Supporting Online Material for

**Nanoplasmonic Probes of Catalytic Reactions**

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Materials and methods

Indirect sensing structure for LSPR studies of kinetic phase transitions and associated adsorbate coverage changes on Pt nanoparticles

Au nanodisks (diameter = 76 nm, height = 30 nm) were fabricated onto borofloat glass using hole-mask colloidal lithography.(1) This nanofabrication method yields a quasi-random distribution of nanodisks, which in combination with a large particle-particle separation, eliminates both far and near-field coupling between the particles, so that the measured optical properties reflect the optical response of a single particle(2). A heat treatment (670 K for 2 h in Ar) of the Au nanodisks was used to obtain a thermally stable (in the temperature range of subsequent catalytic experiments) nanoparticle shape. The SEM image in Fig. 1C shows that the Au nanodisks after the heat treatment had the shape of hexagons. A thin, 10 nm, SiO$_2$ film was deposited onto the Au nanoparticle covered substrate using RF sputtering. Subsequently, a 2 nm thick granular Pt film was thermally evaporated (e-beam evaporation, 0.05 nm/s) onto the SiO$_2$ film. After cyclic treatment (10-20 cycles) of the sample in H$_2$ and O$_2$ at ~500K, single crystal Pt clusters with an average diameter of ca. 12 nm and a projected surface coverage of ca. 20 % were formed from the granular film. The cycling was done to get reproducible results, not plagued by aging effects, in the catalytic experiments. A TEM image of Pt clusters identical to those on the sensing structure (see further details below) is shown in Fig. 1D and their size distribution is shown in Fig. S1. The particle diameter was calculated from the particle area by assuming a spherical particle shape.
Figure S1: Size distribution of Pt clusters formed after annealing of a 2 nm (nominal thickness) Pt film on sputtered SiO$_2$.

The function of the SiO$_2$ layer is twofold (i) it makes the sensing structure more stable at high temperatures and (ii) it eliminates any interaction between the Au nanoparticles and the Pt clusters (e.g. alloying or direct electronic interaction). It also protects the Au nanoparticles from the surrounding environment, which is an advantage in many catalysis applications, since the reactions often take place in a harsh environment (e.g. in the car exhaust).

**Indirect sensing structure for NO$_2$ storage and reduction**

Au nanodisks (diameter = 110 nm and height = 30 nm) were fabricated and heat-treated as above. A ~30 nm thick Ba film, and subsequently, a 0.5 nm granular Pt film, was thermally evaporated onto the particle covered substrate. The evaporated Ba film was converted to BaO upon exposure to air and later during an oxygen treatment (6% O$_2$ in Ar) at ~500 K in the flow reactor.
Direct sensing structure for LSPR studies of kinetic phase transitions and associated adsorbate coverage changes on Pt nanodisks

Pt nanodisks (diameter = 170 nm, height = 60 nm) were fabricated onto a borofloat glass substrate using hole-mask colloidal lithography(1). A stable optical signal was obtained from the Pt disks after 10-20 cycles in H$_2$ and O$_2$ and an $\alpha$H$_2$ sweep at 500 K. Catalytic reshaping(3) of the nanodisks to a more irregular shape was observed after the latter treatment. SEM images of nanodisks after catalytic reshaping are shown in Fig. S2. Fig. S2 also shows a schematic of the sensing structure.

![Schematic of sensing structure](image)

**Figure S2:** “Direct sensing” structure used to detect changes in adsorbate coverage at the kinetic phase transition of the H$_2$-O$_2$ system. A) Schematic illustration. B-C) Top view (B) and 70° tilt (C) SEM images of the sensing structure in A after catalytic reshaping.

**Catalyst flow reactor measurements**

Measurements were carried out in a quartz tube reactor (diameter = 25mm) heated with a resistive heating coil. The reactor temperature was kept constant 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 (10pc) 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 during each measurement.

Optical spectra were collected using a fiber-coupled array spectrometer. An optical fiber
(Ocean optics) was used to bring the light from the light source (Avantes) 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 (Avantes). In the present case, when time resolution was not an issue, spectra
were collected every 20s to avoid too large data sets. However, it is possible to collect spectra
every second or even more frequently if desired, in order to follow relatively fast kinetic
processes.

All data collected using the indirect sensing structure in Fig. 1 B-D was corrected for a
small signal arising from the interaction of gasses with the SiO₂ spacer layer(4). The
correction was carried out by performing an identical measurement using an almost
identical sample without Pt nanoclusters. The signal measured during the calibration
measurement was subtracted from that obtained during the actual measurement before
displaying the data. This small correction has no influence on the analysis in the main
text or the conclusions.
Electron microscopy

Scanning electron micrographs, of the nanostructured glass samples, were collected with a low vacuum SEM (FEI Quant 200 FEG ESEM, 15kV) using water vapor to obtain a pressure of about ~0.7 Torr.

The Pt structures in the TEM image (Philips CM200 FEG 200 keV) in Fig. 1D were fabricated by first sputtering 10 nm SiO$_2$ and, subsequently, evaporating 2 nm Pt onto a TEM window(5). Before imaging, the TEM window was inserted into the reactor and was exposed to H$_2$, O$_2$ and CO at 500 K to mimic the conditions for the actual sensing structure.

Supporting online text and figures

Raw data

The raw data for a typical H$_2$ oxidation measurement is shown in Fig. S3. In the beginning of the measurement the hydrogen concentration is 4 % and the oxygen concentration 0 %, with Ar constituting the remaining (carrier) gas. The hydrogen (oxygen) concentration is subsequently decreased (increased) in steps until the hydrogen concentration is 0% and the oxygen concentration 4%. During the complete measurement the total reactant concentration was kept constant at 4 %. Subsequently, the hydrogen concentration is increased back to 4 % in steps while the oxygen concentration is decreased accordingly.
Fig. S3: Raw data showing the plasmon peak position and temperature during a typical H₂ oxidation measurement using the sample in figure 1 B-D. The total reactant concentration was 4 %. The hydrogen concentration is indicated in the figure. After reaching 0 % H₂ and 4 % O₂ the hydrogen concentration is increased and the oxygen concentration decreased in steps back to the original values. The same concentration steps are used for increasing and decreasing α. Note the large steps in $\Delta \lambda_{\text{max}}$ at ca. 50 mins and ca. 122 mins, which is due to the kinetic phase transitions to/from an oxygen saturated from/to a partially hydrogen covered surface.

Varying the temperature for the H₂+O₂ reaction - hydrogen poisoning effect at low T
**Figure S4:** Plasmon peak shifts (A-B) and temperature variation (C) during $\alpha^{\text{H}_2}$ sweeps at three different temperatures, 340K, 380K and 500K (temperatures due to external heating only, i.e. without reaction induced heating). The graph in panel B is a magnification of the phase transition region in panel A. Triangles pointing upwards and downwards are used to symbolize $\alpha^{\text{H}_2}$ sweeps up and down, respectively. The sensing structure in Fig. 1 B-D was used. The total reactant concentration was 4 % and the flow rate 16.7 ml/s. Note the hysteresis in the orange curves corresponding to the lowest temperature. At high temperatures the hysteresis disappears as predicted by theory(5).

Fig. S4 shows $\alpha^{\text{H}_2}$-sweeps, similar to those presented in Fig. 2A, at three different temperatures, using the “indirect sensing” structure in Fig. 1 B-D. The notable new features, as the temperature is lowered are; (i) the step in $\Delta \lambda_{\text{max}}$ and the position of $\Delta T_{\text{max}}$ move together to lower $\alpha^{\text{H}_2}$ values, (ii) a hysteresis develops along the $\alpha^{\text{H}_2}$ scale between the up and down steps in $\Delta \lambda_{\text{max}}$, (iii) the T versus $\alpha^{\text{H}_2}$ curves change from a symmetric, triangular to an asymmetric shape (the latter similar to the CO+O$_2$ case in Fig. 2B), and also exhibit hysteresis. All these observations are explained by the kinetic phase transition for the reaction: The asymmetry of the T versus $\alpha^{\text{H}_2}$ curve at low temperature is due to surface hydrogen poisoning (similar to the well known CO poisoning in CO+O$_2$; see the main text in the article), and an accompanying lower reaction rate in the hydrogen rich regime. Higher hydrogen coverage is strongly promoted by lower temperature, since hydrogen desorption depends exponentially on temperature, while sticking has a weak temperature dependence. The shift of the $\Delta \lambda_{\text{max}}$ step and $\Delta T_{\text{max}}$ to lower $\alpha^{\text{H}_2}$ as temperature is lowered, are due to an earlier (in $\alpha^{\text{H}_2}$) transition to the hydrogen-poisoned regime. The hysteresis in $\Delta \lambda_{\text{max}}$ and $\Delta T_{\text{max}}$ versus $\alpha^{\text{H}_2}$ is an inherent property of kinetic phase transitions at certain conditions(6), when the temperature is not too high. An additional general feature is that the hysteresis increases with decreasing temperature. All these observations relate to well-known properties of the actual reaction(5), and demonstrate the ability of LSPR sensing for catalysis.
Varying the total reactant concentration – reaction exothermicity and LSPR temperature effect

**Figure S5:** A) Plasmon peak shifts for $\alpha_{H_2}$ sweeps at four different reactant (i.e. H$_2$+O$_2$) concentrations, 1 %, 2 %, 4 % and 6 %. The “indirect sensing” structure in Fig. 1 B-D was used. Triangles pointing up and down are used to symbolize $\alpha_{H_2}$ sweeps up and down, respectively. The temperature without reaction, i.e. with only external heating, was 507 K and the flow rate 16.7 ml/s. The inset shows the maximum temperature increase during the $\alpha_{H_2}$ sweeps. The temperature increase is due to reaction induced heating, i.e. it is caused by the chemical power dissipation in the exothermic reaction. B) Change in temperature when $\alpha_{H_2}$ increases/decreases from $\alpha_{H_2}=0.7$ to $\alpha_{H_2}=1$ for the four different reactant concentrations, 1 %, 2 %, 4 % and 6 %. The inset shows the slope $\delta \Delta \lambda_{\text{max}} / \delta \alpha_{H_2}$ for $\alpha_{H_2} > \alpha_{H_2}^{\text{cr}}$ in A as a function of reactant concentration. The reaction induced temperature increases essentially linearly with the reactant concentration.

Fig. S5 shows an extension of the measurements in Fig. 2A, where different reactant (H$_2$+O$_2$) concentrations (1 - 6 %) were used. The two most important observations are (i) a constant magnitude of the $\Delta \lambda_{\text{max}}$ step at $\alpha_{H_2}^{\text{cr}}$, which does not depend on gas phase concentration and (ii) increasing slopes of $\Delta \lambda_{\text{max}}$ to the left and right of the kinetic phase transition with increasing reactant concentration. Both features are explainable in terms of what is known about the actual reaction (for (i)) and about the T-dependence of $\Delta \lambda_{\text{max}}$ (for (ii)). Regarding
(i) the magnitude of the step in $\Delta \lambda_{\text{max}}$ is almost constant independent of reactant concentration, because the kinetic phase transition for all four reactant concentrations involves a surface coverage change on the Pt nanoparticles, from an oxygen saturated surface to a partly hydrogen covered surface, and it is primarily the removal of a saturated oxygen monolayer that is detected (see Discussion). (The $\Delta \lambda_{\text{max}}$ step size is also independent of flow rate for the same reason, see Fig. S6.) The temperature maximum at $\alpha_{\text{H}_2}^{\text{cr}}$ also here coincides with the stepwise change in $\Delta \lambda_{\text{max}}$ (not shown). However, the amplitude of $\Delta T_{\text{max}}$ increases linearly with the reactant concentration (see the inset), as expected, since the total chemical power dissipation (i.e. the reaction rate) in the exothermic reaction increases linearly with concentration. (ii) An interesting and important feature in Fig. S4 is that the slopes of $\Delta \lambda_{\text{max}}$ versus $\alpha_{\text{H}_2}$ at $\alpha_{\text{H}_2} < \alpha_{\text{H}_2}^{\text{cr}}$ and $\alpha_{\text{H}_2} > \alpha_{\text{H}_2}^{\text{cr}}$ increase with increasing reactant concentration. This effect, which is connected with temperature variations(7) and the influence of temperature on $\Delta \lambda_{\text{max}}$, was initially regarded as an undesired perturbation, but then realized to be an additional valuable observable of the LSPR measurement. The effect can be calibrated by external heating and recording of $\Delta \lambda_{\text{max}}(T)$ in inert gas, and was found to be 0.015 nm/K. Thus we have a built in thermometer in the measurement, which can be used to calculate the sample temperature. An example of this is shown in Fig. S4 B. The inset shows the slope $\delta \Delta \lambda_{\text{max}} / \delta \alpha_{\text{H}_2}$ for $\alpha_{\text{H}_2} > \alpha_{\text{H}_2}^{\text{cr}}$ for four different reactant concentrations. The linear fits to the data are forced through the origin. Good fits to the data are obtained indicating that the slope is, at least primarily, caused by a change in the sample temperature. The change in $\Delta \lambda_{\text{max}}$ was, subsequently, used to calculate the temperature change when $\alpha_{\text{H}_2}$ was decreased/increased from 1 to 0.7, using the calibrated temperature sensitivity 0.015 nm/K. This effect can be integrated, by multiplexing, in a measurement where both the catalytic effects and the temperature effects are measured simultaneously (see brief comment in the main text and the Discussion).
Varying the flow rate – mass transport vs. kinetic control

Figure S6: Plasmon peak shift during $\alpha^{H_2}$ sweeps at different flow rates. The “indirect sensing” structure in Fig. 1 B-D was used. Triangles pointing up and down are used to symbolize $\alpha^{H_2}$ sweeps up and down, respectively. Data are shown for three different flow rates, 8.3, 16.7 and 50 ml/s. The temperature without reaction was 507 K and the total H$_2$+O$_2$ reactant concentration was 4 %. The inset shows the maximum temperature increase versus flow rate during the $\alpha^{H_2}$ sweeps.

The position of $\Delta T_{\text{max}}$ and the step in $\Delta \lambda_{\text{max}}$ at $\alpha^{H_2}_{\text{cr}} = 0.5$ in Fig. 2A show that the overall reaction is largely mass transport controlled, since a kinetically controlled reaction occurs at $\alpha^{H_2} \leq 0.2$. A fully mass transport controlled reaction would occur at the reaction stoichiometric mixture $\alpha^{H_2} = 2/3$, however this value is reduced to $\alpha^{H_2} = 0.55$ if gradients do not extend through the whole reactor, due to the different diffusion rates of H$_2$ and O$_2$ in the carrier gas(8). To further verify the mass transport control of the reaction, $\alpha^{H_2}$ sweeps were performed at different flow rates (Fig. S6). An increased flow rate shifted $\alpha^{H_2}_{\text{cr}}$ towards the kinetically controlled regime (lower $\alpha^{H_2}$ values), as expected for a primarily mass transport controlled reaction. $\Delta T_{\text{max}}$ versus $\alpha^{H_2}$ shifted in the same direction (not shown) and increased linearly with the increase in flow rate (see inset), because the reduced mass transport control, due to the increasing flow rate, provided more reactants to the sample. The latter are all signals of mass transport limitations that decrease with increasing flow.
Direct sensing of the kinetic phase transition in the H\textsubscript{2}/O\textsubscript{2} system on Pt nanodisks

Figure S7: Plasmon peak shift and temperature increase during $\alpha^\text{H2}$ sweeps using “direct sensing”. The “direct sensing” structure in Fig. S2 was used. Triangles pointing up and down are used to symbolize $\alpha^\text{H2}$ sweeps up and down, respectively. The total reactant concentration was 2 % and the flow rate 16.7 ml/s. The temperature without reaction was 507 K.

We finally studied the kinetic phase transition in the H\textsubscript{2}/O\textsubscript{2} system using “direct sensing”, where the catalyst particles and the LSPR sensing particles are the same. The structure consisted of Pt disks (170 nm diameter, 60 nm high, $\lambda_{\text{max}} \approx 540$ nm) as shown in Fig. S2. Such Pt disks have previously been shown to exhibit LSPR type resonances\(^9\) similar to those of gold. Data from two representative $\alpha^\text{H2}$-sweeps (2 % reactant, 507 K, 16.7 ml/s) are shown in Fig. S6. The result is essentially the same as described in the main article for the indirect sensing structure, with a stepwise change in $\Delta \lambda_{\text{max}}$ at the kinetic phase transition, however with a significantly smaller step amplitude. Although the indirect sensing is of much broader applicability and generally more interesting, the direct sensing may in some cases be preferred, or used as a complement, since the Pt disks can be converted to well-defined single crystals and can thus represent well defined model catalysts with single crystal properties.
Discussion

Detection mechanism: kinetic phase transitions

To elucidate the sensing mechanism, measurements were performed at 590 K where the indirect sensing structure in Fig. 1B-D was exposed alternatively to \( \text{O}_2 \), \( \text{H}_2 \) and \( \text{CO} \). The gas concentrations were 2 \% \( \text{O}_2 \), 3.5 \% \( \text{CO} \) and 1.3 \% \( \text{H}_2 \), respectively. From the known pressure and the hydrogen chemisorption energy on Pt it was estimated that the hydrogen coverage should be less than 0.01\% under these conditions, while there would be a close to full monolayer of \( \text{CO} \) and \( \text{O}_2 \). For a monolayer of \( \text{O}_2 \) a spectral red-shift of ca. 1 nm was observed while a monolayer of \( \text{CO} \) gave rise to a blue shift of about 0.1 nm. Since the peak shifts observed during the kinetic phase transition are about 1 nm this indicates that it is mainly the oxygen chemisorption layer that is detected, i.e. the sensitivity is about one order of magnitude larger for oxygen compared to \( \text{CO} \). From the data we thus obtain that a monolayer of oxygen causes an LSPR red-shift of ca. 1 nm, with the present sensing structure (which can be optimized further, see below).

The ultimate sensitivity with the present sensing structure and optical set up was estimated from calibration measurements where a spectral peak shift of 1 nm was obtained for a monolayer of oxygen. In the current measurements the peak-to-peak noise level was < 0.02 nm giving an absolute sensitivity of less than 0.02 monolayers of oxygen. Similarly the spectral peak shift for a monolayer of \( \text{CO} \) was measured to be ca. 0.1 nm giving an absolute sensitivity of 0.2 monolayers of \( \text{CO} \). These values are far from optimal generally speaking. There are in principle to ways of improving the optical resolution. We estimate that the sensitivity can be improved by a factor of 20 by optimizing the optical equipment and setup\(^{10}\). Further improvement can be made by optimizing the size, shape and material of the
plasmonic particles, as well as the thickness of the separating layer. However, it is more
difficult to estimate the magnitude of these latter improvements. In any case a sensitivity of
0.001 monolayer of oxygen is a modest sensitivity limit, which we believe can be further
improved.

It is of interest to compare our observed sensitivities with those reported in literature in spite
of the fact that our sensitivities were obtained by indirect sensing (except for one case) and
those in literature by direct sensing. Our observed sensitivities were; 1 nm shift for the
indirect sensing of one monolayer of oxygen on Pt nanoparticles covering 20 % of the
surface. The latter suggests a 5 nm shift for a Pt particle film covering nearly 100 % of the
surface (ignoring particle-particle interactions). For CO we observed about ten times less
sensitivity. For the conversion of the surface layer of BaO to a surface layer of Ba(NO)\(_x\)
the signal was much larger, up to ca. 14 nm, i.e. more than an order of magnitude larger
compared to the oxygen/Pt case. In the BaO/ Ba(NO)\(_x\) case we expect more than a monolayer
to be affected. For the direct sensing case we obtained about 0.4 nm shift for a monolayer of
oxygen on Pt particles.

These observed sensitivities match reasonably those observed previously for molecular thiol
layers and oxide layers on plasmonic nanoparticles, considering the difference in the studied
systems and the different sensing situations (indirect versus direct). For thiol layers,
sensitivities in the range of 0.7 - 5.9 nm/CH\(_2\) have been reported(11-13). Experimental and
theoretical data on the formation of oxide layers on Al(14) and Cu(15) nanoparticles give
sensitivities of ca. 1-14 nm per oxygen monolayer. The latter can be compared with our direct
sensing value, which was a spectral shift of 0.4 nm.
It is interesting to what extent the current measurements can be extended to real porous catalysts. The sensing function is proportional to the enhanced electromagnetic field, which decays exponentially as a function of distance away from the nanoparticle surface. The decay length of the enhanced electromagnetic field is typically 10-30nm. The sensitivity of the plasmon resonance to dielectric changes in its environment is proportional to the field enhancement and therefore decays from the structure surface in a similar manner as the enhanced field. A nanoplasmonic sensor is therefore only sensitive to changes occurring in its nano-environment. For thicker catalyst layers only the region closest to the plasmonic nanostructures can, therefore, be sensed. For the Au nanoparticles used here the sensing volume is estimated to be ca. $10^5 \text{nm}^3$ which would mean sensing of several monolayers of catalyst particles, a few nm in size, dispersed in a porous support. Work in this direction is in progress.

In order to get a feeling for the magnitude of the observed LSPR red-shift of ca. 1 nm, caused by a monolayer of oxygen, we compare this value with a value recently calculated using established Mie theory(16). A peak shift of 0.97 nm was obtained by increasing the thickness of a SiO$_2$ film, covering a silver ellipsoid particle with a LSPR resonance at 750 nm, from 10 nm to 10.1 nm. In the present case we have a monolayer of oxygen on, or almost embedded in, the Pt surface layer of nanoparticles covering ca. 20% of the SiO$_2$ surface. What the calculation tells is that a hypothetical SiO$_2$ layer 1 Å thick (10 nm from the plasmonic nanoparticle surface) and 20% of a Pt-O$^{\text{chemisorbed}}$ monolayer yield approximately the same signals. A shift of ca. 1 nm for an oxygen layer therefore seems very reasonable. Similar spectral sensitivities have also been observed experimentally for aluminum nanoparticles during the formation of a thin oxide layer on the nanoparticle surface(14). A more detailed analysis requires further experiments and theoretical modeling.
The detailed sensing mechanism thus still remains to be determined. Work function changes, change in surface polarizability and structural changes, caused by the chemisorbed oxygen (and CO) are all likely to play a role. Higher precision measurements in ultra high vacuum with complementary techniques for coverage determination will be required for unraveling the quantitative sensitivities to different adsorbates and adsorbate coverages. (See also discussion on NO\textsubscript{x} sensing below).

Regarding the generality of the method we note that many catalytic reactions are dominated by one species close to the rate maximum. In redox reactions there are usually dominant oxygen coverage on the oxygen rich side of the maximum and dominant or very low reducing agent coverage on the other side, as in the hydrogen and CO reactions demonstrated here. Other examples are ammonia production on iron catalysts, with dominant nitrogen coverage, and many hydro-treatment reactions. There are of course situations where the coverage composition is more complex and where multiple species of comparable coverage exist. In these cases the simple approach shown here must be modified, or one may just have to accept that some cases are not available for the present approach. However, the simplicity of the method plus the many reactions where single species coverage are at hand, in our view makes this an extremely interesting method for catalysis research. In such situations the multiplexing approach, briefly outlined in the main text and articulated below, is highly interesting and promising.

**Detection mechanism: NO\textsubscript{x} storage in BaO**

The BaO+NO\textsubscript{2} reaction is converting a thin surface layer of BaO to Ba(NO\textsubscript{3})\textsubscript{2}. This has two consequences of importance for the sensing; first the dielectric properties are changing
towards a lower dielectric constant (from $n \approx 1.97$ to $n \approx 1.87$), which should cause a blue-shift\textsuperscript{(14, 19)}, second the formation of Ba(NO\textsubscript{3})\textsubscript{2} is associated with a large volume expansion ($\sim 3x$), which should cause a red-shift. (The volume expansion was calculated from the densities and molecular masses of BaO and Ba(NO\textsubscript{3})\textsubscript{2}\textsuperscript{(20).}) Both looking at the shear numbers and since the experimental observation is a red-shift, we conclude that the latter effect is largest. This assumption is also supported by calculations using the electrostatic spheroid model. The observed red-shift is about 4-14 times larger than for a monolayer of oxygen on the dispersed Pt particles. The reason for the larger $\Delta \lambda_{\text{max}}$ shift in the NO\textsubscript{x} case is probably a combination of the larger dielectric change caused by the BaO $\rightarrow$ Ba(NO\textsubscript{3})\textsubscript{2} conversion, a larger total surface area involved in the storage - release and a possible 3D character of the Ba(NO\textsubscript{3})\textsubscript{2} layer, i.e. not only surface but also bulk incorporation of NO\textsubscript{x}\textsuperscript{(21).}

**Multiplexing**

In multiplexing, sensors with different sensitivities and/or measuring different quantities are combined into arrays. In the present case, different sensitivities for a given catalytic material can e.g. be obtained by changing the size, shape and material of the plasmonic nanoparticles, and/or the thickness of the spacer layer. Using fingerprinting, the combined response from all sensors can, via pattern recognition, provide a highly accurate and informative response about several properties even though the response of each sensor may be complex and imprecise. Such more complex sensing structures can be anticipated also for the NO\textsubscript{x} sensing to separate the different effects there (e.g. 2D versus 3D storage layers). Furthermore, by incorporating areas with and without catalytic material on the spacer layer, one can e.g. discriminate signals from the catalyst material and the spacer surface and also use the temperature sensitivity of the LSPR signal to integrate a temperature measurement. The idea can be extended to rapid screening by depositing arrays of different catalytic materials. Only areas of a few
micrometers in linear dimension will be needed for each material and each quantity to be measured.