# Supporting Information

# The Impact of Surfactants and Stabilizers on Palladium Nanoparticle-Hydrogen Interaction Kinetics: Implications for Hydrogen Sensors

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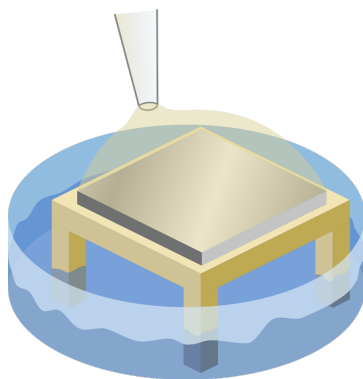*kasper.moth-poulsen@chalmers.se; clangham@chalmers.se

***Figure S1*** *Schematic of the deposition of CTAB, TOAB, CTAC, PVP onto a nanofabricated Pd substrate using a pipette.*

**Table S1** *Quantitative XPS elemental analysis for Pd@CTAB, Pd@TOAB, Pd@CTAC, and Pd@PVP before and after surfactant/stabilizer coating. Relative atomic percentage (at.-%) of relevant elements are presented.*

| _ | Pd | C | N | O | Br | total |
|---|---|---|---|---|---|---|
| bare Pd | 6% | 14% | 0% | 80% | 0% | 100% |
| CTAB@Pd | 3% | 45% | 2% | 49% | 1% | 100% |
| CTAB@Pd (H$_2$ flushed) | 2% | 35% | 2% | 60% | 1% | 100% |

| | Pd | C | N | O | Br | total |
|---|---|---|---|---|---|---|
| bare Pd | 6% | 17% | 1% | 76% | 0% | 100% |
| TOAB@Pd | 3% | 64% | 2% | 29% | 1% | 100% |
| TOAB@Pd (H$_2$ flushed) | 3% | 27% | 0.5% | 69% | 0.5% | 100% |

| | Pd | C | N | O | Cl | total |
|---|---|---|---|---|---|---|
| bare Pd | 6% | 12% | 1% | 81% | 0% | 100% |
| CTAC@Pd | 3% | 55% | 3% | 34% | 6% | 100% |
| CTAC@Pd (H$_2$ flushed) | 2% | 41% | 2% | 53% | 2% | 100% |

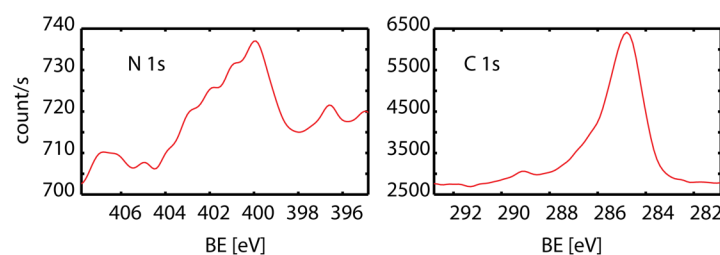| | Pd | C | N | O | total |
|---|---|---|---|---|---|
| bare Pd | 6% | 15% | 2% | 77% | 100% |
| PVP@Pd | 1% | 75% | 10% | 14% | 100% |
| PVP@Pd (H$_2$ flushed) | 2% | 43% | 6% | 50% | 100% |

***Figure S2*** *N 1s and C 1s XPS peaks obtained from bare silicon substrate after rinsing in Milli Q water.*

Nitrogen was identified on the bare silicon substrate after rinsing in MilliQ water, as indicated by the N 1s peak in the corresponding XPS spectrum in **Figure S2**. The ratio between nitrogen carbon surface species is 3 at.-% : 97 at.-%. This ratio is similar to the ratio between nitrogen and carbon found for all bare Pd nanoparticle sample sets used in the surfactant experiments (**Table S1 and S2)**. Thus, we conclude that the initial nitrogen contamination found on our bare Pd samples, prior to surfactant deposition, predominantly stems from the silicon substrate. This is reasonable because only ca. 10 % of the sample surface are covered by Pd nanoparticles.

***Table S2*** *Atomic percentage ratio between nitrogen and carbon as obtained by XPS from uncoated Pd samples presented in Table SI 1.*

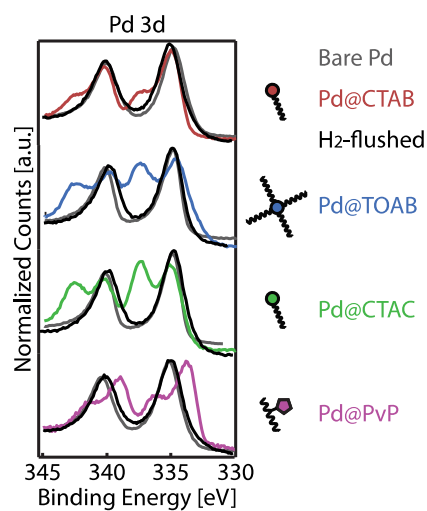| Sample set | N (at.-%) | C (at.-%) |
|:---:|:---:|:---:|
| CTAB | 0 | 100 |
| TOAB | 5.6 | 94.4 |
| CTAC | 7.7 | 92.3 |
| PVP | 11.8 | 88.2 |

**Figure S3** *Pd 3d XPS spectra of bare Pd, surfactant/stabilizer-coated Pd, hydrogen-flushed surfactant/stabilizer-coated Pd. The oxidation "shoulder" peak disappears after hydrogen exposure.*
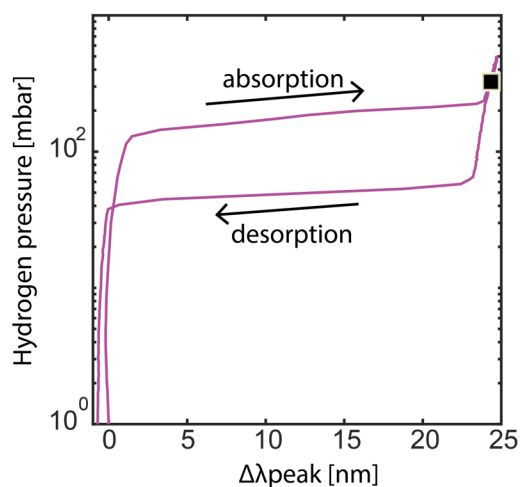


**Figure S4** *Optical pressure-composition isotherm for pure Pd nanoparticles measured at 60°C. The square symbol (■) denotes P = 320 mbar, at which the system is in the hydride phase.*
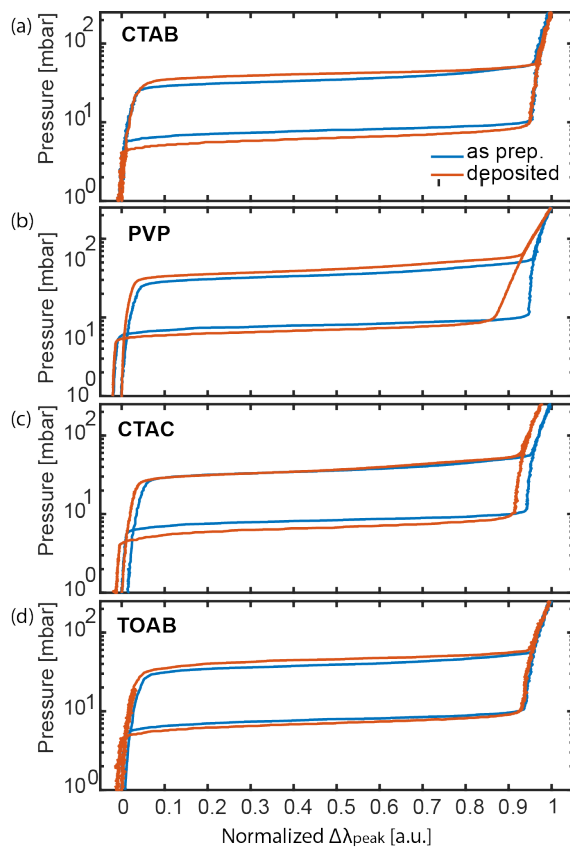
***Figure S5*** *Pressure-composition isotherms of as prepared (blue) and surfactant-coated Pd nanodisks (red). The isotherms appear basically unchanged after coating with surfactant, which indicates that the surfactants do not prevent hydrogen sorption despite the observed deceleration of the sorption kinetics for CTAB, CTAC and TOAB.*
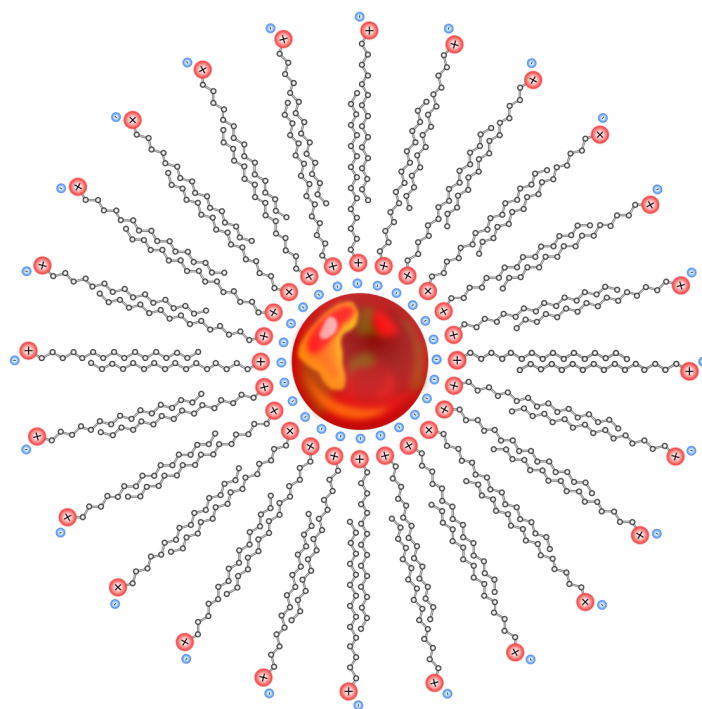
***Figure S6*** *Schematic illustration of the colloidal Pd nanoparticle stabilization by surfactants. The image schematically depicts the electrostatic interaction between halide anions (blue circles) and cationic head groups (red circles), and the steric stabilization of the colloid by formation of a surfactant bilayer by the alkyl chains.*
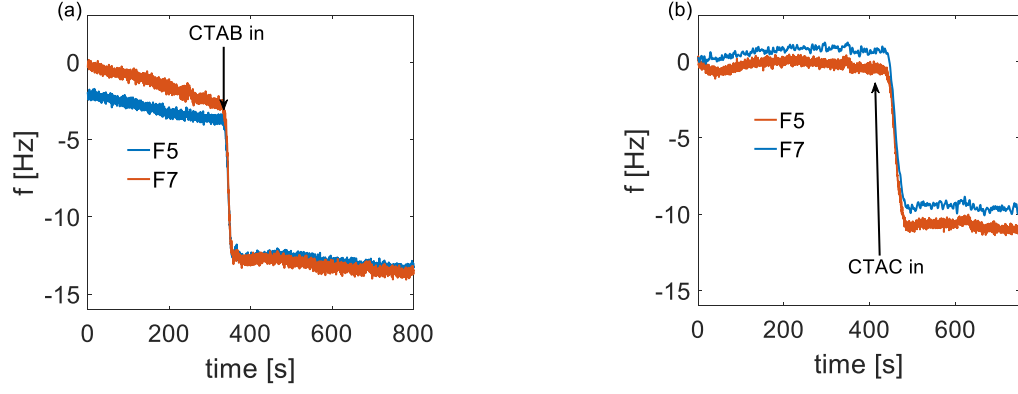
**Figure S7** *Quartz microbalance (QCM) measurement of 10 mM CTAB (a) and 10 mM CTAC (b) adsorption on an annealed Pd film. The $5^{th}$ and $7^{th}$ overtones were used. CTAB adsorption induces a frequency shift of -8.8 Hz and -10.3 Hz for the $5^{th}$ and $7^{th}$ overtones, respectively. CTAC induces a frequency shift of -8.6 Hz and -10.2 Hz for the $5^{th}$ and $7^{th}$ overtones, respectively.*

The obtained QCM frequency shift can be translated to the surfactant adsorption coverage the using Sauerbrey relation.

$$\Delta m = \Delta n. Mw = -C\Delta f \qquad\qquad\qquad eq.\ 1$$

$$\Delta n = -\frac{C\Delta f N_A}{M_w} \qquad\qquad\qquad eq.\ 2$$

Where:

$\Delta m$: mass change ($ng/cm^2$)

$\Delta n$: molecule number change ($1/cm^2$)

$M_w$: molecular weight (ng/mol)

$C$: sensitiviy factor (17.7 $ng/Hz/cm^2$)

$\Delta f$: frequency shift (Hz)

$N_A$: Avogadro constant ($6.02 \times 10^{23}$ /mol)

For CTAB, the amount of adsorbed molecules is:

$$\Delta n = \frac{-C\Delta f NA}{M_w} = -\frac{17.7\,\frac{ng}{Hz\,cm^2} \times -8.8\,Hz \times 6.02 \times 10^{23}\,mol^{-1}}{364.45 \times 10^{-9}\,\frac{ng}{mol}}$$

$$= 2.6 \times 10^{14}\,\frac{molecules}{cm^2}$$

$$= 2.6\ molecules/nm^2$$

If we assume the CTAB molecules to form a bilayer structure, then the adsorption density can be estimated to 1.3 molecules/nm².

For CTAC, the number of adsorbed molecules is:

$$\Delta n = -\frac{C \Delta f N A}{M_w} = -\frac{17.7 \frac{ng}{Hz\,cm^2} \times -8.6\,Hz \times 6.02 \times 10^{23}\,mol^{-1}}{320 \times 10^{-9} \frac{ng}{mol}}$$

$$= 2.9 \times 10^{14} \frac{molecules}{cm^2}$$

$$= 2.9\,molecules/nm^2$$

If we assume the CTAC molecules form a bilayer structure, then the adsorption density can be estimated to 1.5 molecules/nm².

Finally, we motivate the validity of using a thin films here as model system for the nanodisks used in the optical experiments of hydrogen sorption in the following way: (i) both systems are grown in the same evaporation system and using the same parameters, which renders them very similar by definition; (ii) the used nanodisks are large (170 nm diameter) and can thus be regarded as small patches of a film (they are grown as a film through a mask); (iii) the large particle size is guaranteeing that the surface of the nanoparticles is orders of magnitude larger than the cross-section of CTAX molecule. Therefore, one can reasonably assume that the adsorption on the film and the nanodisks are similar.
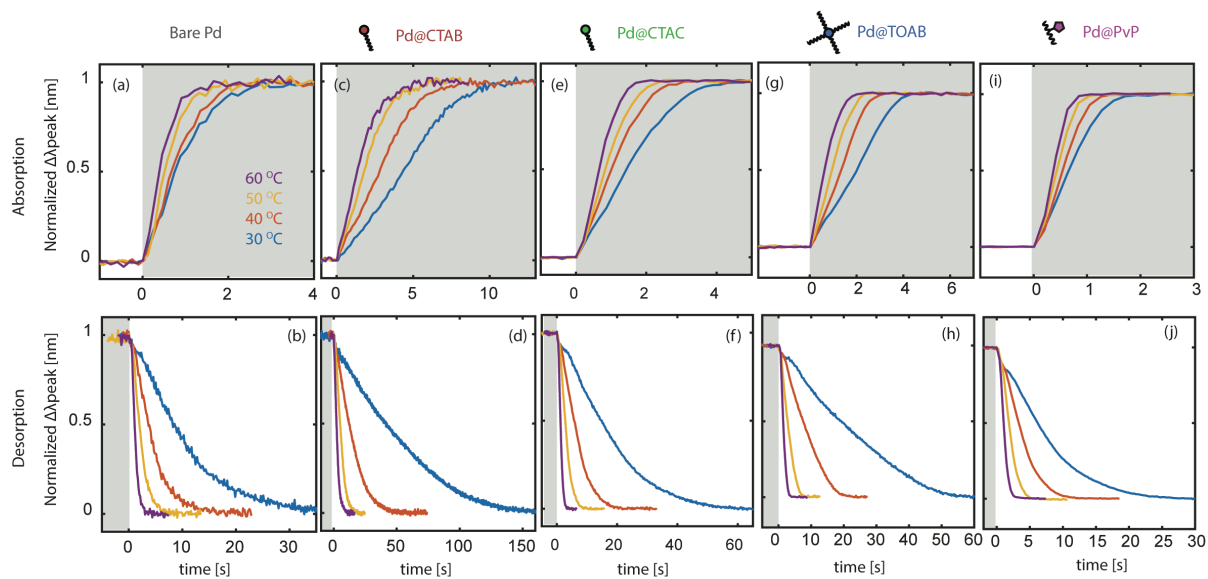
***Figure S8*** *Examples of hydrogen absorption and desorption kinetics raw data measured at different temperatures and used for Arrhenius analysis for (a,b) bare Pd, (c,d) CTAB coated Pd, (e,f) CTAC coated Pd, (g,h) TOAB coated Pd and (i,j) PVP-coated Pd. The grey-shaded area corresponds to 320 mbar hydrogen pressure.*

The activation energy, $E_a$, is calculated from Arrhenius plot of the Arrhenius equation:

$$k = Ae^{-E_a/RT} \qquad\qquad eq.\ 3$$

Which is equivalent to:

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right) \qquad\qquad eq.\ 4$$

Where:

k = rate constant

A = pre-exponential factor

Ea = activation energy

R = gas constant

T = absolute temperature in K.

The rate ($k$) is proportional to the inverse of reaction time. For the reaction time, we use $t_{50}$, obtained from the LSPR signals in **Figure S7** in the supporting information. $t_{50}$ is defined as the time needed to reach 50% of the maximum signal. Therefore, *eq. 4* can be written as:

$$\ln\frac{1}{t_{50}} = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

*eq. 5*

or

$$\ln t_{50} = -\ln A + \frac{E_a}{R}\left(\frac{1}{T}\right)$$

*eq. 6*

By plotting *eq. 6* as in Fig. 3 in the main text, $E_a$ is obtained from the slope.
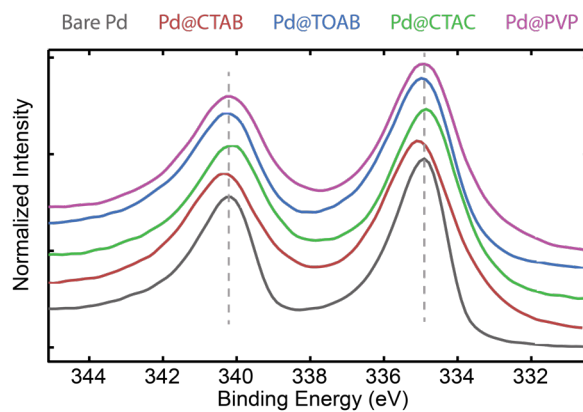
**Figure S9** *Pd 3d peaks of bare Pd and H₂-flushed surfactant-coated Pd. The dashed-lines correspond to 340.21 eV (3d₃) and 334.86 eV (3d₅) peaks of bare Pd.*

**Table S3** *Peak position and FWHM of Pd 3d peaks obtained from* **Figure S9.**

|  | Pd 3d$_3$ | | Pd 3d$_5$ | |
|---|---|---|---|---|
|  | Energy | FWHM | Energy | FWHM |
| Uncoated | 340.21 | 1.81 | 334.86 | 1.67 |
| PdCTAB | 340.34 | 2.14 | 334.99 | 2.19 |
| PdCTAC | 340.15 | 2.08 | 334.79 | 2.09 |
| PdTOAB | 340.29 | 2.10 | 334.91 | 2.07 |
| PdPVP | 340.23 | 2.18 | 334.81 | 2.20 |