Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Internal Structure of pH-Sensitive Gold Nanoparticles in Strong Polyelectrolyte Brushes: A Neutron and X-Ray Reflectivity Study

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TEM image of 5 nm AuNPs

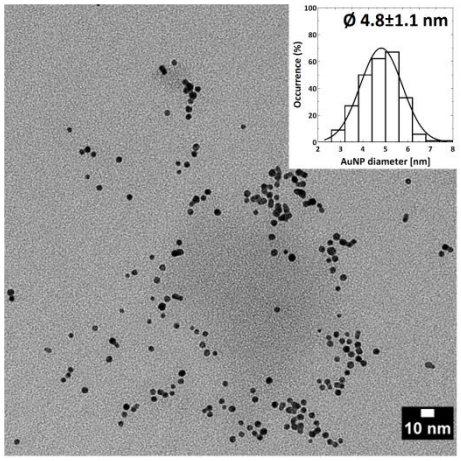

Fig. S1: TEM image of 3-MPA-capped AuNPs and the particle size distribution (inset). The diameter of AuNPs are 4.8±1.1 nm and was determined using ImageJ for the size determination.

Three-layer-model for XRR

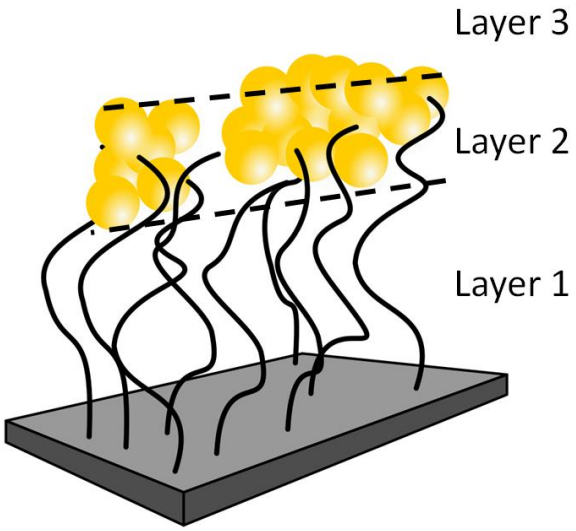

Fig. S2: Three-layer model for fitting the XRR data after attachment of AuNPs.

XRR data of PMETAC brush incubated in AuNP suspension at pH 4 for 99 %rh. Data has been plotted in $R \cdot q^4$ representation for better visualization of features.

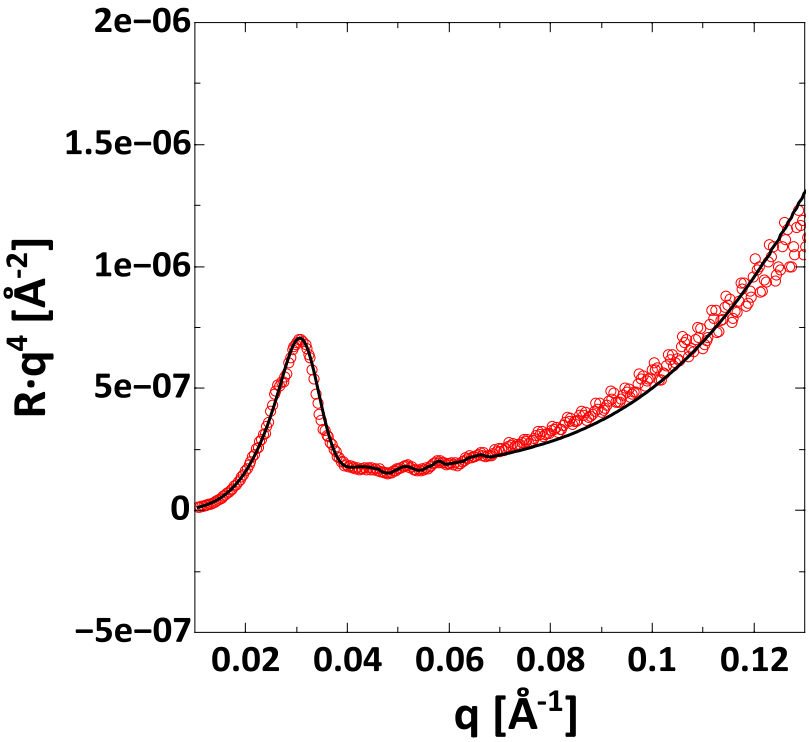

Fig. S3: XRR data (symbols) and fits (line) for PMETAC/AuNP composite after incubation at pH 4 measured at 99 %r.h.. The data were fitted using a three-layer model. Reflectivity curves and fit are represented as $R \cdot q^4$ against q.

XRR data of PMETAC brush incubated in AuNP suspension at pH 4. Data has been fitted using a 2-layer model

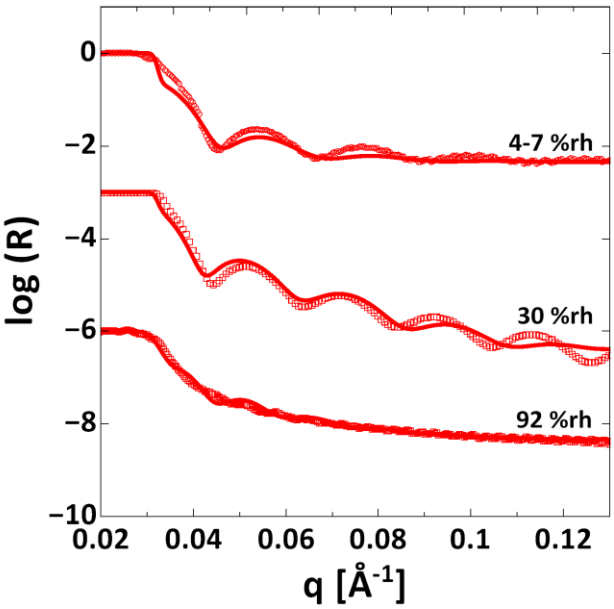

Fig. S4: XRR data (symbols) and fits (line) for PMETAC/AuNP composite after incubation at pH 4 measured at different r.h.. The data were fitted using a two-layer model. Reflectivity curves are shifted vertically for clarity.

XRR data of PMETAC brushes incubated in AuNP suspension at pH 8. Data has been fitted with a three-layer model

In contrast to the aforementioned composites as well as to the neat PMETAC brush, PMETAC/AuNP composites after incubation at pH 8 show different electron density profiles across the entire brush (Fig. S5). Here, layer 1 has the highest electron density, which decreases with increasing humidity. Further, layer 1 has a higher thickness for the brush after AuNP incubation compared to the neat PMETAC brush at the same humidity value. The thickness of layer 1 increases with increasing humidity while the electron density decreases. The electron density for layer 2 is lower than for layer 1 and decreases as well with increasing humidity. Further, the thickness of layer 2 decreases with increasing humidity. The thicknesses and electron densities for layer 3 show no systematic behavior with changing of the humidity level. The sum of the thickness of layer 2 and 3 is smaller than the particle size, indicating less particle protrusion towards the vapor phase.

Table S1: Data for PMETAC/AuNP composites after incubation at pH 8 at different r.h. obtained by XRR measured at room temperature

	XRR Layer 1		XRR Layer 2		XRR Layer 3	
Humidity [%rh]	h_1 [nm]	ρ_e [Å^{-3}]	h_2 [nm]	ρ_e [Å^{-3}]	h_3 [nm]	ρ_e [Å^{-3}]
4-7	22.1	0.925	2.3	0.714	1.1	0.649
30	24.8	0.886	2.1	0.710	0.6	0.675
92	37.8	0.684	1.9	0.648	0.9	0.531

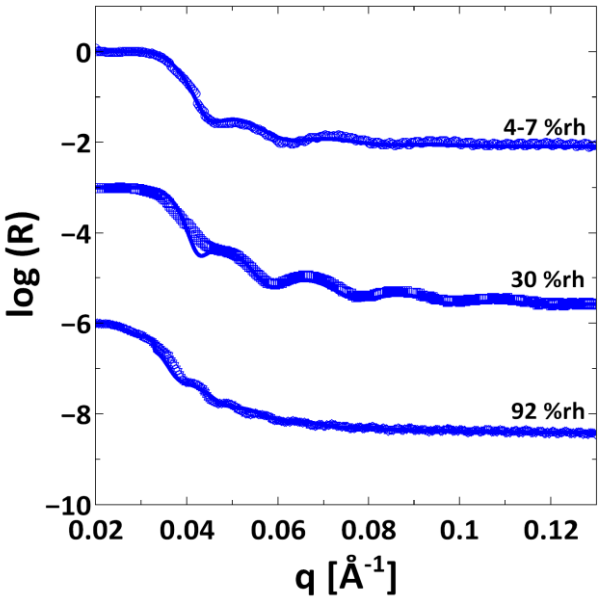

Fig. S5: XRR data (symbols) and fits (line) for PMETAC/AuNP composite after incubation at pH 8 measured at different r.h.. The data were fitted using a three-layer model. Reflectivity curves are shifted vertically against each other due to sake of clarity.

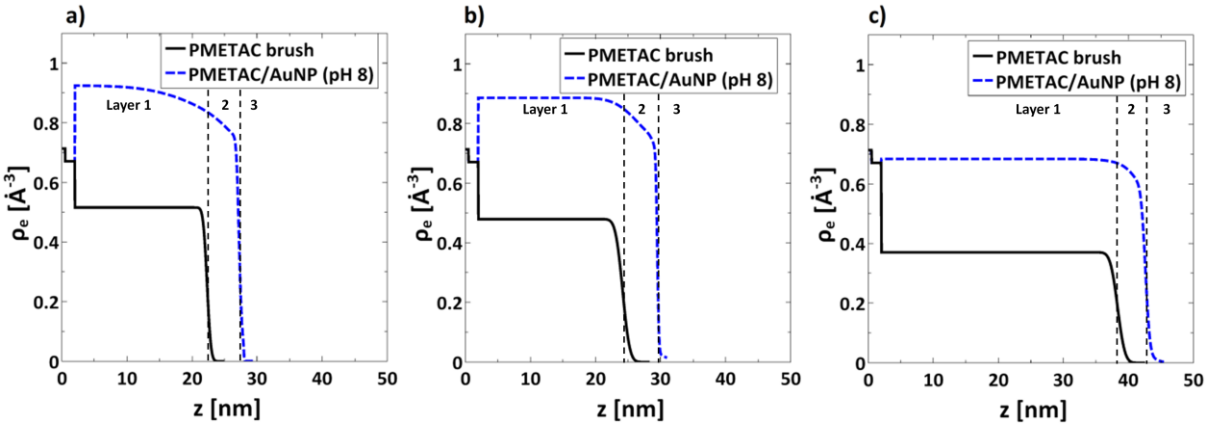

Fig. S6: Electron density profiles in the z-direction from the substrate surface (z=0) for PMETAC/AuNP composite after incubation at pH 8 (blue broken lines) and neat PMETAC brush (black solid lines) measured at different r.h. for a) 4-7 %rh, b) 30 %rh, and c) 92 %rh.