Supporting Information

Ellipsometric characterization of the P2VP brush in the dry and swollen states

We carried out in situ ellipsometric measurements of the 7.8-nm-thick P2VP brush in water at pH 5.5 and pH 2.5 to determine changes in the brush thickness upon the transition between the collapsed and swollen states. The refractive index and thickness of the collapsed brush (pH 5.5) was the very close to those in the dry state, specifically 1.59 and 8.9 nm, respectively. At pH 2.5, however, the strong swelling was observed with the corresponding values of the refractive index and thickness of 1.394 and 36.5 nm, respectively. The obtained value of the thickness of the swollen brush implies that the brush comprises 79% of water. A degree of swelling, defined as a ratio of the brush thickness in the swollen state to that in the collapsed state, is 4.7. We used the rule of mixtures, i.e. $n = n_{P2VP} \cdot v_{P2VP} + n_{water} \cdot v_{water}$, where n_{P2VP}=1.59 is the refractive index of P2VP, v_{P2VP}=0.21 is the volume fraction of the P2VP component in the swollen brush, n_{water} = 1.333 is the refractive index of water, and v_{water}=0.79 is the volume fraction of water in the swollen brush, to assess the effective refractive index of the swollen brush; the calculated value of 1.391 is very close to the experimental one (1.394).

Some discrepancy in the values of the swelling degree between the AFM and ellipsometric measurements can be rationalized by the well-established fact that the highly swollen polymer brush exhibits a parabolic profile of the chain density in the direction normal to the substrate surface. It is reasonable to assume that at the SP value of 98% the AFM tip probed the brush region related to the tail of the density profile and hence the measured thickness is expected to be close to the maximum brush height. In the case of ellipsometry, we simulated the experimental data using a model, in which the brush was assumed to have the step-like profile of a refractive index; consequently, the calculated layer thickness represents the effective height of the brush.

The swelling behavior and compressibility of the swollen hybrid layer as studied by AFM

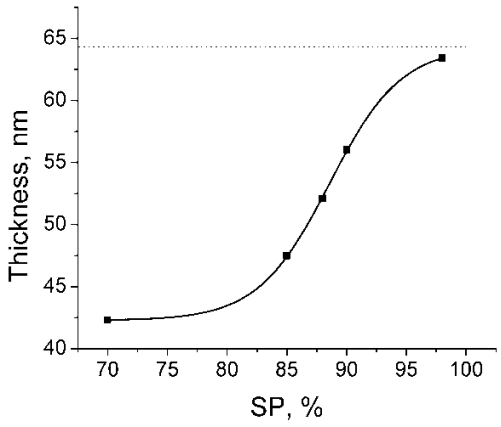

Figure S1. The plot displaying the dependence of the thickness of the swollen hybrid layer at pH 2.5 on the SP value. The experimental data are shown with the squares, while the solid and dotted lines denote the best fit to these data using the Boltzmann function (the coefficient of determination > 0.999) and the asymptote to the upper part of the fitting curve, respectively.

This conclusion that the hybrid layer experience minor compression at SP 98 % is in accord with the results of our previous study of the conformation of single P2VP chains adsorbed on the surface of a solid substrate.[1] In particular, we demonstrated that at this SP value the conformation of the chains

was not affected by an AFM tip even after continuous scanning of the same area for many hours. At SP 70%, however, the chain conformation was significantly altered by the tip during the first scan.

The reversible behavior of the hybrid layer can be concluded from the AFM data presented in Figure S2. In this experiment, we monitored changes in the average thickness of the hybrid layer (Au islands + PGMA + P2VP brush + Au particles) by varying the solution pH and applying different forces to the layer by an AFM tip. All the measurements were carried out in the same location near the edge of the needle scratch.

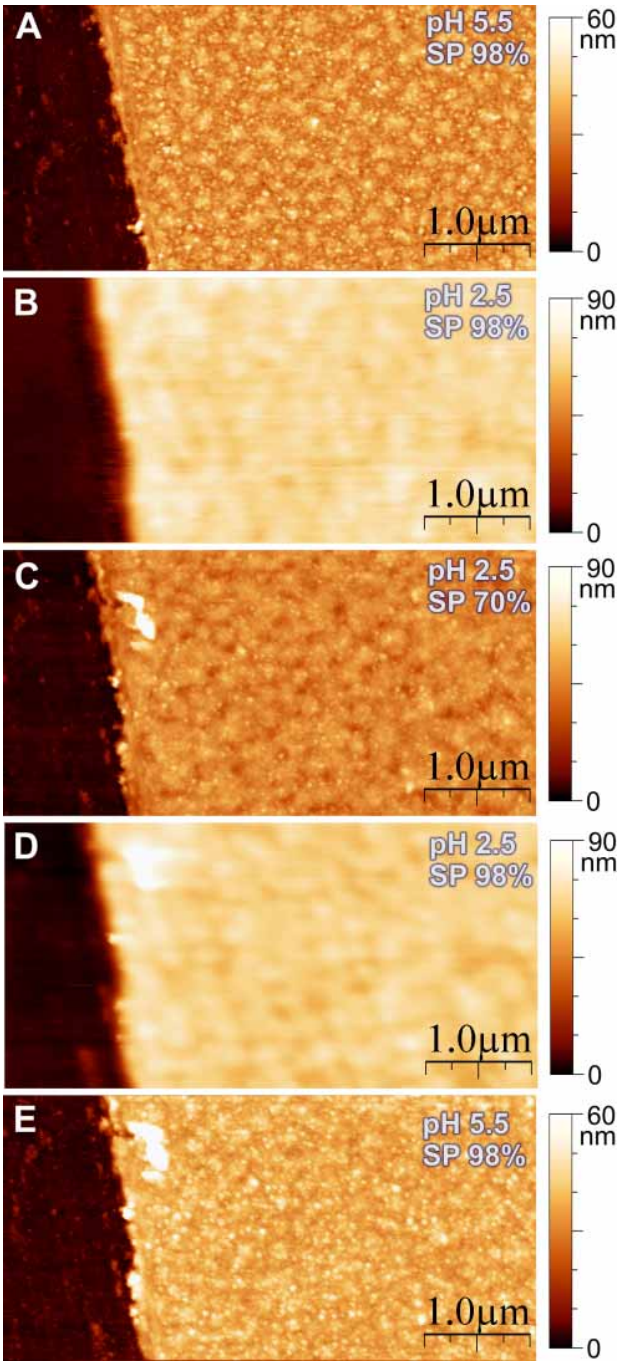

Figure S2. The AFM topography images of the hybrid layer recorded under different conditions varied in the following order:

(A) pH 5.5, SP 98%; thickness*: 30.4 nm;

(B) pH 2.5, SP 98%; thickness*: 63.4 nm;

(C) pH 2.5, SP 70%; thickness*: 42.3 nm;

(D) pH 2.5, SP 98%; thickness*: 63.7 nm;

(E) pH 5.5, SP 98%; thickness*: 33.6 nm.

* The thickness of the hybrid layer was determined from the AFM scratch analysis; the step-height function available in the commercial software was used in the thickness calculations.

Spectroscopic data

Table. S1. The numerical results of the fitting of the LSPR bands acquired from the grafted P2VP layer with Au nanoparticles (NPs) and nanoislands (shown in Figure 3 of the manuscript), the grafted layer with particles only (reference), and the grafted layer with islands only (reference). The deconvolution procedure was carried out using the Gaussian function*. The LSPR peak positions of Au nanoislands on a glass slide and a dispersion of Au nanoparticles are also provided for reference.

Sample	**Peak I**			**Peak II**			**Peak III**			**Peak IV**		
	Au NPs			Au islands			Au NPs plasmon coupling			Au islands plasmon coupling		
	λ, nm	FWHM	Amp.	λ, nm	FWHM	Amp.	λ, nm	FWHM	Amp.	λ, nm	FWHM	Amp.
Au islands				530	-	-						
Au islands + P2VP brush				557	-	-						
Au islands + P2VP brush + Au NPs **pH 5.5**	536	57	0.047	577	85	0.086	640	136	0.204	748	221	0.138
Au islands + P2VP brush + Au NPs **pH 2.5**	530	54	0.048	564	78	0.103	619	125	0.116	703	223	0.066
P2VP brush + Au NPs **pH 5.5**	536	68	0.047				622	139	0.079			
P2VP brush + Au NPs **pH 2.5**	538	73	0.061				619	125	0.067			
Au NPs in dispersion	520	-	-									

*The Gaussian function in the form $f(x) = ae^{-\frac{(x-b)^2}{2c^2}}$ was used to fit the spectral data. The full width at half maximum of the peak is defined as $\mathrm{FWHM} = 2\sqrt{2\ln 2}\, c = 2.35482\ldots \cdot c$.

References

[1] Supporting information in "Roiter, Y.; Minko, S., AFM single molecule experiments at the solid-liquid interface: In situ conformation of adsorbed flexible polyelectrolyte chains. *J. Am. Chem. Soc.* **2005,** 127, (45), 15688-15689".