Supporting Information for:

Active Control of SPR by Thermo-Responsive Hydrogels for Biosensor Applications

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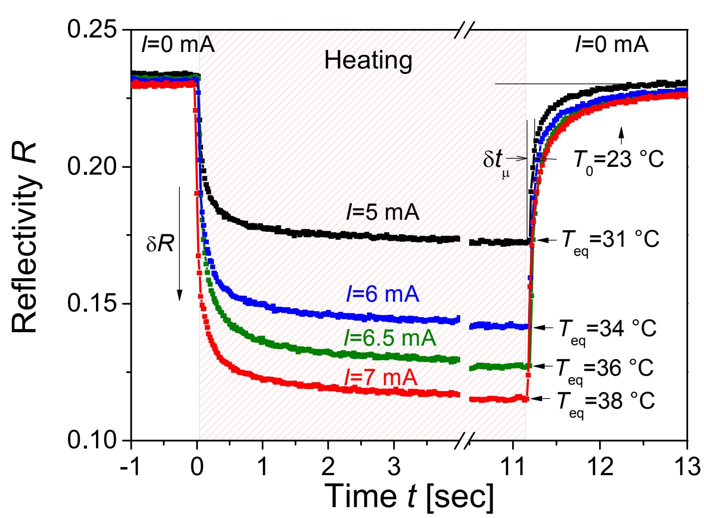
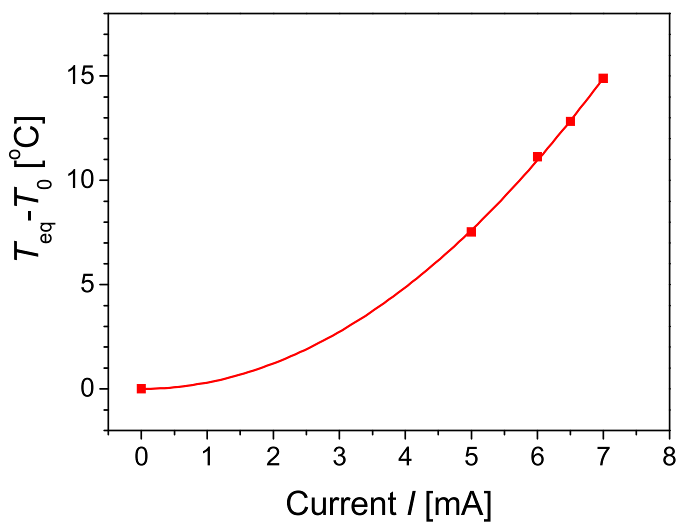
1. Calibration of local temperature changes induced by the micro-heater.

For the calibration of the local temperature changes induced by the micro-heater, water was pumped over the gold sensor surface (without the hydrogel layer) and series of current pulses *I* were applied through the ITO micro-heater. From the measured reflectivity changes upon the coupling to long range surface plasmons (LRSPs) presented in Figure S1a, there can be seen that the current flow I leads to a drop of the reflectivity signal R. This effect is due to a decrease in the refractive index of water when increasing the temperature.[1] After the current was switched off I=0, the heat in vicinity to the micro-heater rapidly dissipates leading to a decrease in the local temperature to that of the background T_0 and to respective increase in the reflectivity R. The response time of the ITO micro-heater δt_μ was defined as the time in which the change in reflectivity signal R reached half of that in equilibrium (see Figure S1a). The analysis of the measured kinetics revealed that the response time of δt_μ=50 ms was identical for the heating and the cooling phases. The dependence of the equilibrium temperature T_{eq} on the current flow I was determined by comparing reflectivity changes δR as a function of the current flow I with those induced by changing the background temperature T_0 with a Peltier element. A typical calibration curve that is presented in Figure S1b shows a quadratic dependence of the temperature T_{eq} on the current I. It illustrates that the developed micro-heater allows for increasing the temperature on the sensor surface to more than 15 K above to the background temperature T_0.



(a)



(b)

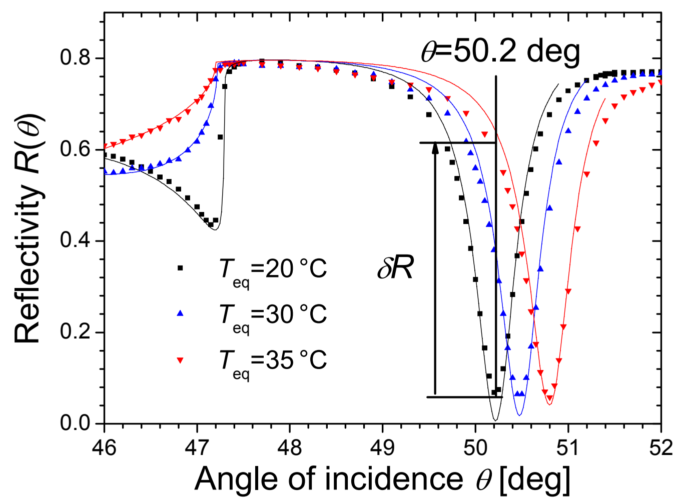
Figure S1 Micro-heater calibration: (a) SPR response measured at a fixed angle of θ=48.7 deg for the bare gold surface in contact with water upon its heating and relaxing back to the background temperature T_0=23 °C and (b) typical calibration curve showing the equilibrium temperature T_{eq} depending on the current flow I through the ITO pad.

2. Determining of swelling ratio by the analysis of SPR reflectivity spectra

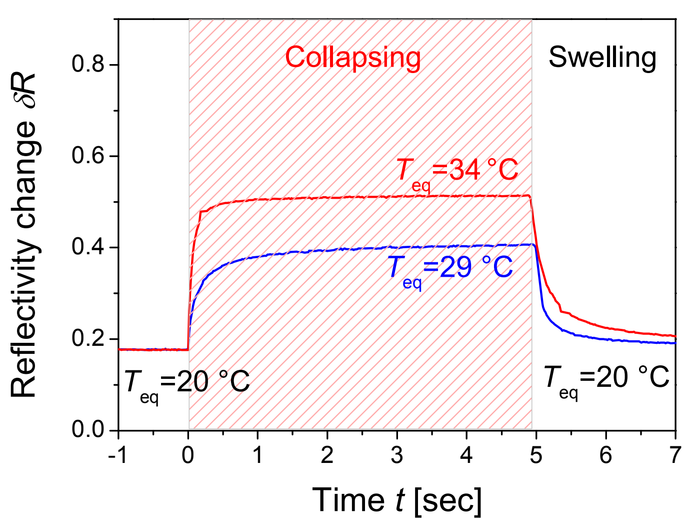
As seen in Figure S2a, the resonance coupling to long range surface plasmons and hydrogel layer-guided optical waves (HOW) is manifested as respective dips in reflectivity spectra located at distinct angles. This coupling shifts to higher angles when increasing the refracting index of the dielectric adjacent to the gold surface n_h. In order to determine the thickness d_h (related to the swelling ratio SR) and the refractive index n_h (related to the density) of the hydrogel film, the angular reflectivity spectrum exhibiting LRSP and HOW resonance dips was fitted by a transfer matrix-based model (implemented in the software Winspall developed at the Max Planck Institute for Polymer Research in Mainz, Germany). Similar to our previous investigation[2], we assumed a constant refractive index of the gel n_h perpendicular to the surface from which the gel surface mass density was calculated as $\Gamma = (n_h - n_b) d_h \partial c / \partial n_h$, where n_b is the refractive index of buffer and d_h is the thickness of hydrogel. The refractive index of the hydrogel layer was assumed to change with the concentration of the captured protein molecules and with the NIPAAm polymer chains as $\partial n_h / \partial c$ = 0.2 mm^3 mg^{-1}.

3. Swelling and Collapsing Kinetics of IgG-modified Hydrogel Films.

The swelling and collapsing kinetics of IgG-modified hydrogel film in contact with PBS buffer was observed from reflectivity measurements. In this experiment, the hydrogel film was modified with mIgG with a surface mass density of Γ=20.6 ng/mm^2. Figure S2a shows a series of angular reflectivity spectra taken at temperature between T_{eq} =20 °C and 35 °C. The kinetics measurements in Figure S2b was performed with the background temperature set to T_0 =20 °C and an angle of incident of θ=50.2 deg. The sensing spot was heated in order to reach equilibrium temperature between T_{eq}=29 and 34 °C by applying current to the ITO microheater at t=0 sec and subsequently allowed to cool down to the background temperature at t=5 sec by switching off the current. The characteristic time when the reflectivity change reaches to half its maximum value was about 100 ms which is comparable to what observed with unmodified hydrogel film in water.



(a)



(b)

Figure S2 (a) Angular reflectivity spectra measured for IgG-modified hydrogel film in contact with PBS buffer upon heating to temperature of T_{eq}=20, 30, and 35 °C. (b) Kinetics of collapsing and swelling of IgG-modified hydrogel in contact with PBS upon a current pulse applying to the ITO micro-heater.

4. References:

(1) Schiebener, P.; Straub, J.; Sengers, J.; Gallagher, J. S. REFRACTIVE-INDEX OF WATER AND STEAM AS FUNCTION OF WAVELENGTH, TEMPERATURE AND DENSITY *J. Phys. Chem. Ref. Data* **1990**, *19*, 677-717.

(2) Aulasevich, A.; Roskamp, R. F.; Jonas, U.; Menges, B.; Dostalek, J.; Knoll, W. Optical Waveguide Spectroscopy for the Investigation of Protein-Funcionalized Hydrogel Films *Macromol. Rapid Comm.* **2009**, *30*, 872-877.