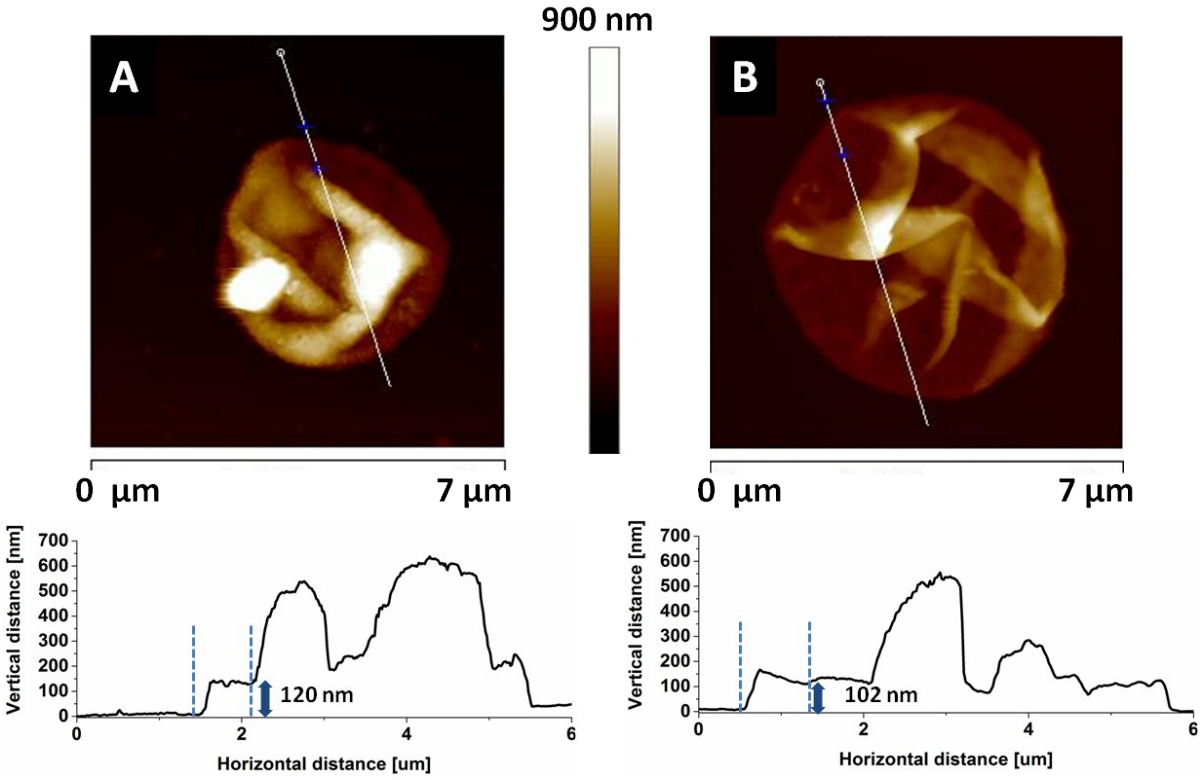


Figure S5. Representative AFM images of (A) $(PDADMAC/PSS)_5$ and (B) MWCNTs-$(PDADMAC/PSS)_5$ capsules with respective cross-section profiles.

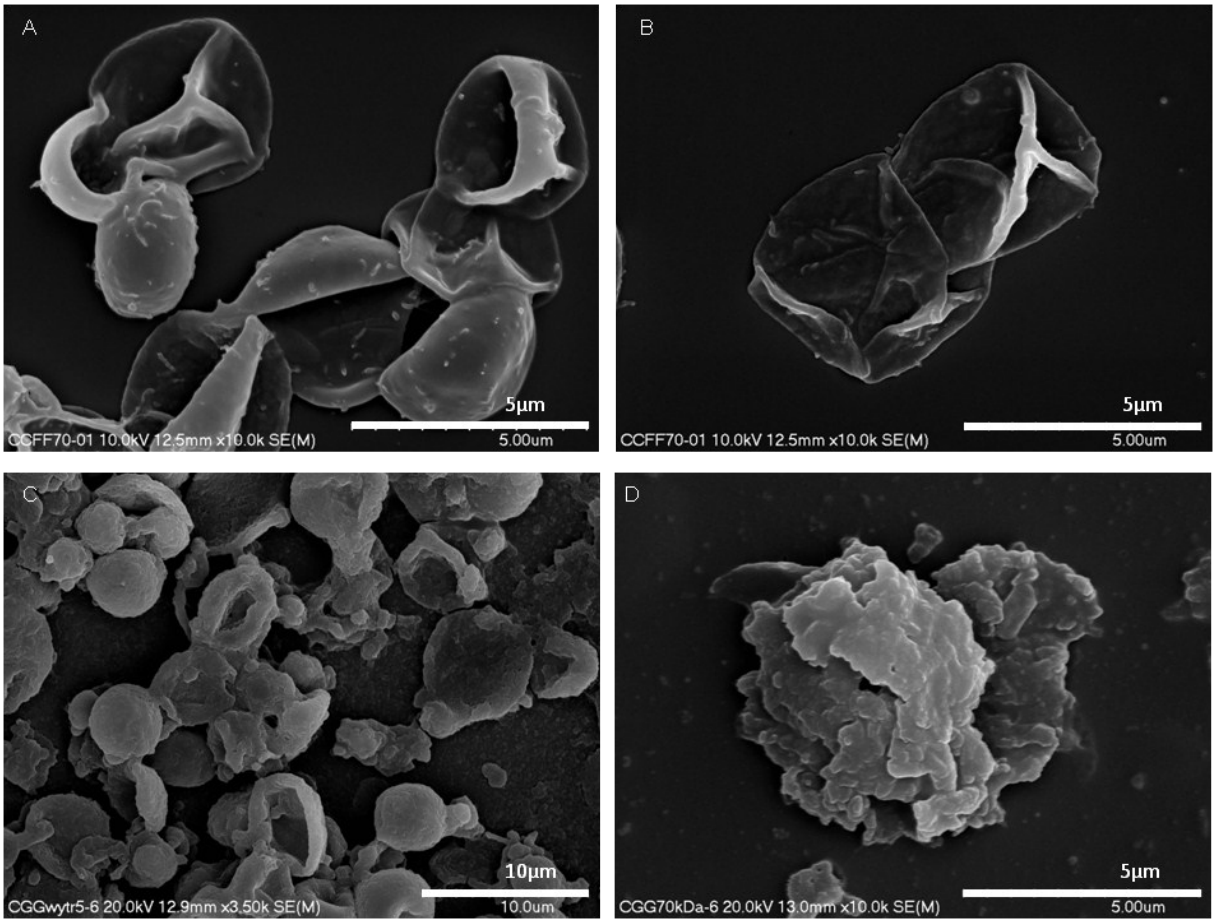


Figure S6. Representative SEM images of MWCNTs-(PDADMAC/PSS)$_5$ capsules (A) before and (B) after incubation in 1 g/L FITC-dextran(70 kDa) solution; and (PDADMAC/PSS)$_5$ capsules (C) before and (D) after incubation in 1g/L FITC-dextran(70 kDa) solution.

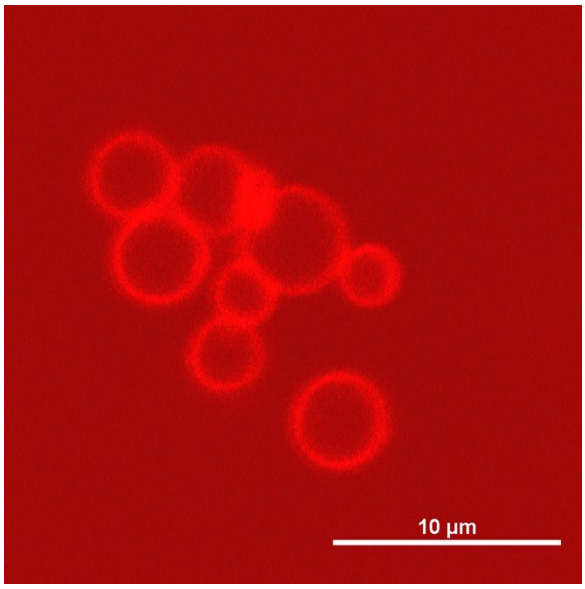


Figure S7. CLSM image of MWCNTs-(PDADMAC/PSS)$_5$ capsules incubated in Rhodamine B solution for 10 min.

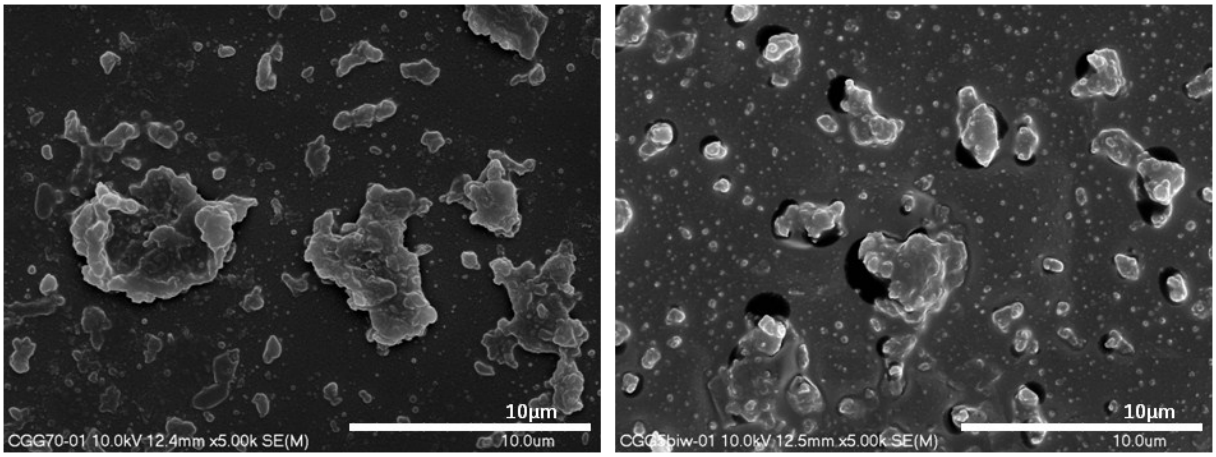


Figure S8. SEM images of $(PDADMAC/PSS)_5$ capsules kept 4 weeks in water.

[1]W. Tong, W. Dong, C. Gao, H. Möhwald, *J. Phys. Chem. B.*, **2005**, 109, 13159.
[2] S. Leporetti, A. Voigt, R. Mitlöhner, G. Sukhorukov, E. Donath, H. Möhwald, *Langmuir*, **2000**, *16 (9)*, 4059.
[3] Y.-H. Nien, The Application of Carbon Nanotube to Bone Cement, Carbon Nanotubes - Polymer Nanocomposites, Dr. Siva Yellampalli (Ed.), ISBN: 978-953-307-498-6, InTech, **2016**.