

Supporting Information

1. Materials and Methods

1.1 Sensing platform fabrication.

The first step comprised fabricating Au nanodisks onto Borofloat glass substrates using Hole-Mask Colloidal Lithography (HCL)¹. The latter yields a random distribution of nanodisks on the surface. Mean diameters $D=74$ nm and heights $h=30$ or 40 nm were targeted, respectively. The Au evaporation was carried out in an electron beam evaporation system, at a base pressure of about 2×10^{-6} mbar and 1 Å/s evaporation rate. After evaporation, the samples were thermally annealed for 3h at 350°C in Ar in order to thermally stabilize the microstructure and shape of the Au nanodisks. This step was important in order to avoid temperature-induced irreversible spectral shifts during experiments at elevated temperature, caused by (micro)structural reshaping of the sensor particles. Typically, as seen in SEM, this thermal annealing step leads to a recrystallization of the nanodisks. After the structural stabilization, the subsequent fabrication step comprised RF-sputtering of a 10 nm thick SiO_2 spacer layer onto the sensor particles. When needed, the sputtering step was followed by the e-beam evaporation of granular Pd films (base pressure 2×10^{-6} mbar; evaporation rate 0.5 Å/s) to produce Pd nanoparticles. Films between 2.5 Å and 20 Å were deposited. After deposition, the samples were again thermally anneal in the tube furnace in Ar flow at 250°C for 2h to further stabilize the structures and relax fabrication induced stresses from SiO_2 sputtering and Pd evaporation.

1.2 Polystyrene nanosphere T_g experiments.

To measure the glass transitions in the PS nanospheres (sulfate latex, Interfacial Dynamics Corporation), the latter were deposited from a Milli-Q water suspension containing the negatively charged PS particles in a similar fashion as in the HCL mask fabrication step¹, leaving the sensor surface covered with uniformly distributed PS-spheres. The glass transition experiments were the carried out in a heated stainless steel chamber, connected to a vacuum pump, with optical windows for extinction measurement. The samples were, in a first cycle, under vacuum, heated to 80°C (below T_g of the polymer) for stabilization and remaining water desorption. During the second cycle (the actual measurement), the samples were heated at $2^\circ\text{C}/\text{min}$ and optical extinction was measured. To correct for the LSPR peak shifts induced by the external heating of the sensor, a calibration measurement was carried out on the blank sensor and the T-induced spectral shifts subtracted from the measured data with PS spheres on the sensor (supplementary material). The optical response of the sensor was followed by measuring extinction spectra in a spectrophotometer (Varian Cary 5000), in transmission mode with the experimental chamber placed in the sample compartment.

The same measurement procedure was used for the thin atactic PMMA films. The final thickness of the latter was controlled by varying the revolution rate during spin coating of $950\ 000$ MW atactic PMMA in Anisole (Microchem Corporation) onto the INPS surface.

1.3 Optical Calorimetry of hydrogen oxidation over Pd nanocatalysts.

The measurements were carried out in a quartz tube reactor (diameter = 25mm) heated with a resistive heating coil. The reactor temperature was controlled using an electronic feedback loop and by measuring the temperature with a thermocouple placed, upstream the sample, inside the reactor. During the measurement, the sample temperature was recorded with a thermocouple in contact with the sample surface. A set of mass flow controllers (Bronckhorst) with different working ranges was used to obtain the desired flows and concentrations of the reactants and the carrier gas (Ar). The flow of the Ar carrier gas was adjusted to keep the total gas flow constant at 1000 ml/min (3.4 cm/s plug flow velocity) during each measurement. The total reactant concentration was 4%.

Optical spectra were collected using a fiber-coupled array spectrometer (Avantes AvaSpec). An optical fiber (Ocean optics) was used to bring the light from the light source (Avantes, AvaLight-Hal) into close proximity (5-10 cm) of the reactor tube. A collimated light beam from the optical fiber, which was obtained using a collimating lens (Ocean optics), was shone through the front wall of the reactor tube, through the sample and finally through the back wall of the reactor where it was collected into an optical fiber (equipped with a collimating lens) and transmitted to the spectrometer.

For freshly fabricated samples, after Pd evaporation, a stable optical signal was obtained after 10-20 cycles in H₂ and O₂ at 250 °C. The observed optical shift during this structural stabilization can be attributed to catalytic reshaping and sintering^{2, 3} of the Pd catalyst particles on the SiO₂ spacer.

To correct for the LSPR peak shifts induced by the external heating of the sensor, a calibration measurement was carried out in 4% H₂ in Ar (i.e. without any reaction taking place) and subtracted from the data obtained under reaction conditions. The error introduced by having only H₂ and not H₂ + O₂ for the calibration is very small since the dominant cooling gas is Ar in both cases.

1. 4 Indirect sensing hydrogen storage experiments.

The experiments were carried out in a heated stainless steel chamber which was connected to a vacuum pump as well as molecular hydrogen (6N purity) and molecular oxygen gas. The chamber was heated with an active temperature control feedback from a thermocouple in close contact with the sample inside the chamber. The hydrogen pressure was controlled with two capacitance pressure gauges (MKS Baratron). Prior to every experiment the chamber was pumped over night at 100°C. Subsequently, the sample was catalytically cleaned by 2 oxygen-hydrogen cycles. After the catalytic cleaning, several (typically 20-40) hydriding-dehydriding cycles were run at 105°C, until a stable and reversible optical signal was reached. Stabilization of the optical response of the sensor was interpreted as the Pd clusters having reached a stable geometrical and internal structure state (i.e. no further hydrogen-induced sintering or other irreversible (micro)structure transformation processes occurred). Thereafter, the sample was cooled down to 30°C while pumping the chamber and the first isotherm was measured at 30°C by increasing the hydrogen pressure in steps and waiting after each step for the optical signal to become stable. The optical response was obtained by measuring extinction spectra

in a spectrophotometer (Varian Cary 5000) in transmission mode with the experimental chamber being placed in the sample compartment of the latter. The hydriding and dehydriding kinetics were obtained by measuring optical extinction at a constant wavelength (640 nm) on the low energy "tail" of the peak of the Au disk LSPR. The integration time of the spectrophotometer (Varian Cary 5000) was set to 0.05 s. The pressure was then instantaneously increased from 1 mbar (where the H/Pd ratio is small) to 500 mbar (the cell filling time constant being ca. 0.06 s) and the change in the optical signal was monitored, yielding a hydriding kinetic curve. At 500 mbar pressure, Pd was to 100 % converted to hydride. After reaching a stable optical extinction signal, attributed to the full conversion of metallic Pd to the hydride phase, the experiment was reversed by instantaneously evacuating the chamber down to 1 mbar hydrogen pressure (evacuation time constant ca 0.25s). The corresponding dehydriding kinetics was, similarly to the hydriding kinetics, obtained by following the optical extinction signal in real time. Four sorption-desorption cycles were measured for each temperature.

1.5 Quartz Crystal Microbalance hydrogen storage experiments.

The QCM hydrogen storage measurements were carried out in a setup built in-house. The QCM chamber was connected to a vacuum pump as well as molecular hydrogen (6N purity) and oxygen gas and equipped with capacitance pressure gauges (MKS Baratron) for pressure control. The QCM-crystals (10 MHz fundamental mode SC-cut, Laptech) were mounted onto spring-loaded Au contacting-pins inside a heatable small volume of a copper block inside the QCM chamber. The required temperature stability was obtained by heating the copper block having an active temperature control through a controller with feedback from a chromel-alumel thermocouple placed in close vicinity of the QCM crystal. As reference temperature for the controller, an Omega IcePoint Calibrator was used. After mounting of the QCM crystal, the chamber was baked at 80°C over night while pumping. Subsequently the chamber was exposed to several oxygen-hydrogen cycles for catalytic cleaning of the Pd surfaces. After that, in order to reach the necessary stability of the system, the sample was annealed in hydrogen for 12-24 h at 1 atm pressure and at 80°C. For the actual measurements, the QCM was then operated at 30°C at its fundamental frequency, 10 MHz, using QSoft® software (QSense AB). To correct for hydrostatic pressure induced effects, calibration measurements of frequency shifts induced by changes in hydrostatic pressure on the QCM crystal were carried out on the blank crystal. The obtained frequency shifts were later subtracted from the ones obtained when measuring the sample with the Pd nanostructures. The studied Pd nanoparticles were fabricated onto a QCM crystal by sputtering 30 nm SiO₂ onto both electrodes, followed by subsequent evaporation of a granular 1nm Pd film on both sides.

2. Supporting Results

2.1 Tuning the sensitivity of the indirect sensing platform

It has been demonstrated extensively in the plasmonic biosensing literature that altering the size and shape of the LSPR nanoparticles in the nanoplasmonic sensor is an effective way to control and improve its sensitivity. It is therefore to be expected that our indirect nanoplasmonic sensing platforms can be improved and optimized for specific applications in a similar way. The first steps in this direction are shown in figure S1 with hydride formation isotherms as an example. Four different sensor nanodisk geometries were investigated, i.e. both nanodisk diameters D and height h were varied for constant spacer layer thickness and size of the deposited Pd nanoparticles. It is clearly seen that significant improvements in the sensitivity can be made for the three readout parameters $\Delta\lambda_{\max}$ (peak shift), Δf_{whm} (fwhm shift) and $\Delta E_{\max}$ (extinction shift). Interestingly, the different readout parameters respond very differently to the altered nanodisk sensor geometries. For example, the particles that give the largest extinction shift ($D = 76$ nm, $h = 40$ nm; red curve in Fig. S1 c) of all investigated LSPR particles, show the smallest peak shift (Fig S1 b) and intermediate fwhm shift (Fig S1 a). We predict that the sensitivity of the indirect sensing platforms can easily be improved by 5-10 times or more, over what has been shown here, by nano-engineering of the sensor particle geometry.

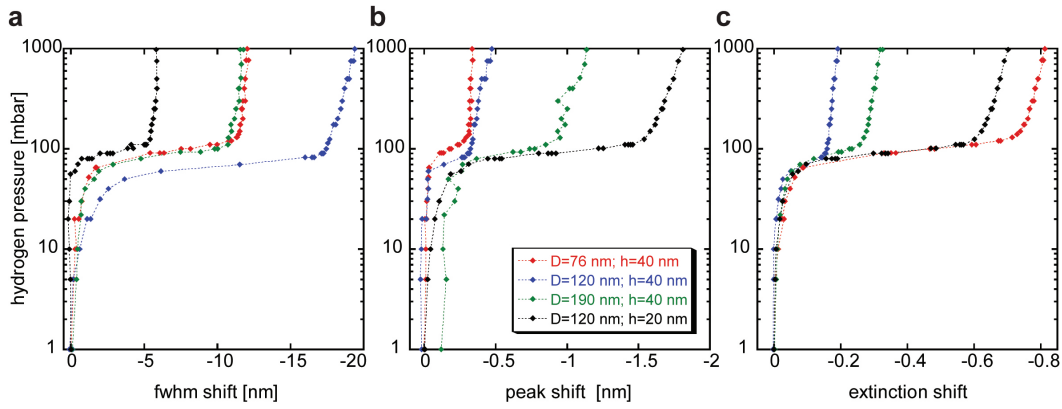


Figure S1: Sensor particle size dependent sensitivity. The figure depicts hydride formation isotherms, measured at 30°C, for identical Pd nanoparticles and four different Au nanodisk sensor geometries. The response for the readout parameters (a) Δf_{whm} , (b) $\Delta\lambda_{\max}$, (c) $\Delta E_{\max}$ is shown.

2.2 Sensor response to the amount of deposited metallic nanomaterial

The presence of a metallic shell around Au nanoparticles can significantly dampen and eventually quench the Au plasmonic resonance. It is therefore interesting to briefly explore how the presence of small metallic nanoparticles on the spacer layer of an indirect nanoplasmonic sensor influences the response. We illustrate the latter with the example of Pd nanoparticles. The presence of the Pd nanoparticles on the

spacer layer, when compared to the case without particles, is a significant broadening (i.e. damping) and spectral red-shift of the Au-LSPR peak (with respect to the blank sensor) for increasing size and surface coverage of the Pd nanoparticles (figure S2f and g). These shifts nicely reflect the coupling between the Au sensor LSPR and the Pd nanoparticles. This study also indicates that measurements with high metallic nanoparticle densities as well as thin metallic films on the sensor surface are feasible without quenching the Au LSPR.

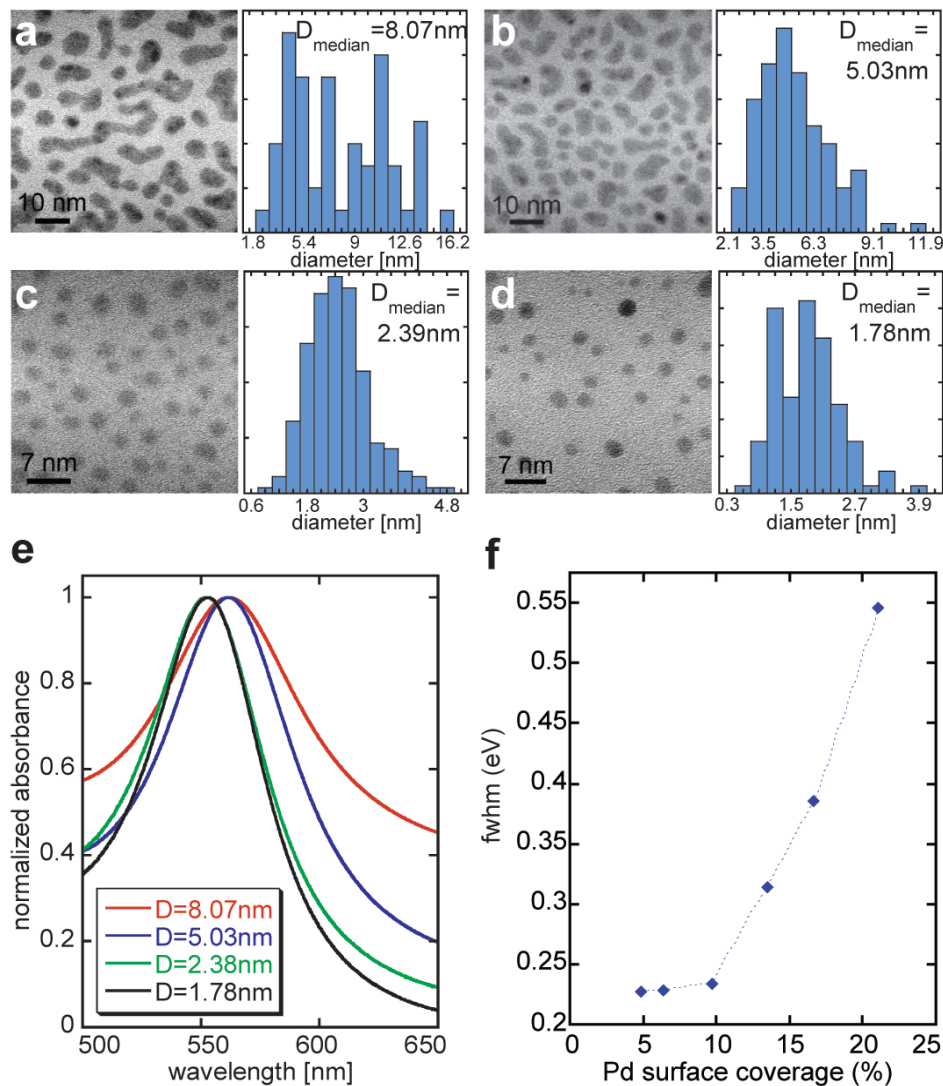


Figure S2: Sensor response to different amounts of deposited nanomaterial. (a)-(d) TEM images of Pd clusters deposited by evaporation and hydrogen annealing of granular Pd films. (e) Optical extinction spectra measured in vacuum for different amounts of deposited Pd, i.e. Pd cluster sizes. The Au sensor LSPR is significantly spectrally red-shifted and broadened for increasing Pd nanoparticle size. (f) Quantification of the Pd particle surface coverage dependent fwhm of the Au sensor LSPR, illustrating the coupling between the Au LSPR and the material deposited onto the sensing platform. Increasing amounts of Pd on the sensor give rise to stronger damping of the coupled system.

2.3 Glass transition in confined polymers raw data

The glass transition measurements were carried out in a heated stainless steel chamber. The measured $\Delta\lambda_{\max}$ -values thus had to be corrected for the peak shift caused by heating of the samples during the temperature ramp, due to the intrinsic temperature sensitivity of the indirect sensing platform. In figure S3 the response to increasing temperature of the blank sensor (blue), the sensor decorated with $\langle D \rangle = 110$ nm PS spheres (a) and a 40 nm thick PMMA film (b) is shown. By subtracting the calibration measurement from the blank sensor from the raw data with polymer, the true temperature response of the latter is obtained (red curves).

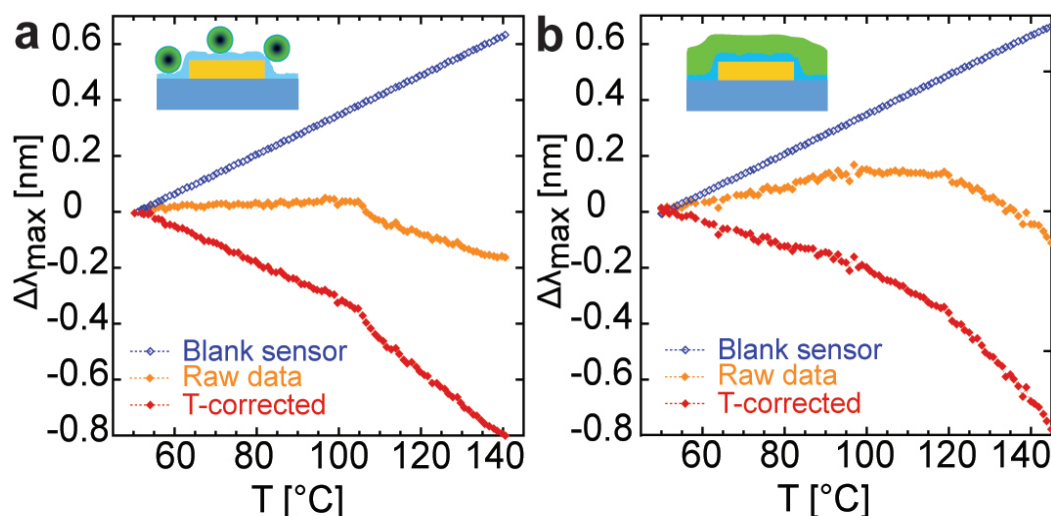


Figure S3: Correction for temperature induced peak shifts. Temperature response of blank sensor platforms and sensors decorated with (a) $\langle D \rangle = 110$ nm PS spheres and (b) a 40 nm thick PMMA film.

2.4 Optical Calorimetry: Reactant flow rate and heating rate

In figure S4a we show the correlation between the measured sensor temperature shifts (with a thermocouple in contact with the sensor surface) and $\Delta\lambda_{\max}$ shifts (which is a measure of the exothermically induced, local temperature rise). Both temperature shifts were obtained by quenching the $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ reaction (at $\alpha = 0.35$, reactor temperature 180°C) by shutting down the reactant gas. This was performed at four different gas flow rates in the reactor. The larger total temperature shift ($\Delta T_{\text{thermocouple}}$) and the larger $\Delta\lambda_{\max}$ upon quenching of the reaction for higher gas flow rates reflect that there is, due to mass transport limitations, a higher total reaction rate when the reaction is running and thus higher chemical power after light-off, because the higher flow rates supply more reactants to the sample. The linear correlation between the global sensor temperature, measured by a thermocouple, and $\Delta\lambda_{\max}$ in the steady state for different flow rates confirms our interpretation of $\Delta\lambda_{\max}$ being a direct measure of the local catalyst temperature. On

the abscissa a $\Delta\lambda_{\max}$ value of -1 nm corresponds to a temperature change of -80 °C upon quenching of the reaction.

In figure S4b light-off traces, i.e. $\Delta\lambda_{\max}$ versus $\Delta T_{\text{thermocouple}}$, are plotted for three different reactor heating-rates. Note that in the figure the $\Delta\lambda_{\max}$ is due to a combination of the external heating and reaction heating – here the important thing is that all curves coincide and show no sign of temperature lag time between $\Delta T_{\text{thermocouple}}$ and the local surface temperature.); clearly the total $\Delta\lambda_{\max}$, the general shape of the curve and the light-off temperature are not changed by varying the reactor heating-rate.

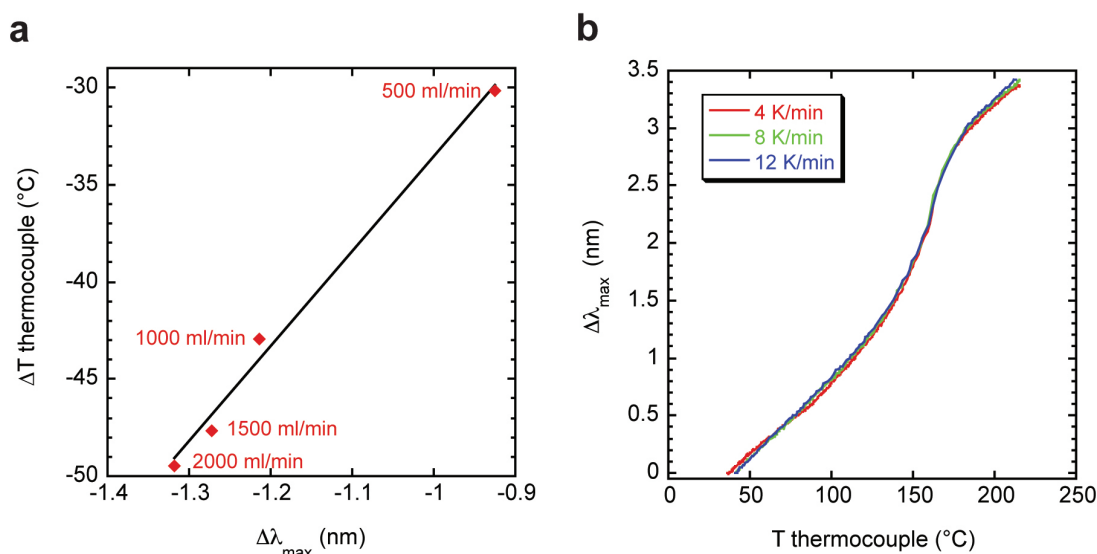


Figure S4: Reactant flow rate and reactor heating rate. (a) $\Delta\lambda_{\max}$ and sensor temperature measured by a thermocouple after quenching of the $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ reaction for different gas flow rates in the reactor. (b) Light-off traces, i.e. $\Delta\lambda_{\max}$ versus the sensor temperature measured by a thermocouple, for three different reactor heating-rates.

2.5 Hydrogen Storage: Van't Hoff analysis

The enthalpy of formation of the palladium hydride phase can be calculated from the temperature dependence of the plateau pressure in the p- Δf_{whm} isotherms, using of the Van't Hoff relation $\ln(p/p_0) = \Delta S - \Delta H/T$. Figure S5 shows Van't Hoff plots as obtained from p- Δf_{whm} isotherms by using the “center of mass” of the sloping plateaus as reference point for reading out plateau pressures. The plots for the different Pd cluster sizes clearly indicate the expected destabilization of the hydride phase in the smallest clusters.

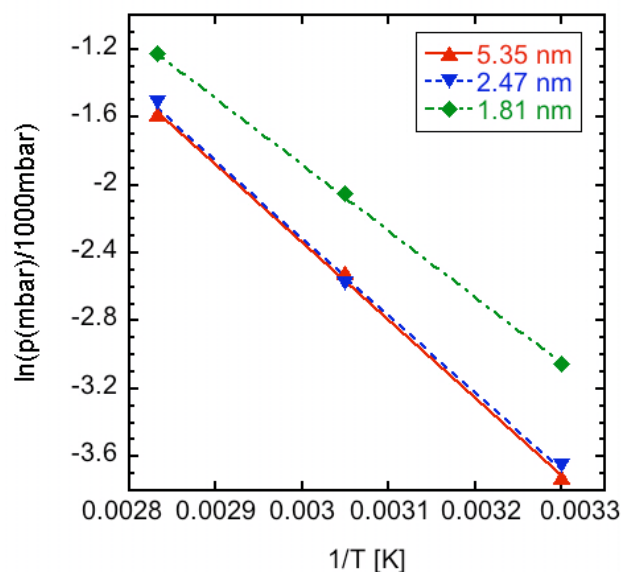


Figure S5: Van't Hoff analysis. Van't Hoff plots for three different Pd nanoparticle sizes indicate clearly the destabilization of the hydride phase for the 1.8 nm clusters.

References

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