On the Promotion of Catalytic Reactions by Surface Acoustic Waves

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1. Pt electrical characterization

The Pt thin film structures used in this study were characterized electrically by resistivity measurements in a two point probe method, using tips applied to two samples: A control sample with a pristine Pt film (nominal thickness: 20 nm) and the very same sample as used to obtain the work function oscillations in Fig. 2 of the main manuscript, after extracting it from the UHV system. The in situ surface preparation of the second sample included three cycles of Ar$^+$ ion sputtering (10 min, 500 V, 5×10$^{-6}$ mbar, 3 µA, incidence 45°) and oxygen treatment (2×10$^{-5}$ mbar, 600 K, 10 min), which are expected to reduce the Pt thickness. Measured resistance data along 100 µm wide stripes, defined by optical lithography, are shown in Fig. S1, together with the results of linear fits. Similar constant offsets correspond to the contact resistance of the measurement setup, while the slopes of the linear fit indicate the Pt resistivity. From the data of the pristine film, a resistivity of 13.8×10$^{-8}$ Ωm is calculated, in reasonable agreement with the bulk value for Pt 10.8×10$^{-8}$ Ωm at 300 K (K. H. Hellwege, Ed., Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology, Group III, Vol. 15, Subvol. a, Springer-Verlag, Heidelberg, 1982.), indicating good metallic behavior of the deposited Pt film. The sputter cleaned sample shows an increased sheet resistance, which we ascribe predominantly to a reduction of thickness during the in situ surface cleaning by Ar$^+$ sputtering. Assuming the resistivity of both Pt samples is the same, it translates into a reduced thickness of around 9 nm.

These results rule out the possibility of an incomplete electric screening of the LiNbO$_3$ surface electric potential through the Pt layer to be the origin of the observed work function oscillation in Fig. 2. Note that the ratio between the potential oscillations in LiNbO$_3$ (1.04 V peak to peak) and the measured work function oscillation (0.910 mV peak to peak) correspond numerically to only 8 - 9 screening lengths.

Figure S1: The resistance of a pristine 20 nm thick Pt film and a sputter-cleaned 20 nm thick Pt film as measured using a two-point probe method.
2. Film morphology characterization

The Pt films were prepared by magnetron sputtering from a Pt target at room temperature. In this way polycrystalline Pt film are obtained, with the roughness mainly determined by the surface morphology of the LiNbO₃ substrate single crystal. The low annealing / oxygen treatment temperature of 600 K is not sufficient to cause an atomically flat surface with large corn grains. Due to the small size of the Pt grains in the film, a LEED characterization is not possible in this case. However, we expect a broad distribution of surface orientations with a large portion of the grains representing low index planes of (111) or (100) orientation, as a result of the prolonged high temperature / oxygen treatment. An FTIR characterization of a similar system, a Cu film on LiNbO₃, showed that 3 h annealing at 573 K suffices to generate a surface consisting predominantly of Cu(111) (Inoue, Y., Surf. Sci. Rep., 2007, 62: 305). A dominant (111) orientation is also what is expected from thermodynamics. In order to obtain an estimate of the quality of the Pt film used for the SAW experiments on a macroscopic scale, white light interferometry 3D microscopy (WLI) was used. Fig. S2 shows three WLI images recorded on different areas of the Pt/LiNbO₃ sample. The first image in Fig. S2 gives an overview of the Pt microstructure. Two horizontal and three vertical Pt lines of ~9 nm height are seen on the LiNbO₃ substrate. One notices several bright features, which are particles probably caused by scratching the Pt film during the electrical characterization. The microstructured Pt film represents a cross pattern, which would have allowed several parallel current paths. In order to achieve a well-defined single current path, some intersections were removed carefully with a knife.

The bottom left image shows a magnification of a horizontal Pt stripe and the LiNbO₃ substrate, the bottom right image shows a magnified portion of a Pt stripe. The average $R_q$ roughness, calculated as:

$$ R_q = \sqrt{L^{-2} \sum (h(\vec{r}) - \bar{h})^2}, $$

with $\vec{r}$ being the position vector, $L$ the length of the platinum film and $\bar{h}$ its mean height

$$ \bar{h} = L^{-2} \sum h(\vec{r}), $$

measured over entire field of view of the top image is 96 nm.
The nanoscale roughness was characterized by atomic force microscopy (AFM). A representative $5 \times 5 \mu m^2$ AFM image of the Pt sample used in the SAW experiments is shown in Fig. S3A, together with an AFM image of an unprepared reference sample of the same batch. Both samples have been stored in air for $\sim 8$ months between film preparation (and SAW experiment) and AFM characterization. Fig. S3B shows three-dimensional representations of the data in A. Fig. 3C shows two line profiles taken along the white lines depicted in Fig. 5A. The AFM measurements demonstrate a strong effect of the sample preparation (repeated cycles of $Ar^+$ ion sputtering and oxygen treatment at 600 K) on the film quality. On the Pt/LiNbO$_3$ sample used in the SAW experiments a $R_q$ roughness averaged over the imaged area of 0.64 nm is determined, whereas the corresponding value of the unprepared reference sample is 2.24 nm. The roughness of both films is comparable with values reported in the literature (Dolatshahi-Pirouz, A., et al. Phys. Rev. B, 2008, 77: 115427).
Figure S3: AFM images of the Pt film used in the SAW experiments (left) and of an unprepared reference sample (right). The AFM characterization was performed eight months after film growth and SAW experiment. During this period, the sample was stored in air. In case of the SAW sample, the Pt film was additionally touched with needle contacts for the electrical characterization. A) 2D AFM images of the Pt film used in the SAW experiments (left) and of a pristine reference sample (right). B) 3D representation of the data in A. C) Representative line profiles taken along the white lines shown in A.
3. **Conversion of image intensity into work function change**

In order to reduce noise and to amplify the signal, SAW difference images have been calculated in the following way:

\[
\frac{I_0 - I_\pi}{I_0 + I_\pi}
\]

with \(I_0\) and \(I_\pi\) being the images recorded with the SAW phase 0 and \(\pi\). Due to the subtraction of the images, the intensity variation caused by the phase shifted SAW double in the numerator, whereas the their influence cancels out in the denominator. The denominator is used to normalize the image intensity of the difference image and removes most of the background intensity.

To translate the image intensity into work function change \(\Delta w_f\) between the opposite SAW phases, we use the linear approximation

\[
\frac{I_0 - I_\pi}{I_0 + I_\pi} = \frac{\Delta I}{2I} \approx \frac{1}{2I} \frac{dI}{dV} \Delta w_f,
\]

thus, the whole image has to be multiplied by two times the intensity of the Pt surface at \(-0.5\) V bias voltage \((I(-0.5\) V)), the voltage at which the difference image was recorded, and divided by the slope of the secondary electron emission onset \((d'(-0.5\) V)), these values are shown in Fig. 2c:

\[
\Delta w_f = \frac{I_0 - I_\pi}{I_0 + I_\pi} \cdot \frac{2I(-0.5 \text{ V})}{I'(-0.5 \text{ V})}.
\]

In our case, the average conversion factor for the two phases is 0.50 eV, calculated as:

\[
\frac{1}{2} \cdot \left( \frac{2 \cdot I_0(-0.5 \text{ V})}{I_0'(-0.5 \text{ V})} + \frac{2 \cdot I_\pi(-0.5 \text{ V})}{I_\pi'(-0.5 \text{ V})} \right) \cdot e = \frac{1}{2} \cdot \left( \frac{2 \cdot 60.84}{231.8 \text{ V}^{-1}} + \frac{2 \cdot 67.46}{281.4 \text{ V}^{-1}} \right) \cdot e.
\]
4. SAW amplitude as function of distance

Figure S4: WF changes in the Pt thin film under SAW as determined from stroboscopic XPEEM images (Fig. 2). Shown is the intensity of the SAW induced brightness variations as a function of distance from the Pt/LiNbO$_3$ interface. Left: color coded differential image, showing the Pt surface (top) and the uncovered LiNbO$_3$ substrate (bottom). Right: seven line profiles taken along the horizontal white lines in the image on the left side. The line profiles 1 and 2 were taken in the vicinity of the interface Pt/LiNbO$_3$ / (phase jump). Line profiles 3 to 7 were taken in steps of roughly 9 μm from the interface towards the center of the Pt stripe. The intensity of the line profiles 3 to 7 is multiplied by 500, in order to allow for comparison with the line profiles 1 and 2. The area used for quantification of the SAW induced work function change in Fig. 2 of the main manuscript is the area enclosed by two horizontal black lines in the left frame, far from the stripe edge.
5. **Strain calculation**

![Graph showing strain calculation](image)

**Figure S5**: Calculated strain ($S_{xx}$ and $S_{zz}$) for a SAW of 8 µm wavelength propagating along the $x$ direction of a LiNbO$_3$ substrate partially covered by a 10 nm Pt film. The dashed lines are the strain components at the surface of the Pt-free LiNbO$_3$, while the solid lines are the strain calculated at the Pt film. The strain tensor components are calculated by numerically solving the coupled differential equations of the mechanical and electric displacements and setting a linear power density of 29.5 W/m to obtain the same piezoelectric voltage amplitude at the surface of the Pt-free LiNbO$_3$ as measured experimentally (1.3 V). The Pt film screens the piezoelectric field at the sample surface and modifies the amplitude of the strain fields.
6. Determination of surface potential change over LiNbO₃

**Figure S6:** Determination of the SAW piezoelectric voltage amplitude. Left: XPEEM image recorded at a bias voltage of -0.65 eV at a photon energy of 300 eV. Right: Intensity vs. bias voltage curves showing the onset of secondary photoelectron emission. The intensity is integrated over the two white rectangles shown in the right frame. The amplitude of the SAW is evaluated by numerically fitting the intensity onset with sigmoid functions (not shown). A shift of 2.6 eV between the two curves indicates a SAW piezoelectric voltage amplitude of 1.3 V.

With the SAW piezoelectric voltage amplitude of 1.3 V we calculate the amplitude of the strain components $S_{xx} = +2.03 \times 10^{-4}$ and $S_{yy} = -1.23 \times 10^{-4}$, resulting in a total volume change of:

$$\alpha = (1 + 4.06 \times 10^{-4}) \times (1 - 2.46 \times 10^{-4}) - 1 = 1.6 \times 10^{-4}.$$  

Taking the experimentally measured work function difference of 910 µeV we arrive at 28.4 meV/% volume change, taking into account, that the difference image includes an effective factor 2. For comparison, a value of approximately 13.4 meV/% volume change is reported in the literature (Wang, X. F., et al. *Appl. Phys. Lett.*, 2013, 102: 223504).
7. Work function changes due to SAW treatment

Figure S7: Measurement of the onset of secondary photoelectron emission. Changes of the local work function are reflected by an energy shift to lower energy (lower work function) or to higher energy (higher work function). The black squares represent a measurement recorded before the sample was exposed to SAW for 11 h. Data acquired after 11 h of SAW at different positions on the Pt surface (X-ray beam irradiated area and non-irradiated area) exposure are represented by filled circles. For comparison, the corresponding measurement outside the acoustic path on the Pt surface (no SAW exposure) is represented by blue triangles. The application of SAW for 11 h causes a work function decrease of 30 – 75 meV, compared to the situation before SAW excitation. On the Pt surface not exposed to SAW, a work function increase of 200 meV is measured, probably due to adsorption from the residual gas.