Supporting information

for

Yttrium hydride nanoantennas for active plasmonics

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Methods

Optical characterization

The spectra are recorded using a Fourier-transform infrared spectrometer (Bruker Vertex 80), equipped with an infrared microscope (Bruker Hyperion). The incident light is focused using a Cassegrain objective with numerical aperture $NA = 0.4$, and the transmitted intensities are detected with Si and InGaAs diodes. The incident polarization is set along the long axis of the nanorods with infrared polarizers. The measured transmittance spectra I_T are normalized with respect to the substrate signal I_S and converted into extinction values via $I_{ext} = -\ln(I_T/I_S)$.

Diffusion model

The diffusion model developed in the manuscript is based on the continuity of the chemical potential for all layers of the system, similar to Pasturel et al.¹.

Figure S1: Sketch of a cut through an yttrium antenna, illustrating the important quantities of the diffusion model.

To be able to solve Eq. (1) from the manuscript,

$$\frac{D_{Pt}}{V_{Pt}} \cdot \frac{c_s - c_i}{L_{Pt}} = \frac{L_Y}{V_Y} \cdot \frac{dc_Y}{dt} \quad (1)$$

one needs to link the hydrogen concentrations at the surface of the caplayer c_s and at the interface c_i to the concentration in the Yttrium/YH_x layer c_Y . At the surface thermodynamic equilibrium implies that the chemical potential of molecular H₂ is related to the chemical potential of H in Pt in the following way

$$\frac{1}{2} \mu_{H_2} = \mu_{Pt} \quad (2)$$

as hydrogen dissolves atomically into Pt. The chemical potential of gaseous H₂ can be written as

$$\mu_{H_2} = RT \ln p_{H_2} + H_{H_2} - TS_{H_2}, \quad (3)$$

with $S_{H_2} = 130.77 \text{ J/Kmol H}_2$, the standard molar entropy at 1 bar. The enthalpy H_{H_2} is essentially given by $7/2 \text{ RT}$ where R is the gas constant.

The chemical potential of H at the surface of the caplayer is

$$\mu_{Pt}(x = 0) = RT \ln c_s + H_{Pt} - TS_{Pt} \quad (4)$$

As the solubility of H in Pt is very low due to the positive enthalpy of H solution in Pt. ($c_s \ll 1$)

Substituting Eqs. (3) and (4) into Eq. (2), we obtain

$$\frac{1}{2} RT \ln p_{H_2} = RT \ln c_s + \Delta H_{Pt} - T \Delta S_{Pt}, \quad (5)$$

where

$$\Delta H_{Pt} = H_{Pt} - \frac{1}{2} H_{H_2} \quad \text{and} \quad \Delta S_{Pt} = S_{Pt} - \frac{1}{2} S_{H_2} \cong -\frac{1}{2} S_{H_2} \quad (6)$$

are the enthalpy and entropy of hydride formation. The approximation on the RHS of Eq. (6) is valid, as the entropy of hydrogen in a metal lattice is small compared to the one of gaseous hydrogen.

Solving Eq. (5) for c_s leads to.

$$c_s = g \cdot \sqrt{p_{H_2}} \quad \text{with} \quad g = \exp \left(-\frac{\Delta H_{Pt} + 1/2 \cdot TS_{H_2}}{RT} \right). \quad (7)$$

To obtain a relation between the hydrogen concentration c_Y in the Y layer and the concentration c_i at the Pt-Y interface, we use the continuity of the chemical potential at the interface between the two layers. Thus, with

$$\mu_{Pt}(x = L_{Pt}) = RT \ln c_i + H_{Pt} - TS_{Pt} \quad (8)$$

at the Pt-Y interface, and

$$\mu_Y = RT \ln \frac{c_Y}{1 - c_Y} + H_Y - TS_Y \quad (9)$$

for the chemical potential of H in the Y layer, $\mu_{Pt}(x = L_{Pt}) = \mu_Y$ leads to

$$c_i = f \cdot \frac{c_Y}{1 - c_Y} \quad \text{with} \quad f = \exp\left(\frac{\Delta H_Y - \Delta H_{Pt}}{RT}\right), \quad (10)$$

as S_{H_2} is much larger than S_Y and S_{Pt} .

Substituting Eqs. (7) and (10) into (1) leads to a differential equation (see Eq. (4) in the manuscript) describing both the diffusion in and out of our system

$$\frac{dc_Y}{dt} = \frac{m}{\tau} \left(g\sqrt{p_{H_2}} - f \frac{c_Y}{1 - c_Y} \right), \quad (11)$$

with

$$\tau = \frac{L_{Pt}L_Y}{D_{Pt}} \quad \text{and} \quad m = \frac{V_Y}{V_{Pt}}. \quad (12)$$

During hydrogen loading at a given pressure p_{H_2} we need to solve the full differential equation. This can be carried out in a closed form by integration of the inverse function

$$t(c_Y) = \frac{\tau}{mf} \left(\frac{c_Y}{k+1} + \frac{1}{(k+1)^2} \ln \frac{1}{1 - c_Y \left(1 + \frac{1}{k}\right)} \right) \quad (13)$$

with

$$k = \frac{g}{f} \sqrt{p_{H_2}}. \quad (14)$$

Equation (13) can be approximated for low concentrations c_Y by a simple straight line with slope $dc_Y/dt = (m g \sqrt{p_{H_2}})/\tau$ as shown in Fig. S2a.

To validate the assumptions of a square root pressure dependency for the loading process, we performed loading measurements with various partial pressures of hydrogen on a new nanorod array sample. We used loading pressures of 0.05, 0.1, and 0.2 bar H_2 (in nitrogen) and performed the same extinction measurements as in the manuscript, taking a spectrum every 2 seconds. The time traces of the extinction maxima (particle plasmon resonance) for the three loading pressures are renormalized to the interval [0,1] and plotted in Fig. S2b. By

fitting straight lines to the three curves, we can extract the factor $(m g \sqrt{p_{H_2}})/\tau$ for all three pressures p_{H_2} .

These values nicely resemble a square root dependency on the pressure as predicted by the model (see the log-log plot in the inset of Fig. S2 (b)). The deviations between the slopes from Fig. 4b in the manuscript and Fig. S2b can be explained by fabrication differences between the two samples and different ages and quality of the platinum caplayer.

Figure S2: (a) Comparison between full solution of the diffusion model and a straight line with slope $(m g \sqrt{p})/\tau$. (b) Time trace of hydrogen loading measurements with hydrogen pressures of 0.05, 0.1, and 0.2 bar H_2 , extracted from extinction measurements and renormalized to [0,1]. The inset compares the slopes of the three curves with the expected hydrogen pressure dependence of $\sqrt{p}$ derived in the model.

For the hydrogen unloading process the differential equation Eq. (11) reduces to

$$\frac{dc_Y}{dt} = -\frac{f}{\tau} \frac{c_Y}{1 - c_Y} \quad (15)$$

As the external hydrogen pressure p_{H_2} is zero. This equation can be solved again using the inverse function and subsequent integration to give

$$t(c_Y) = -\frac{\tau}{m f} \left(c_Y - c_\infty + \ln \frac{c_\infty}{c_Y} \right), \quad (16)$$

which reduces to $t = -\tau/(m f) \cdot (c_Y - 1 - \ln c_Y)$, if we assume the concentration limit c_∞ to be approximately unity.

Simulated extinction spectra

We performed FEM simulations using CST MICROWAVE STUDIO 2012, CST AG with periodic boundary conditions (unit cell $700 \times 400 \text{ nm}^2$). The simulation results for plain rod antennas with dimensions $380 \times 160 \times 50 \text{ nm}^3$ on a glass substrate ($n_{\text{SiO}_2} = 1.5$) are shown in Fig. S3 for the case of metallic yttrium dihydride (dielectric data for $\text{YH}_{1.8}$ from ref. 2) and dielectric yttrium trihydride ($\text{YH}_{2.9}$ from ref. 2). The simulations are in good qualitative agreement with the measured data in Fig. 2, showing practically no extinction signal for the trihydride whereas the dihydride exhibits a strong plasmonic resonance in the near-IR region.

Figure S3: Calculated extinction spectra, using tabulated dielectric data from Van Gogh et al.². The metallic yttrium dihydride exhibits a plasmonic resonance at 1800 nm (red line) whereas the dielectric trihydride has a negligible extinction signal (blue line).

Dielectric function modelling

Gartz et al.³ have shown that it is possible to describe the dielectric function of yttrium by the following expression:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{S_{osc} \cdot \omega_{osc}^2}{\omega_{osc}^2 - \omega^2 - i\omega\gamma_{osc}} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_{fe}}$$

Here, the first part represents a standard harmonic oscillator with oscillator strength S_{osc} , an oscillator frequency ω_{osc} and a damping constant γ_{osc} . The last part follows the Drude theory for metals including the plasma frequency ω_p and the free electron damping γ_{fe} .

The model is quite general and can be used to describe many other metals⁴. Therefore we used it as basis to fit the dielectric function of YH_2 (see Fig. S4) and found the following parameters: $S_{osc} = 3.41$; $\omega_{osc} = 4.2 \cdot 10^{15} \text{s}^{-1}$; $\gamma_{osc} = 1.4 \cdot 10^{15} \text{s}^{-1}$; $\omega_p = 6.7 \cdot 10^{15} \text{s}^{-1}$; $\gamma_{fe} = 2.4 \cdot 10^{14} \text{s}^{-1}$. Except for some small deviations, the model reproduces the experimental values of van Gogh et al.². The harmonic oscillator part only plays a role between 500 and 1000 nm (Fig. S4). Therefore, changing the oscillator damping will not affect the plasmonic resonance situated around 2 μm . Hence, the Drude part of the model and in particular the free electron damping needs to be adjusted to explain our experimental data. The red and blue lines in Fig. S4 show how changing the free electron damping to $\gamma_{fe}^* = 3 \cdot \gamma_{fe} = 7.2 \cdot 10^{14} \text{s}^{-1}$ affects the real and imaginary part of the dielectric function.

Figure S4: Dielectric function of YH_2 in the visible and NIR range. The black dashed lines shows the measured dielectric function ($\text{YH}_{1.8}$) by van Gogh et al.² on a continuous yttrium film. The green lines represent the best fit to the van Gogh et al. data using a combined harmonic oscillator and Drude (HO+D) model. The blue and the red curve show the real and imaginary part of the modified dielectric function that describes well the present nanoantenna data. This dielectric function is calculated with the HO+D model and a 3 times enhanced γ_{fe} compared to the green line.

Bibliography

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