Programmable co-assembly of oppositely charged microgels

Dennis Go,[a,b] Thomas E. Kodger,[b] Joris Sprakel,[c] and Alexander J. C. Kuehne[a]

[a] DWI - Leibniz Institute for Interactive Materials, RWTH Aachen University, 52074 Aachen, Germany.
[b] Harvard University, School of Engineering and Applied Sciences, Cambridge, MA 02138, USA.
[c] Laboratory of Physical Chemistry and Colloid Science, Wageningen University, 6703 HB Wageningen, The Netherlands.

SUPPORTING INFORMATION

Experimentals

Field emission scanning electron microscopy is performed on an S-4800 microscope (Hitachi) to determine the morphology of the synthesized core particles. Before imaging, particles dispersions are deposited and dried on a silicon wafer (CrysTec GmbH).

Zeta potential measurements are carried out at 25 °C using a Zetasizer Nano ZS from Malvern Instruments. The samples are prepared by diluting 50 µL of particle dispersions with 2 mL of the corresponding buffer solution. Every data point represents an average value of three measurements (except for the time-dependent measurement in Fig. 2d, where only one measurement was performed for each data-point). Each measurement consists of a set of runs, which is performed until convergence (max. 100 runs). The Malvern software calculates the zeta potential from the electrophoretic mobility based on the Helmholtz-Smoluchowski relationship.

Confocal laser scanning microscopy is performed on a Leica TCS SP8 to visualize the mixture of fluorescently labeled particles and to analyze their dynamics. The sample chamber is made from a glass substrate and three stacked cover slides to form a closed channel. The channel is sealed using commercial fast curing adhesive. The anionic and amphoteric particles are imaged using different excitation laser lines and separate detectors, each corresponding to the fluorescence profiles of the employed fluorescent markers.

Transmission electron microscopy is carried out using a Zeiss Libra 120 operating at 120 kV in zero-loss energy-filter mode. Microgel dispersions are dried on carbon-coated copper grids (Electron Microscopy Sciences) at room temperature before imaging.

Dynamic light scattering measurements are performed with a laser light scattering spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000/EPP multiple digital time correlator and laser goniometry system ALV/CGS-8FS/N025 with a helium-neon laser (Uniphase 1145P, output power of 22 mW and wavelength of 632.8 nm) as a light source.

Synthesis of the poly(2,2,2-trifluoroethylmethacrylate) core particles: The fluorescent core particles are synthesized by emulsion polymerization of 2,2,2-trilfuoroethyl methacrylate (TFMA) initiated with 0.2 mol% of potassium peroxodisulfate (KPS). 10.0 mg of the fluorescent marker, either Nile Red or Coumarin 7, is dissolved in 10.0 ml (0.07 mol) TFMA. The organic phase is transferred into a three-necked round bottom flask and 30.0 ml of deionized water is added. 0.32 mg of the sodium dodecyl sulfate (SDS) is added as a surfactant and 0.94 g of *N*-isopropylacrylamide (NIPAAm) is added to the emulsion. While degassing the reaction mixture with argon, it is heated up to a temperature of 80 °C and

reacted for 4 hours after addition of KPS in 2.5 mL of water. The resulting dispersion is filtered and dialyzed against deionized water for at least 3 days to remove residual reactants.

Synthesis of PTFMA-core-PNIPAAm-shell particles: 3.90 g (0.03 mmol) of NIPAAm, 1.0 wt% of the cross-linker *N*,*N*'-methylenebis acrylamide (MBA) and 8 wt% of acrylic acid (AAc) are dissolved in 150 ml of deionized water. The amount of added core particles dependends on their volume fraction and the desired final size of the core-shell particles. The reaction mixture degassed using argon and heated up to a temperature of 70 °C and then initiated by the addition of 4.0 ml of aqueous solution of 0.15 mg (0.06 mmol) of KPS. The core-shell particle solution is filtered and purified by centrifugation and washing with deionized water.

Post-modification with 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC)/ N-Hydroxysuccinimid (NHS)-coupling: To obtain amphoteric particles, the Coumarin 7 labeled core-shell particles are modified via EDC/NHS-coupling. First a solution of NHS (10 fold excess with respect to AAc groups inside the microgel) in 5.0 mL MES buffer (2-(*N*-morpholino)ethansulfonic acid, 20 mM, pH 5) is added. Then, 5 mL of MES buffer solution containing 4 fold excess of EDC with respect to AAc in the microgel is added. After 15 minutes, a 10 fold excess with respect to AAc of *N*,*N*-dimethylethylendiamine in 5.0 mL HEPES buffer (2-[4-(2-hydroxyethyl)piperazin-1- yl]ethanesulfonic acid, 100 mM, pH 7.5) is added to the dispersion and agitated for a min. of 4 hours. The post-modified core-shell particles are purified by centrifugation.

Characterization of PFEMA core particles

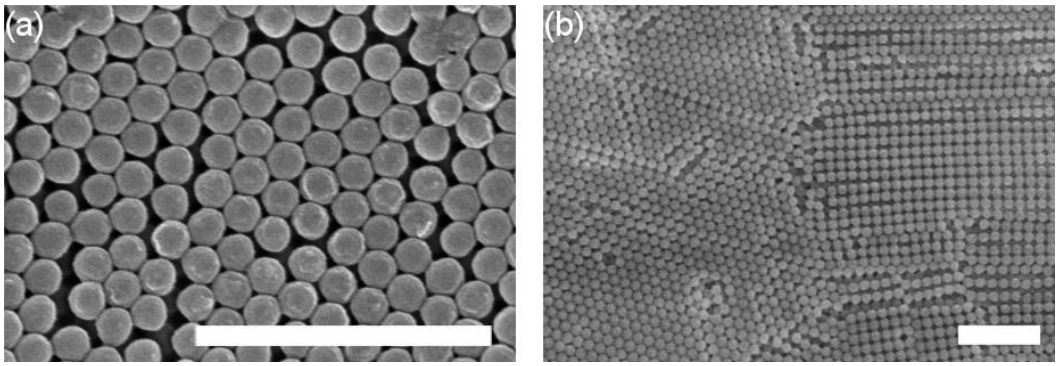

Fig.S1 (a,b) Scanning electron micrographs display monodisperse and dense poly(TFMA) core particles, prepared in an emulsion polymerization using KPS as the initiator. Scale bars indicate 1.0 μm.

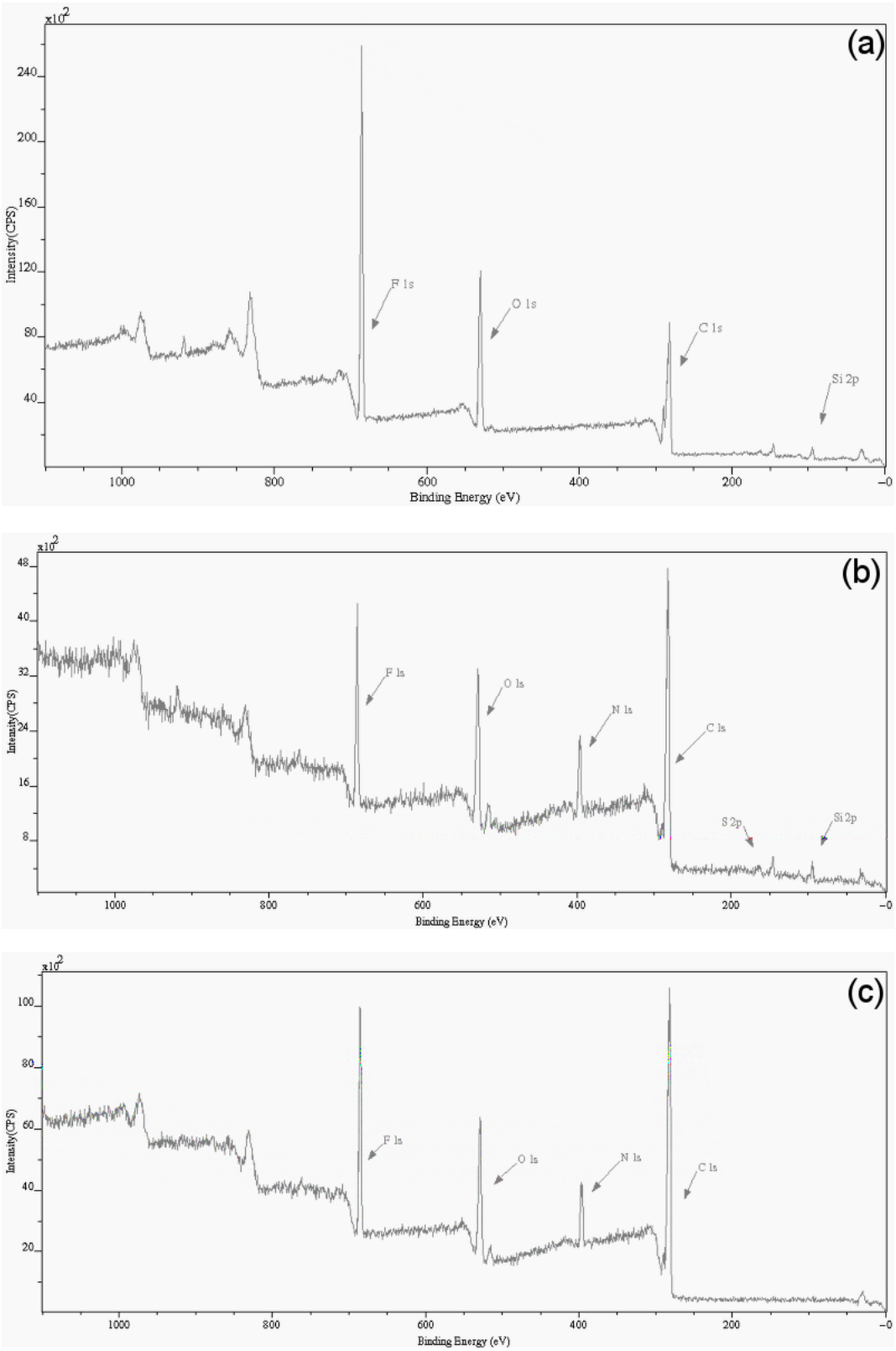

Fig.S2 XPS-spectra of fluorescently labeled poly(TFMA) core particles. (a) shows the XPS spectrum without and (b) and (c) with added NIPAAm during polymerization. (b) and (c) show XPS for either of the two species one with a green and the other with a red fluorescing dye. (b) and (c) both show a clear N(1s)-peak illustrating that the NIPAAm groups accumulate on the particle surface.