Electronic Supplementary Information

Fabrication of 3D supramolecular hybrid particle microstructures with controllable morphology and dimensions

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Experimental Section

Materials. Adamantyl-terminated poly(propylene imine) dendrimer of generation 5 (G5-PPI-$(Ad)_{64}$) was synthesized as described before.[27] Lissamine rhodamine B sulfonylchloride, fluorescein, 2-naphthoic acid were obtained from Sigma Aldrich, Germany. Carboxylate-functionalized polystyrene particles of 500 nm were purchased from Polysciences Inc. Gold nanoparticles (Au-CD, d ~ 3 nm) and CD-functionalized polystyrene particles (PS-CD), prepared from the carboxylate-functionalized particles, were prepared as described before.[14,28] Milli-Q water with a resistivity higher than 18 MΩ·cm was used in all experiments.

Substrate and monolayer preparation. Flat silicon substrates were cleaned by immersion in piranha solution (conc. H_2SO_4 and 33% H_2O_2 in a 3:1 volume ratio, **Warning!** piranha should be handled with caution; it is a highly corrosive oxidizing agent) for 15 min to form a SiO_2 layer on the surface. The substrates were then sonicated in Milli-Q water and ethanol for 1 min, and dried with N_2.

Nanoimprint lithography (NIL) was performed by putting a hard silicon master (e.g. 10 μm hexagons at 3 μm spacing with a height of 500 nm) in contact with a 800 nm thick layer of PMMA on a SiO_2 substrate.[9] A pressure of 40 bar was applied at a temperature of 180 ºC using a hydraulic press (Specac). Oxygen plasma etching (Tepla 300E) was applied for 30 s to remove the residual polymer layer also rendering the resulting polymer pattern hydrophilic.

Formation of hybrid structures. The hybrid structures were prepared by layer-by-layer (LbL) assembly of Au-CD nanoparticles (d ~ 3 nm) and G5-PPI-$(Ad)_{64}$ on the NIL-patterned substrate, according to a published procedure.[14] The positively charged Ad dendrimers were first adsorbed onto the slightly negatively charged PMMA template. Complementary Au-CD nanoparticles were subsequently adsorbed. Up to 30 LbL cycles were performed. After each adsorption step, the substrate was blown dry with N_2.

Encapsulation of fluorescent molecules within the hybrid structures. Infiltration of fluorescent molecules into the hybrid structures was performed prior to the release process. The hybrid structures on the NIL-patterned substrate were immersed in an aqueous solution of 1 mM lissamine-rhodamine, fluorescein or naphthoic acid for 10 min. The hybrid structures were subsequently rinsed gently with Milli-Q water and dried with N_2.

Attachment of PS-CD nanoparticles on the hybrid structures. Prior to the release process, the hybrid structures on the NIL-patterned substrate were immersed in 5 wt% of PS-CD nanoparticle aqueous solution. for 10 min. The hybrid structures were subsequently rinsed gently with Milli-Q water and dried with N_2.

Lift-off of the hybrid structures. Rinsing the hybrid structures in acetone for 2 s created cracks

at the edges between the PMMA patterns and the substrate, which facilitated the lift-off process thereafter. The hybrid structures on the patterned NIL substrate were sonicated in water in a vial in Branson® Ultrasonic Cleaner (Model 1510, frequency 40 Hz) for 10 – 30 min to lift off the hybrid objects from the surface. The substrate was removed from the vial after sonication. A few drops of a solution containing the hybrid objects were cast on a silicon surface for visualization.

Scanning electron microscopy (SEM) and Atomic force microscopy (AFM). All SEM images were taken with a HR-LEO 1550 FEF SEM. AFM measurements were carried out using a Dimension D3100 atomic force microscope.

Fluorescence microscopy. Fluorescence microscopy was performed using an Olympus inverted research microscope IX71 equipped with a mercury burner U-RFL-T as the light source and a digital camera Olympus DP70 (12.5 million-pixel cooled digital color camera) for image acquisition. Green excitation, red emission light ($510 \leq \lambda_{ex} \leq 550$ nm, $\lambda_{em} \geq 590$), blue excitation, and green emission light ($450 \leq \lambda_{ex} \leq 480$ nm, $\lambda_{em} \geq 515$ nm), and UV excitation ($300 \leq \lambda_{ex} \leq 400$ nm, $\lambda_{em} \geq 400$) were filtered using a U-MWG Olympus filter cube.