



Supporting Information

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Combining resonant piezoelectric micromembranes with molecularly imprinted polymers

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1. Materials:

Poly(vinyl acetate) (PVAc, MW : 140.000g/mol), trimethylpropane trimethacrylate (TRIM), 4-vinylpyridine (4-VP), 2,4-dichlorophenoxyacetic acid (2,4-D), phenoxyacetic acid (POAc) and 2,2-dimethoxy-2-phenylacetophenone (DPAP) were from Sigma-Aldrich. Diethylene glycol dimethyl ether (diglyme) was from Fluka. All other chemicals were of analytical grade. 4-VP was vacuum distilled before use and kept in the dark at -20 °C.

2. Micromachined piezoelectric micromembranes:

Matrices of piezoelectric membranes were fabricated by standard micromachining techniques.^[1] The membranes are circular shaped with a total radius R_2 equal to 100 μm . Each membrane can be individually addressed by a piezoelectric $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) thin film, this layer being actuated by a Ti/Pt bottom electrode and a Pt top electrode. This active part is circular shaped with a radius R_1 equal to 50 μm . A ZrO_2 ring was deposited before the Pt top electrode, so that the radius of this top layer was 5 μm larger than the PZT circular film, to prevent electro-magnetic interferences between the piezoelectric layer and the substrate. Evaporated circular gold patches ($R=100\mu\text{m}$) were patterned for a preferential individual functionalization of the micromembranes. Once the collective fabrication process of the chips was achieved, the substrate wafer was diced into $5\times 5 \text{ mm}^2$ individual cells corresponding to one matrix of piezoelectric membranes. Each cell was glued on a TO8 package and each membrane wire-bonded to the TO8 pins. A solvent compatible polymeric sealant was used to protect the connecting wires.

3. Electronic set-up:

For an appropriate use of the micromembranes, a dedicated electronic set-up was developed to obtain a precise and multiplexed tracking of their resonant frequencies, thanks to the integrated piezoelectric patches.^[2] Several stages were designed for an autonomous use of the system. Among them, one is dedicated to the dynamic actuation of the structures using the piezoelectric layer. A specific dynamic compensation of the parasitic elements was developed to measure ideal resonance spectra while a synchronous detection was used for the multiplexed resonant frequencies sensing thanks to the PZT active layer. As shown on Figure 1, the electronic set-up permitted the measurement of spectra with a highly compensated resonant peak, allowing a precise determination of the resonant frequency since the signal-to-noise ratio is about 1ppm and switching capability is about 4 membranes/second.

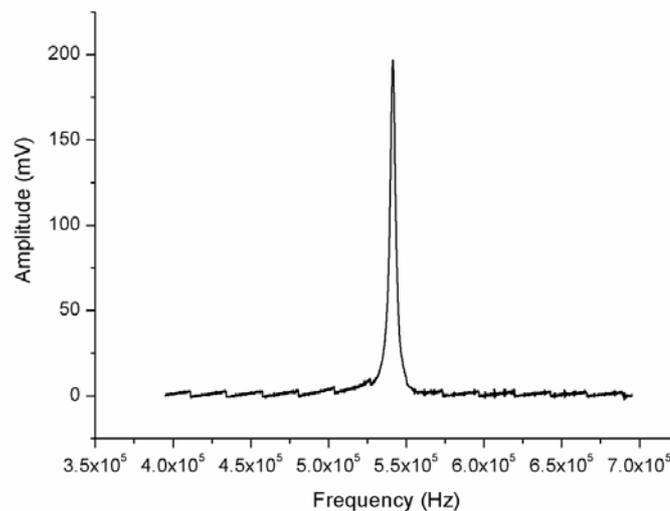


Figure 1: Measured frequency spectrum with the dedicated electronic set-up on a micromachined piezoelectric micromembrane ($R_1=50\mu\text{m}$ and $R_2=100\mu\text{m}$)

4. Molecularly imprinted polymers:

MIPs were prepared using a 1:8:16 molar ratio between the template (2,4-D), the functional monomer (4-VP), and the cross linker (TRIM), respectively. The amount of polymerization

initiator (DPAP) used was 1.2 mol-% relative to the number of moles of polymerizable double bonds. Diglyme was used as the porogen, which contained 1% PVAc as a co-porogen. The volume ratio between the porogen and the monomers was 3:1. Polymerization was initiated under UV light (360 nm, 6 W low-pressure lamp) in a nitrogen atmosphere. Non-imprinted control polymers were synthesized in the absence of the 2,4-D template.

5. Deposition tool and procedure:

The MIP precursor solution was deposited on the micromembranes using a cantilever array-based microspotting tool. The chips used for deposition were fabricated by standard micromachining techniques and mounted on a three-stage automated spotter.^[3] The cantilevers, as shown on Figure 2, are 1500 μm long, 120 μm wide and 5 μm thick and contain a fluidic channel in their tip for liquid loading and deposition.

After loading the cantilevers by dipping them into reservoirs containing the 2,4-D MIP and NIP precursor solutions, droplet deposition occurred by a direct contact between the cantilever tip and the surface of the micromembrane. This specific spotting tool allowed the deposition of variable volumes of precursor solution by controlling the contact time of the tip with the surface. The cleaned 100 μm gold patch on the membrane surface induced the spreading of the droplet from the center to the periphery of the membrane.

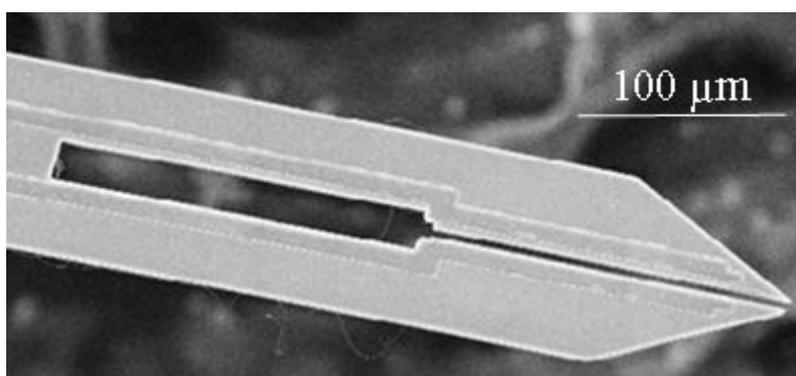


Figure 2: SEM picture of a cantilever used for MIP deposition.

6. Polymerization:

After the deposition of the MIP droplets, the chips were connected with the dedicated electronic set-up for the real-time monitoring of the resonant frequency and placed in a saturated nitrogen atmosphere, immediately followed by starting up the UV lamp to initiate polymerization.

7. Templates removal and rebinding experiments:

The chips with deposited molecularly imprinted polymers were subjected to three washing cycles (15 min each) in a 1:10 mixture of acetic acid and ethanol for template removal, followed by three rinsing cycles with pure ethanol, and dried in a stream of nitrogen. The resonant frequency of the micromembranes was measured after the six cycles until a stable frequency reading was reached. For rebinding experiments, the polymer-coated membranes were incubated in different concentrations of 2,4-D or POAc in 20 mM phosphate buffer pH 7 for 30 minutes at room temperature. The surfaces were rapidly rinsed with water and ethanol and dried in a stream of nitrogen. The resonant frequency of the micromembrane was then measured until the stabilization of the signal.

8. AFM study of MIP and NIP surfaces:

Images of the 2,4-D molecularly imprinted polymer and the non-imprinted polymer were acquired in contact mode using a JPK Nanowizard 2 AFM.

REFERENCES

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