Supplementary Information

Materials

Sodium poly (styrene sulfonate) (PSS, Mw ~70000), poly (allylamine hydrochloride) (PAH, Mw ~70000) were obtained from Aldrich. Dextran amino (Mw 10000) and 4'-(aminomethyl) fluorescein hydrochloride (fluoresceinamine) were purchased from Molecular Probes. Poly (ethylene glycol) acrylate (acrl-PEG, Mn ~375) and acrylate-poly(ethylene glycol)-NHS (acrl-PEG-NHS, Mw ~3400) were obtained from Aldrich and Nektar respectively. UV initiator Irgacure 184 (Ciba) was freshly prepared at 20 mg/mL in DMF solution. Monodisperse $MnCO_3$ microparticles (5 μm) were synthesized as described in our previous work (ref. 8). For confocal fluorescence microscopy, dextran amino and PAH were labeled with rhodamine isothiocyanate (RITC, Aldrich) and fluorescein isothiocyanate (FITC, Aldrich) respectively in pH 8.5 sodium bicarbonate buffer and precipitated in acetone.

Fabrication of polyelectrolyte multilayers microcapsules

The PSS and PAH solutions used for alternating adsorption of {PSS/PAH} multilayers on $MnCO_3$ template were prepared in DI water at 2 mg/mL with 0.5 M NaCl. The $MnCO_3$ particles were suspended in DI water via vortexation and ultrasonication for 10 min prior to layer-by-layer assembly. The positively-charged particles were coated with eight bilayers of {PSS/PAH}, where each adsorption step reaction time was 20 min, followed by triple rinsing with DI water. The $MnCO_3$ cores were then dissolved by 0.1 M HCl solution, followed by 0.01 M EDTA solution treatment to remove residual manganese ions. The microcapsules obtained were again triple rinsed with DI water.

Polymerization of PEG monomers in polyelectrolyte multilayer microcapsules

For polymerization of PEG monomers in microcapsules, 25 μL of acrl-PEG, 25 μL of UV initiator, and 20 μL of the microcapsules were mixed with 430 μL of DI water (total 500 μL) in 1 mL microcentrifuge tube. The mixture was then exposed to UV light for 10 min with gentle stirring. The obtained highly viscous product was rinsed with DI water and then centrifuged three times. Alternatively, 20 mg of acrl-PEG-NHS

and 10 μL of acrl-PEG (rather than 25 μL of acrl-PEG) were used for the functionalization of PEG microspheres.

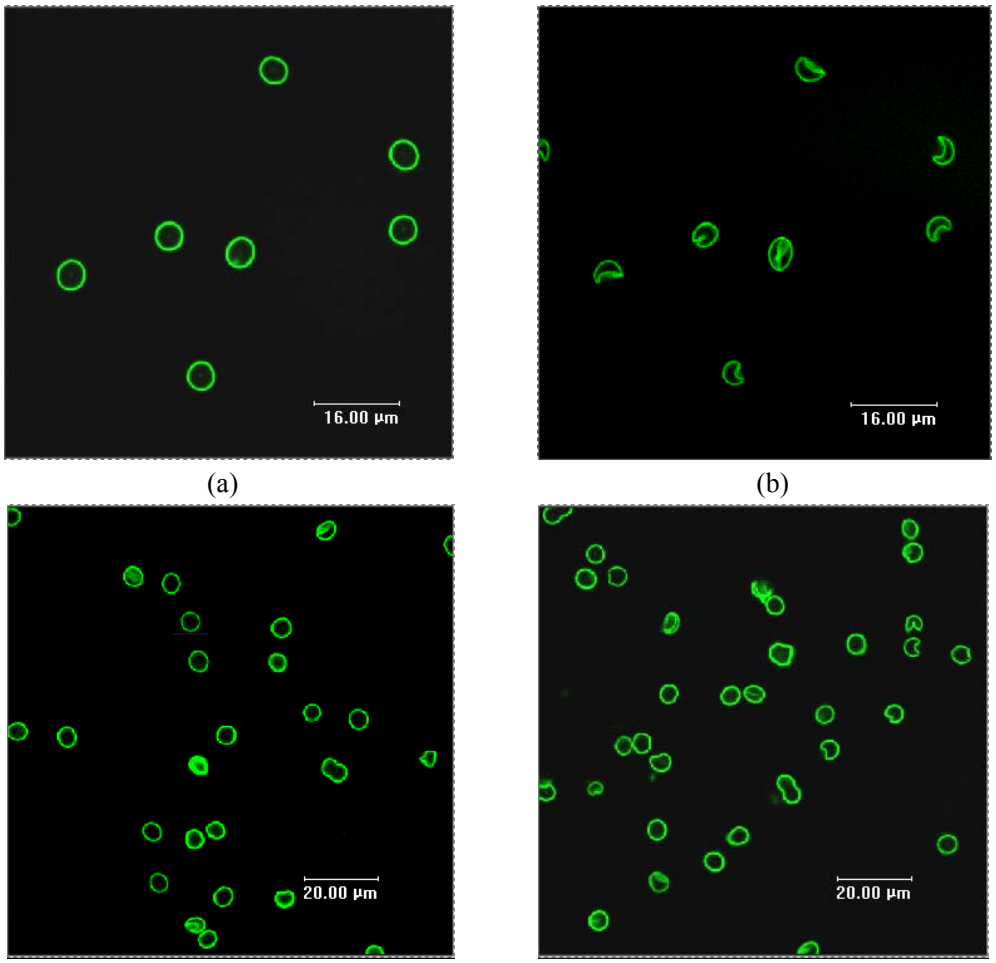
Functionalization of PEG microspheres

For functionalization of PEG microspheres, two conjugation techniques were used. One is pre-mix and conjugates acrl-PEG-NHS monomer with amine containing molecules (fluoresceinamine) and then polymerize within microcapsules; the other is polymerize acrl-PEG-NHS monomer first and then conjugate amino containing molecules (dextran amino) to PEG hydrogel microspheres after rinsing. For NHS/amine conjugation step, a pH 8.5 sodium bicarbonate buffer was used and the reaction was kept for 1 hr.

Instrumentation and Measurement

The assembly of polyelectrolyte layers on colloidal templates was monitored by electrophoretic mobility measurements (ZetaPlus Zeta Potential Analyzer, Brookhaven Instrument Corp.). Fourier transform infrared spectroscopy (Nexus 470 FTIR) was used to analyze the PEG hydrogel microspheres after polymerization and rinsing with DI water. PEG microspheres samples (PEG hydrogel microspheres and dextran amino functionalized PEG hydrogel microspheres) were also dried on silica wafer at room temperature and sputter-coated with Au-Pd alloy for scanning electronic microscopy (SEM, Amray 1830) study. The acceleration potentials used to collect SEM images was 10 KV in our study. Confocal micrographs were taken with a Leica TCS SP2 equipped with a 63× oil-immersion objective, using the 488/514 nm lines of an Ar/Kr laser for FITC/RITC excitation, respectively. Osmotic pressure measurements were also imaged with confocal microscopy by adding 10 μL of 0.5 M NaCl solution to 10 μL of empty microcapsules or PEG hydrogel microspheres on slide.

Osmotic pressure measurements



(a) (b)

(c) (d)

Figure 1. Confocal images of osmotic pressure measurements. (a) $\{PSS/PAH\}_8$ microcapsules and (c) PEG microspheres in DI water, (b) $\{PSS/PAH\}_8$ microcapsules and (d) PEG microspheres in 0.25 M NaCl solution, PAH labeled with FITC.

Under confocal microscopy, it could be seen clearly that the empty polyelectrolyte multilayer microcapsules collapsed immediately upon adding of the NaCl salt solution because of the osmotic pressure, while most of the PEG microspheres remained spherical because of the existence of hydrogel inside the microcapsules

FTIR analysis

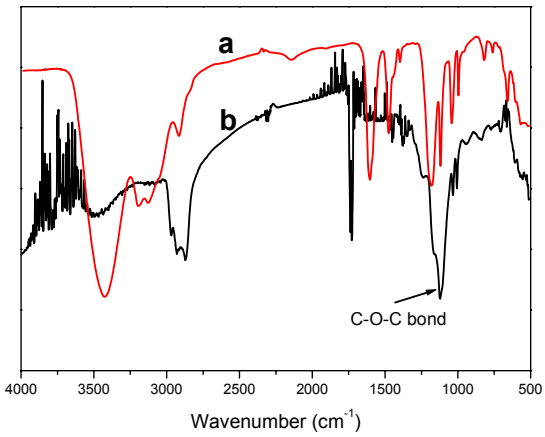


Figure 2. FTIR spectrum of (a) $\{PSS/PAH\}_8$ microcapsules and (b) PEG microspheres.

Comparing with the FTIR spectrum of $\{PSS/PAH\}_8$ microcapsules, it could be seen there is a significant peak at 1100 cm^{-1} on the FTIR spectrum of PEG hydrogel microspheres, which specifically contributes to ether bond on PEG polymer chain.