

Electronic supporting information for *Soft Matter*

Hybrid raspberry microgels with tunable thermoresponsive behavior

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Materials

For the synthesis of the microgel core we used n-Isopropylacrylamide 99% (NIPAM, Accros), with N,N'-methylenebisacrylamide (BIS, Fluka) as crosslinker, hexadecyltrimethylammonium bromide (CTAB, Alfa-Aesar) as surfactant, 2,2'-Azobis(2-methylpropionamide)dihydrochloride (V50, Sigma-Aldrich) as initiator, and 3-Methacryloxypropyltrimethoxysilane (MPS, ABCR) as linking organosilane agent. The deionized water was obtained from a Milli-Q system (resistivity = 18.2 MΩ.cm, Millipore). Absolute ethanol was purchased from Merck. Tetraethoxysilane (TEOS, Sigma-Aldrich) was used as the silica precursor. Ammonia solution (25 %, Sigma aldrich) was used for pH adjustment.

Preparation of SiOH-modified microgels

Poly(N-isopropylacrylamide) (PNIPAM) particles were first synthesized by emulsion polymerization. A given amount of NIPAM was dissolved in 90 mL of water in the presence of BIS and CTAB in a three-neck round bottom flask. The mixture was stirred at 300 rpm and the temperature was increased up to 60°C. After three alternated nitrogen / vacuum flow steps, the temperature was increased to 80°C. The initiator dissolved in deionised water was then added dropwise. After one hour, the linking agent MPS was subsequently added dropwise. Reaction occurred for 24 hours under stirring. In order to remove aggregates, the suspension was then filtered through a glass filter and dialyzed against deionized water for two weeks to remove remaining agents.

Chemicals	Amount
NIPAM	2 g
BIS (5 % mol)	0.072 g
CTAB	5 mL of 7.82 mM aqueous solution
V50	10 mL of 18.4 mM aqueous solution
MPS	0.231 g

Table 1: Chemicals used for the synthesis of the microgel core particles

Silica shell growth

Two different ways were used to grow the silica particles in the outer shell of the silane-modified PNIPAM microgels. In the first synthesis approach the silica particles were formed by continuously adding the TEOS using an infusive pump. First, 1 mL of hybrid microgel suspension (1.9 wt %) was diluted with 4 mL absolute ethanol to which 0.5 mL of ammonia solution (30 %) was added. TEOS diluted in absolute ethanol (1:1, v:v) was added dropwise at 2 mL.h⁻¹ into the stirred suspension at room temperature. We added 0.25 mL TEOS for the batch 1 of and 1 mL TEOS for batch 2.

In the second approach a modified Stoeber method has been used. The polymeric colloid suspension was diluted in absolute ethanol (1:8, v:v) and 0.2 mL of ammonia solution (30 %) was added. After homogenization, 0.5 mL of TEOS was added at room temperature. The reaction was left under stirring for 6 hours.

After synthesis the hybrid microgels were purified by repeated centrifugation against deionized water.

Characterizations

TEM

Particles deposited on a copper grid were imaged in a Philips CM 100 BIOTWIN operating at 80 kV and equipped with a side mounted MORADA CCD camera.

SEM

Scanning electron microscopy (SEM) observations were performed with a FEI XL30 Sirion operating at 15 kV. The samples were deposited on the sample holder, dried and gold-coated prior to examination.

DLS

Dynamic light scattering (DLS) experiments were carried out using a light scattering goniometer instrument from LS Instruments (3D LS Spectrometer) equipped with a HeNe laser light source with a wavelength $\lambda=632.8$ nm. The sample were filled into cylindrical NMR tubes with a diameter of 5 mm and placed in the temperature-controlled index matching bath, where the temperature was varied from 17°C to 45°C. Measurements were performed at scattering angles of 30°, 45°, 60°, 75° and 90°, and the average hydrodynamic radius was obtained through a second order cumulant analysis.