ARTICLE

Supplementary Information to: Surface acoustic wave enhanced water splitting reaction with methanol as sacrifice material

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Experimental

S_{21} transmission signal measurement

To characterize the SAW chip and to check whether the thin catalyst layer possibly alters the SAW propagation mode, we manufactured two otherwise nominally identical SAW delay lines with and without the thin catalyst layer, which is shown in Fig. 1. The geometric structure of these IDTs are the same as the one used for acoustic-catalytic reaction, so the resonance frequency of them is also around 150MHz, the area of the catalyst layer is also kept as 2mm×8mm. Their rf transmission functions S_{21} are measured and compared employing a network analyzer. We measured the S_{21} transmission in the time domain (from 0 to 0.6µsec) as a function of frequency from 50MHz to 800MHz. This way, we are able to quite easily distinguish different acoustic modes. The result is shown in Fig. 2.

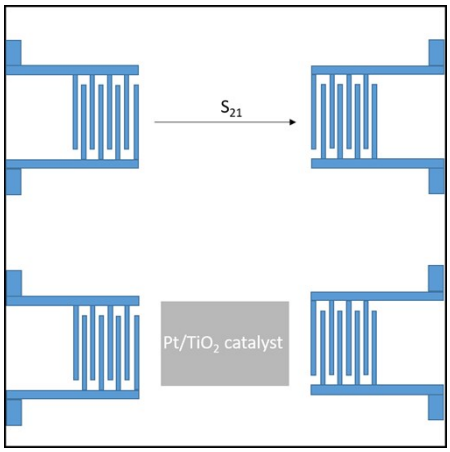

Fig. 1 structure of SAW device with two identical delay lines, one is without catalyst on the delay line and the other is with Pt/TiO_2 catalyst nanoparticle layer on the delay line.

Monitoring temperature changes and resonance frequency shifts

One might argue that the increase in formaldehyde production, indicating H_2 production in the photocatalytic process is due to an increased reaction temperature while the SAW is present. Moreover, the temperature is also critical for the resonance frequency of the IDT. Thus, temperature variation and shifts of the resonance frequency were investigated experimentally. A custom-made tiny temperature sensor was attached to the cylinder reaction chamber. Silver conductive paste was used to fill the gap between the sensor and the chamber. The temperature was recorded during the whole two photocatalytic reaction processes, 30min in dark and 60min under UV illumination, with and without applied SAW with a power level of P_{SAW}=40mW. The temperature change is shown in Fig. 2 and the resonance frequency shift and calculated output SAW energy at 150.3MHz is illustrated in Table. 1.

Monitoring hydrogen evolution using mass spectrometry

A mass spectrometer (Hyden Analytical HAL 201 RC) was coupled to the micro chamber outlet using a cold trap. The partial pressure of hydrogen was logged while the UV illumination was periodically switched on and off during the experiment.

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Results

SAW Transmission

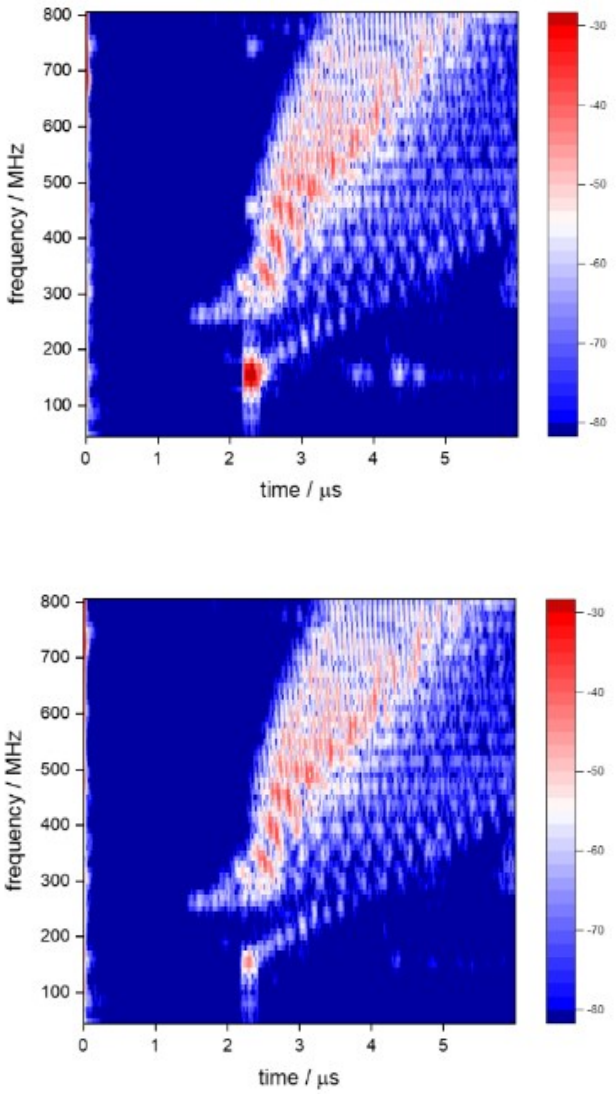


Fig. 2 transmission signal S_{21} at different frequencies in the time domain, the upper graph shows the experiment with no catalyst deposited on the delay line and the lower graph shows the experiment with catalyst on the delay line. The scale bar shows the scale of the S_{21} signal in dB.

Basically, two acoustic modes and a few echoes are seen in Fig. 2: The one with the largest signal (red) at f=150.3MHz and Δt= 2.3µsec represents the Rayleigh SAW, since the velocity of the surface acoustic wave is 3980m/s and the length of delay line is 8.7mm, so the propagation time of the surface acoustic wave from one IDT to the other IDT is around 2.3µs. In the upper graph, where no catalyst is present on the delay line, the S_{21} signal at 150.3MHz and 2.3µs is stronger than the S_{21} signal in right picture at same frequency and same time. This can be understood by the elastic and electric properties of the TiO_2 catalyst film that attenuates the S_{21} signal. The other S_{21} signal above 280MHz which exhibits a large slope results from bulk waves. These bulk waves are excited from the transducers directly. Comparing these two pictures, we can see that except a little damping (around 10dB) at the resonance frequency 150.3MHz and Δt=2.3µs, there is no other obvious difference between the two measurements. This indicates that the catalyst film on the delay line, most likely does not generate any other type of acoustic wave. When the power was applied to the IDT, a certain high percentage thereof will convert into a surface acoustic wave, with most of the acoustic energy being confined to the surface of $LiNbO_3$ and being able to interact and affect the combined catalyst film. The area of the nanoparticle film was kept around 2mm×8mm, and even though the catalyst causes attenuation, the surface acoustic wave could still pass through the whole catalyst film and reaches the opposite IDT. This also demonstrates that the whole catalyst film was affected by SAW.

Temperature Measurement

Fig. 3 shows the temperature change as a function of time. From 0 to 30 minutes, the UV light was turned off, so the recorded temperature is around room temperature (22.5°C). From 30 minutes to 60 minutes, the UV illumination and the SAW have been turned on, and the temperature increased immediately. As can be seen, both curves (UV only and UV plus 40mW SAW) are nearly identical. Thus, the temperature increase of about 20 K obviously is mainly caused by the UV illumination and the SAW with a power level of P_{SAW}=40mW cause a negligible additional temperature rise. Thus, it is safe to state that the SAW at power of 40mW, which clearly produces a doubling in the catalytic efficiency, does not act via an additional temperature increase but rather via intrinsic SAW related effects.

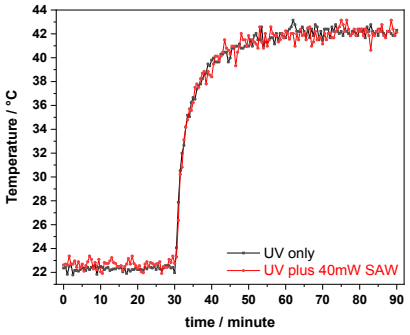


Fig. 3 Temperature change during the photocatalytical reaction process. From 0 to 30minutes, the UV light was off, then the UV illumination was turned on from 30 minutes to 60 minutes. the temperature increase has been measured (black trace). For comparison, the exact same experiment was performed but with the P_{SAW} = 40mW acoustic wave been turned on (red trace). The traces for SAW off and SAW on are nearly identical, indicating that the SAW does not alter the temperature during the experiment. The overall increase is thus mainly caused by the UV illumination.

To estimate the effect of the changing temperature on the SAW resonance frequency $f_{SAW} = v_{SAW} / \lambda_{SAW}$ during the experiment, we separately measured the SAW resonance frequency as a function of temperature, using a network analyzer (see Table 1). As v_{SAW} is known to be temperature dependent, we also expect f_{SAW} to change during the course of the experiment.

Table.1 SAW resonance frequency due to the temperature change during the photocatalytic experiment

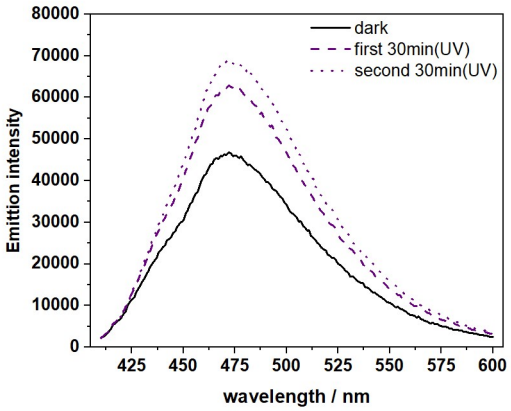
time	T	Measured f_{SAW}	S_{11} at 150.34 MHz	Output SAW power/ input power
After 30min (dark)	22.5 °C	150.34 MHz	-8.98 dB	87.35%
After 30min (UV)	41.1 °C	150.16 MHz	-8.94 dB	87.24%
After 60min (UV)	42.3 °C	150.11 MHz	-8.92 dB	87.18%

The temperature coefficient for 128° rotated y-cut $LiNbO_3$ is 76ppm/°C.[1] Thus, we expect a change of f_{SAW} by about Δf_{SAW}=11.4KHz for every degree of temperature change.

In Table. 1, we show that the temperature increase after one hour illumination turned out to be almost ΔT =20 °C (see also Fig. 3), and the resonance frequency shifted by Δf_{SAW} = -240MHz which nicely agrees with the expected value. During the experiment and over the one hour illumination time, however, we kept the output frequency of the rf generator constant at 150.3MHz. This in turn is equivalent to a slight change of the SAW power, being caused by the temperature induced shift of f_{SAW}. This slight decrease of the SAW power can be estimated once the frequency dependent transmission function S_{12} or the power reflection S_{11} of the IDT is known. In Fig. 9, we show the measured S_{11} of the emitting IDT as a function of the frequency. As we can see, the temperature dependent Δf_{SAW} = -0.24MHz would result in only a very small power change which is estimated to be less than 0.1dB for the for ΔT= +20° being caused by the UV illumination. Hence, the observed nearly 100% increase of the catalytic efficiency due to SAW interaction might even be a bit larger, taking the non-compensated shift of the SAW resonance frequency into account.

Reference Measurement on glass

Fig. 4 shows the fluorescence spectra of reference measurements with the identical catalyst on a glass substrate. The preparation of the catalyst was done in the same way as for the samples. However,



due to the process it is not possible to ensure the presence of the exact same amount of catalyst.

Fig. 4 Fluorescence emission intensity of the adsorption solution after 30 minutes in the dark (black line), after first 30minutes UV illumination of catalyst on glas without SAW (dashed line), and another 30minutes UV illumination without SAW (dotted line)

This results in an amount of produced formaldehyde of about 0.012 µmol. The enhanced activity compared to the reference on $LiNbO_3$ most likely is caused by preparation uncertainties.

Mass spectrometry

Fig. 5 shows the partial pressure of hydrogen in a reference experiment with SAW-application (40 mW). A mass spectrometer with a nitrogen cold trap was connected to the outlet of the reaction chamber. In contrast to the other shown experiments pure nitrogen was used as carrier gas. During the experiment the UV illumination was periodically switched on and off. As can be seen from the partial pressure as function of time, and its time derivative a clear correlation between illumination and detected hydrogen can be seen. This allows for the conclusion that we indeed observe water splitting here.

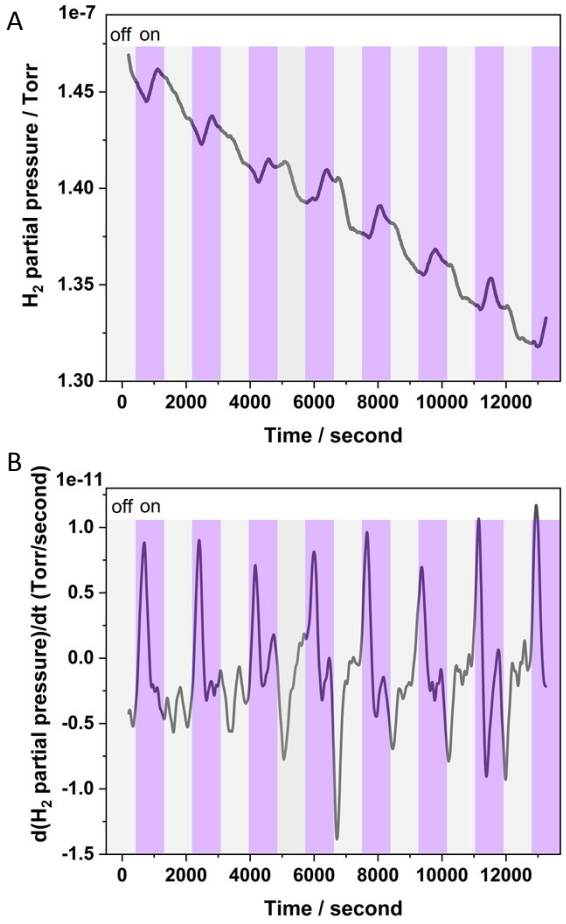


Fig. 5 A) Partial hydrogen pressure as function of time (UV on and off, SAW 40 mW). B) Time derivative of the data in A).

References

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