

Supporting information

Photosensitive Spherical Polymer Brushes: Light Triggered Process of Particle Repulsion

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1. Synthesis

The synthesis of the polyelectrolyte brushes on silica colloids is done following the procedure described elsewhere.¹ In short, the surface initiator is first grafted on the particle surface to allow for a subsequent grafting from polymerization. The amino functionalization is done with 3-aminopropyltriethoxysilane (APTS) in acidic water (acidic acid) and then reacted in toluene with 2-bromo-2-methylpropionyl bromide (BIBB) to place the initiator group on the surface. For polymerization, we use surface initiated ATRP with Cu(I)Br as catalyst and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) as ligand in a methanol–water mixture ($V_{\text{MeOH}}/V_{\text{H}_2\text{O}} = 4:1$), keeping the particle concentration low to avoid fusion of polymer chains from different particles. Polymerization is performed with high monomer and Cu to initiator molar ratio, the monomer concentration is set to 122 mM of *tert*-butyl methacrylate (*t*BuMA) per reaction batch, polymerization time is 6 hours. Anionic polyelectrolyte brushes are obtained by polymerization of *t*BuMA and subsequent hydrolysis in DCM/TFA (trifluoroacetic acid) to get poly(methacrylic acid) brushes (SiO₂@PMAA). After the reaction, polymer-coated SiO₂ particles are transferred into water by dialysis, and charged by adjusting solution pH to 9.

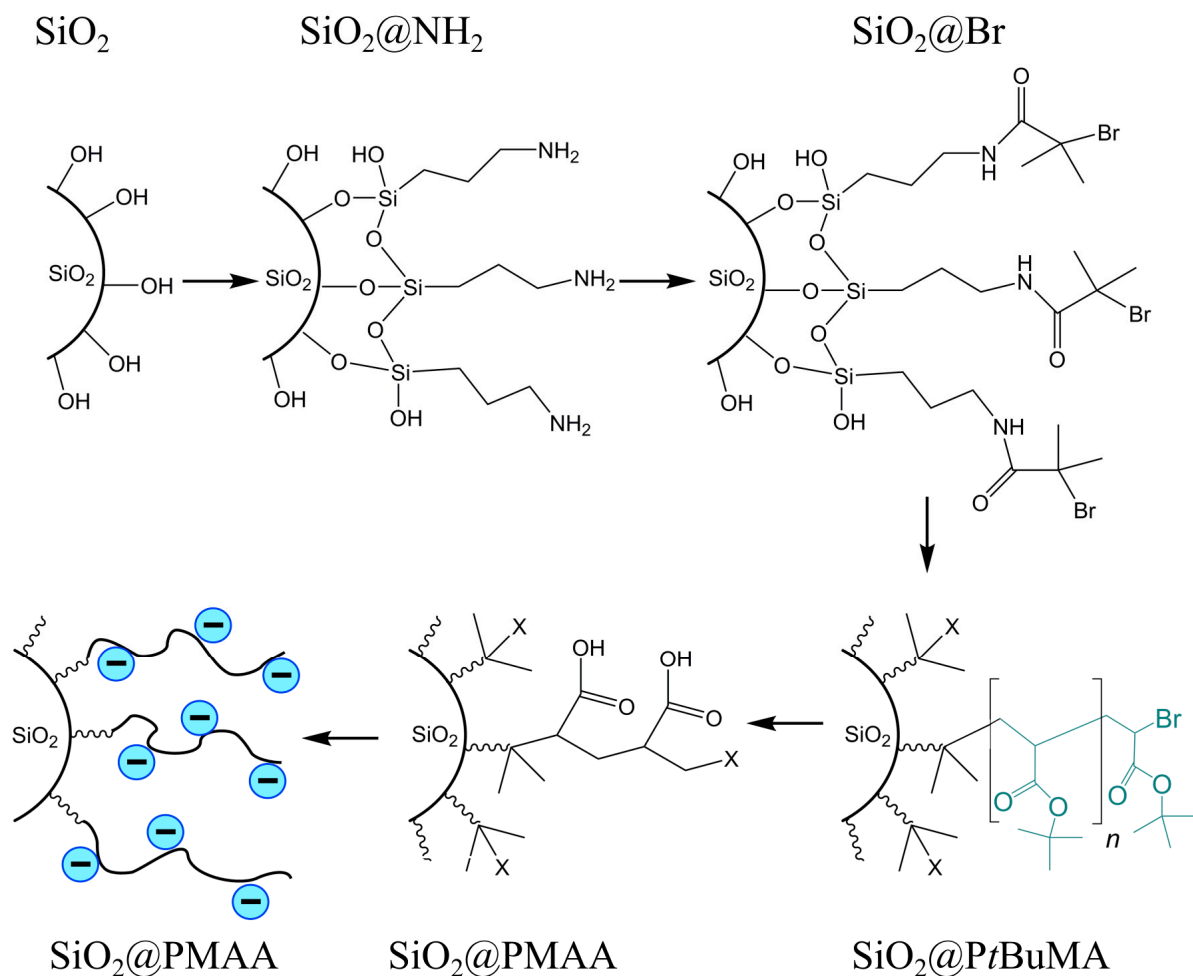


Figure S1. Scheme of the poly(methacrylic acid) brush ($\text{SiO}_2@\text{PMAA}$) synthesis on silica colloid. 1st step: surface functionalization with APTES in acidic water and then grafting the surface initiator with BIBB in toluene. Synthesis of $\text{SiO}_2@\text{PMAA}$ is done by surface initiated ATRP polymerizing the monomer *t*BuMA with following hydrolysis of the *tert*-butyl group in DCM/TFA to yield poly methacrylic acid coated particles.

2. Grafting density estimation

The molecular weight of the silica core, M_{WC} , is calculated from the volume V_C (measured average $D = 4.0 \mu\text{m}$ from **Figure S8**) of the particle multiplying with density $\rho_{\text{SiO}_2} = 1.8 \text{ g/cm}^3$

$$M_{\text{WC}} = N_A \cdot \rho_{\text{SiO}_2} \cdot V_C = N_A \cdot \rho_{\text{SiO}_2} \cdot \frac{4}{3} \cdot \pi \cdot R^3, \quad (\text{S1})$$

with N_A as Avogadro constant, V_C the volume of the silica core.

Calculation of the grafting density of $\text{SiO}_2@\text{PMAA}$ -brush

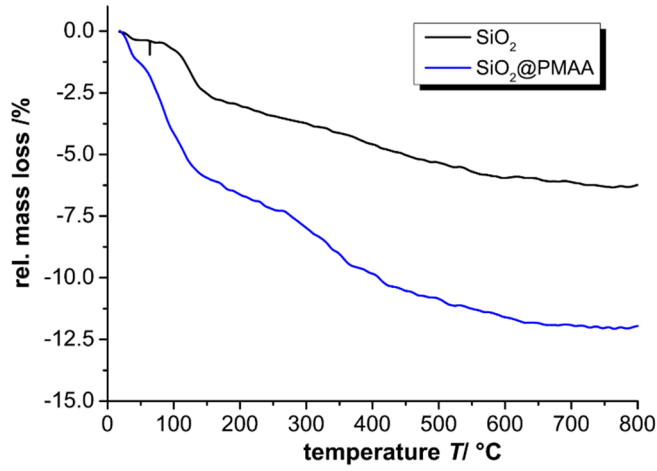


Figure S2. Thermo gravimetric analysis data of bare silica particles (SiO_2) and poly(methacrylic acid) coated silica particles ($\text{SiO}_2@\text{PMAA}$).

First, we determined the weight loss from the pure SiO_2 -NPs which can be attributed to the loss of tightly bound water. The difference from the weight loss of silica (SiO_2) compared to $\text{SiO}_2@\text{PMAA}$ at $T = 700^\circ\text{C}$ is the amount of polymer without the mass of tightly bound water.

$$\Delta m(\text{Polymer}) = \Delta m(\text{SiO}_2@\text{PMAA}, 700^\circ\text{C}) - \Delta m(\text{SiO}_2, 700^\circ\text{C}) \quad (\text{S2})$$

$$\Delta m(\text{Polymer}) = 11.8\% - 6.2\% = 5.6\%$$

$$M_{\text{WP}} = M_{\text{WC}} \cdot \left(\frac{5.6}{100}\right), \quad (\text{S3})$$

Assuming an average molecular weight of 70.000 g/mol per chain the number of chains per particle N_{chains} can be calculated:

$$N_{\text{chains/P}} = \frac{M_{\text{WP}}}{M_{\text{chain}}}, \quad (\text{S4})$$

and divided by the surface area of the silica core, the grafting density σ is estimated:

$$\sigma = \frac{N_{\text{chains/P}}}{A} = \frac{M_{\text{WP}}}{M_{\text{chain}}A} = \frac{4\pi R^3 \cdot 0.056 N_A \rho_{\text{SiO}_2}}{M_{\text{chain}} 4\pi R^2} = 0.58 \text{ nm}^{-2}. \quad (\text{S5})$$

Brush height determination from atomic force microscopy

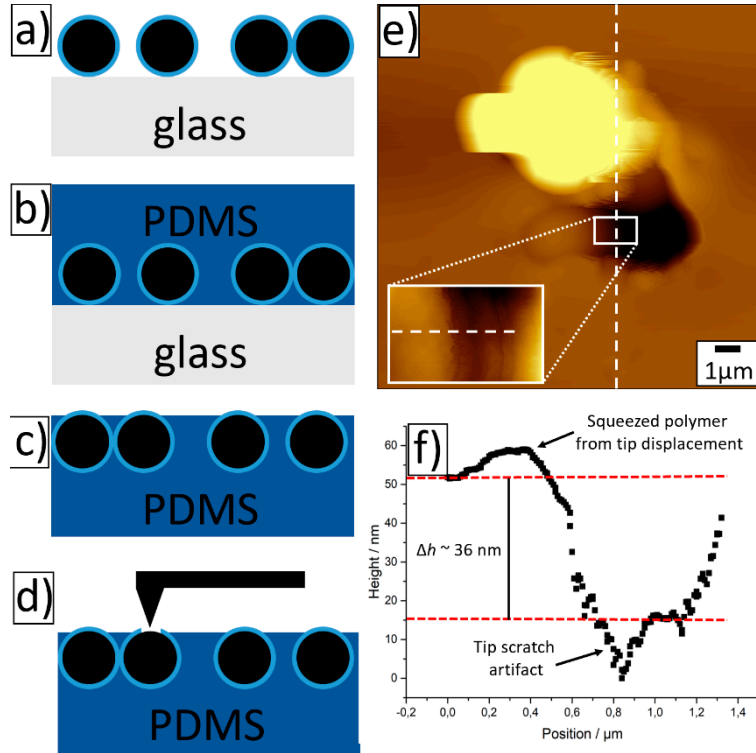


Figure S3. (a-d) Cartoon of sample preparation to lock the particle into a polydimethylsiloxane (PDMS) mask to measure the height thickness of grafted polyelectrolyte layer on SiO₂@PMAA. (a) The particle solution was spin coated on a glass film, then (b) covered by a liquid mixture of silicone elastomer (dimethylsiloxan) and curing agent to polymerize under 24h into the PDMS-matrix. (c) After peeling off the PDMS layer of the glass, the particles were at the PDMS-air interface. (d) The brush of the immobilized particles was scratched with an AFM tip and the height of the brush on the particles was measured by AFM tapping mode. (e) AFM micrograph of embedded particles in PDMS manipulated with an AFM tip. One particle's surface is scratched (black spot), and one particle is pulled upwards by the AFM tip interaction (bright spot). The height difference on the scratched particle is measured and a cross section (dashed line in the inset) analyzed (f).

Measured height:

$$h = h_2 - h_1 = (52 - 15.5)\text{nm} = 36.5\text{nm}.$$

To calculate grafting density knowing the dry thickness of the PMAA layer, $h=36\text{nm}$, we use the following equation:

$$\sigma = \frac{h\rho N_A}{M_n} = 0.39 \text{ nm}^{-2} \quad (\text{S6})$$

Where p is the density of the PMAA, 1.2g/cm^3 , N_A the Avogadro number, M_n the molecular weight of the chain, 70.000g/mol .

3. Zeta-Potential

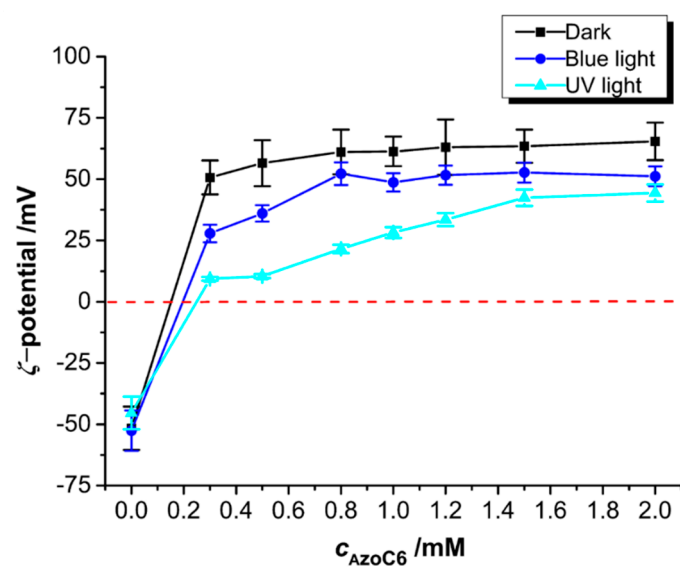


Figure S4. Zeta potential of SiO₂@PMAA for different wavelengths.

4. Calculation of the amount of adsorbed surfactant using UV-Vis absorption spectra

Prior to measurements aqueous surfactant solution is mixed with particle suspension of concentrations $c_{\text{azo}}=2 \text{ mM}$ and $c_{\text{particles}}=0.1 \text{ mg/mL}$, followed by equilibration overnight and then exposed to illumination with the desired light source (10 mW/cm^2) for 15 min. Afterwards the sample is centrifuged at 1500 rpm for 5 min; 10 μL of the supernatant is removed and diluted with 990 μL Millipore water, to achieve a dilution factor of 100. The diluted aqueous surfactant solution is equilibrated under dark conditions for 5 days to allow the surfactant to isomerize into the thermodynamic stable *trans* state. Then the samples are measured in the UV-Vis spectrometer. From pure surfactant solution of well-known concentration ($2\text{mM}/100$) the extinction coefficient, ϵ , is calculated at the wavelength of 353 nm using the Lambert-beer-law:

$$A = \epsilon \cdot c_{\text{UV-Vis}} \cdot d, \quad (\text{S10})$$

with $c_{\text{UV-Vis}}$ as the measured concentration and $d = 1 \text{ cm}$ as the cuvette thickness. Due to the dilution, $c_{\text{UV-Vis}}$ have to be multiplied with a factor of 100. The adsorbed surfactant concentration is calculated from the difference of $c_{\text{UV-Vis}}$ and adjusted surfactant concentration of 2 mM via:

$$c_{\text{ads}} = 2 \text{ mM} - c_{\text{UV-Vis}}. \quad (\text{S7})$$

Finally, the amount of adsorbed surfactant is normalized to the silica particles $c_{\text{ads}}/c_{\text{ads,SiO}_2}$. All calculate values are presented in **Table S1**, adsorption spectra are shown in **Figure S5**.

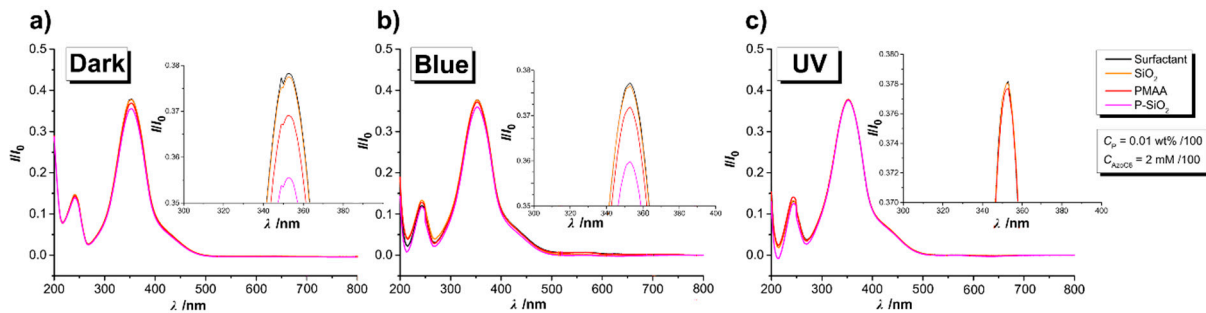


Figure S5. Adsorption spectra of supernatant surfactant solution: a) no illumination, b) blue, c) UV.

Table S1. Sample type, absorbance at $\lambda = 353$ nm, measured concentration multiplied with 100 c_{UV-Vis} , adsorbed surfactant concentration c_{ads} , normalization of c_{ads} to silica samples $c_{ads}/c_{ads,SiO_2}$

sample	Abs	c_{UV-vis} mM	c_{ads} mM	$c_{ads}/c_{ads,SiO_2}$
dark				
SiO ₂	0.3775	1.996	0.004	1.00
PMAA	0.3690	1.951	0.049	13.14
P-SiO ₂	0.3555	1.879	0.120	32.42
blue				
SiO ₂	0.202	1.991	0.003	1.00
PMAA	0.195	1.921	0.028	9.08
P-SiO ₂	0.177	1.745	0.092	29.11
UV				
SiO ₂	0.102	1.993	0.001	1.00
PMAA	0.101	1.978	0.003	3.19
P-SiO ₂	0.094	1.844	0.024	22.48

$$\varepsilon = 18.91 \text{ (mM}\cdot\text{cm)}^{-1} @ 365 \text{ nm}$$

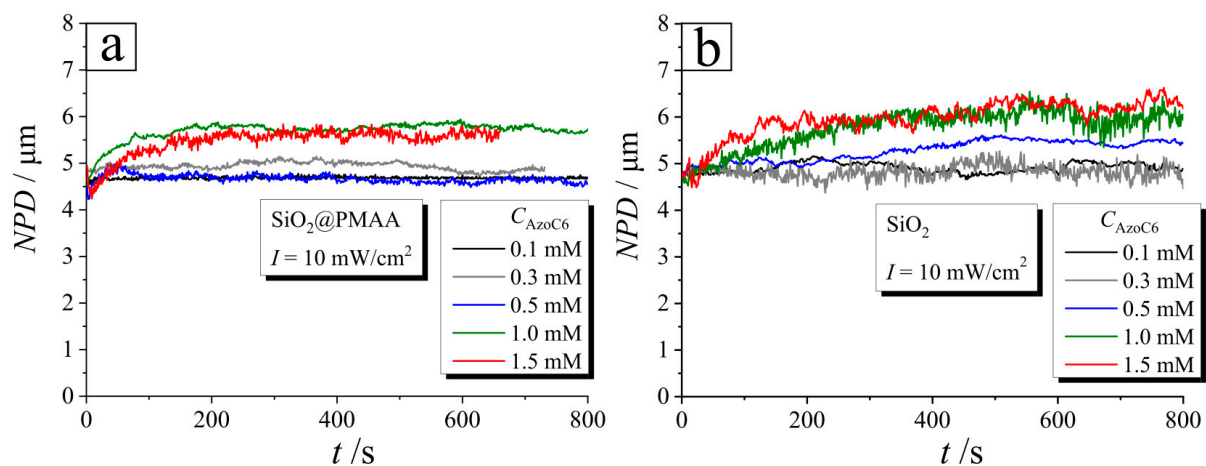


Figure S6. Nearest particle distance (NPD) as a function of time (a) $\text{SiO}_2\text{@PMAA}$ and (b) SiO_2 particles immediately after switching on the blue irradiation (455nm) with an intensity of 10 mW/cm^2 . Shown is the raw data with variation of the surfactant concentration by keeping all other parameters fixed.

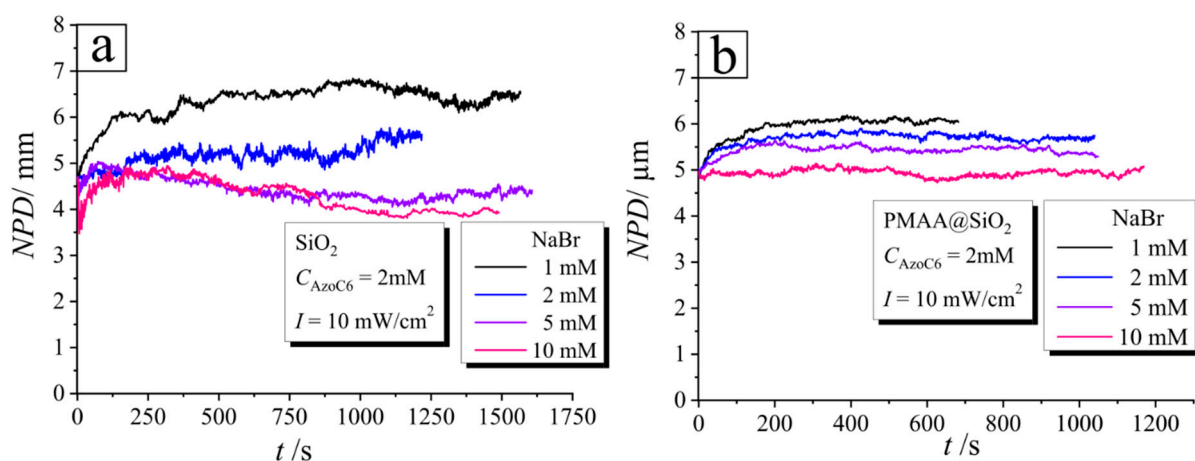


Figure S7. Nearest particle distance (NPD) as a function of time (a) SiO_2 and (b) $\text{SiO}_2\text{@PMAA}$ particles immediately after switching on the blue irradiation (455 nm) with an intensity of 10 mW/cm^2 . Shown is the raw data with variation of the salt concentration by keeping all other parameters (particle and surfactant concentration (2 mM)) fixed.

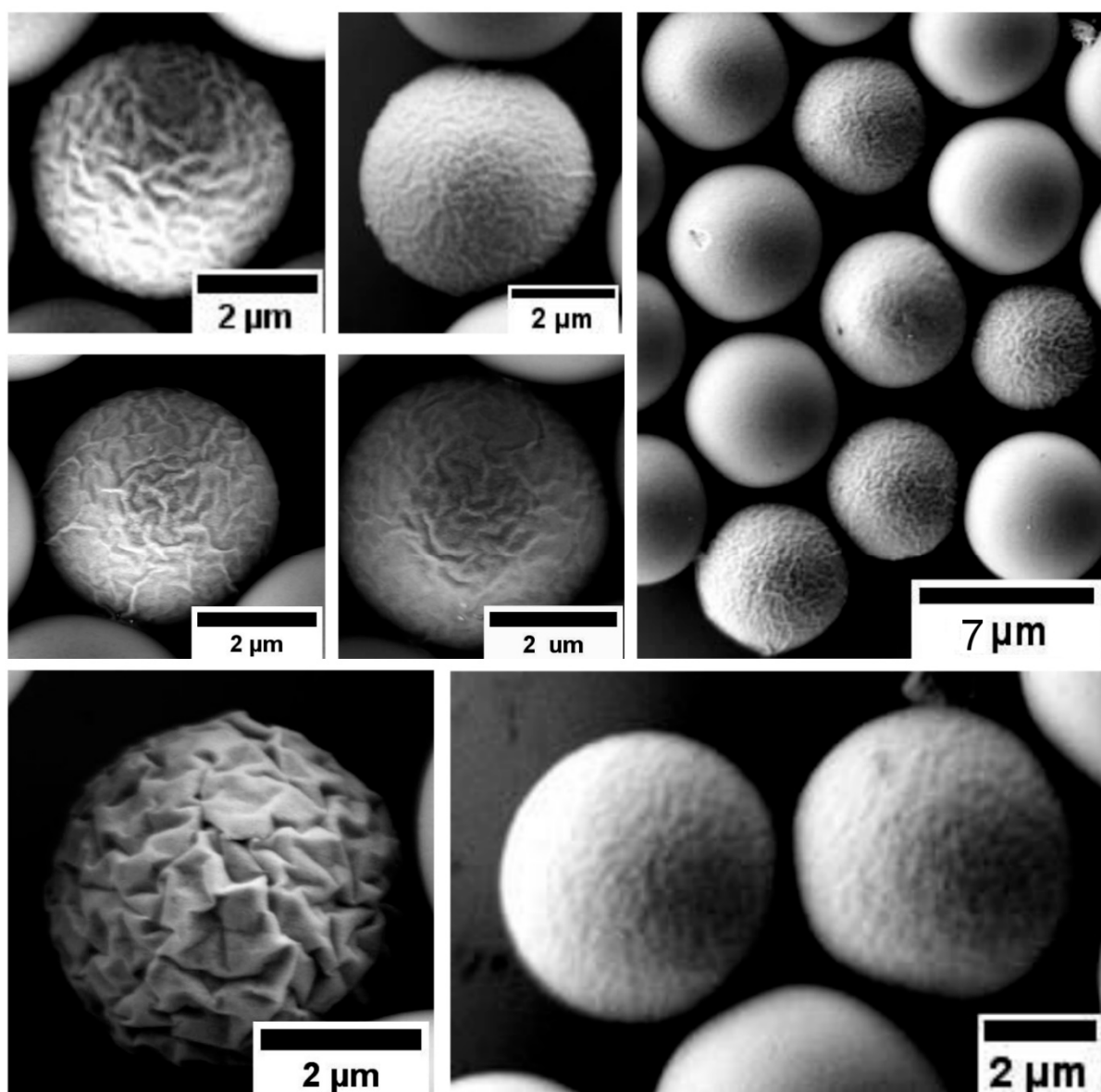


Figure S8. SEM images of PSiO₂@PMAA microparticles.

1. Sokolowski, M.; Bartsch, C.; Spiering, V.J.; Prévost, S.; Appavou, M.-S.; Schweins, R.; Gradzielski, M. Preparation of Polymer Brush Grafted Anionic or Cationic Silica Nanoparticles: Systematic Variation of the Polymer Shell, *Macromolecules* **2018**, *51*, 6936.
2. Masalov, V. M.; Sukhinina, N. S.; Kudrenko, E. A.; Emelchenko, G. A. Mechanism of formation and nanostructure of Stöber silica particles *Nanotechnology* **2011**, *22*, 275718