Flexible and biocompatible pH sensor based on WO_3 nanoparticles

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Outline

- Motivation
- Introduction
- Hydrothermal synthesis of WO_3
- WO_3 characterization
- pH sensor assembly
- Characterization and proof of concept
- Conclusions

Motivation

Wearable Biomedical Devices

Advantages:
- Early diagnosis
- Continuous monitoring

"Segev-Bar, M., et al., ACS Nano 7, **2013**, 8366"

Requirements:
- Cost-effective
- **Flexible**
- Lightweight
- Easy-to-fabricate
- Biocompatible

Examples:
- **pH**
- Temperature
- Pressure
- Humidity
- Surrounding gases

Introduction

pH value can be useful as:

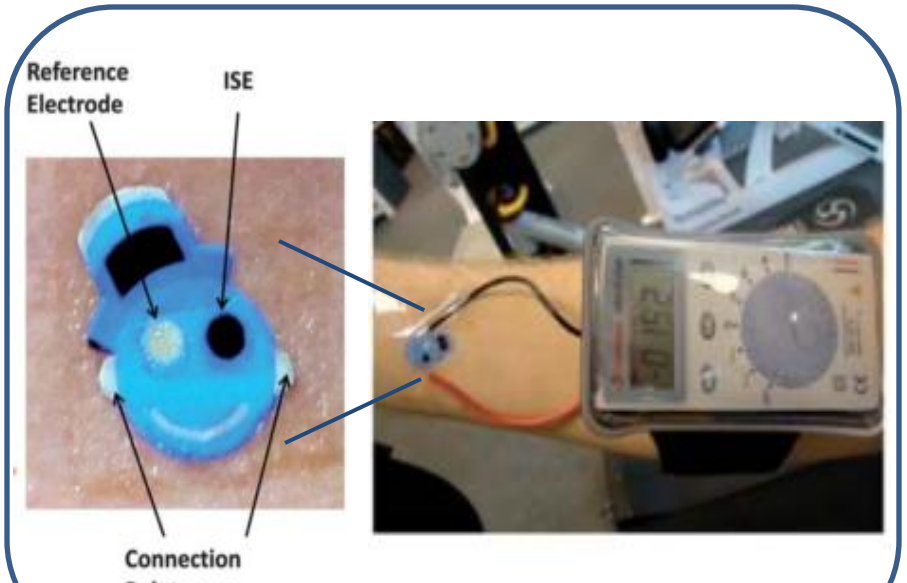
- indicator for diagnosing diseases
- optimizing medical treatments
- monitoring biochemical and biological processes

Metal oxide sensing layer:

- Low manufacture costs
- Compatibility with miniaturization processes
- High sensitivity
- Abundancy

Potentiometric sensor:

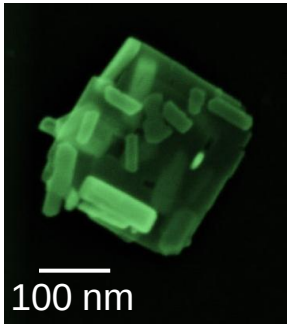
- Simple
- Portable electrochemical technique

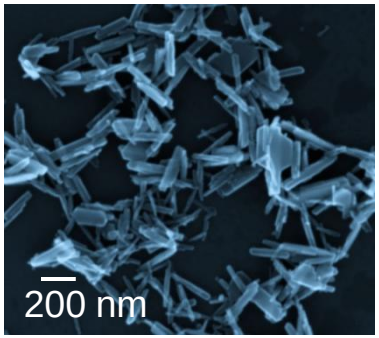


"Bandodkar, A. J., et al., Analyst 138, **2013**, 123"

Introduction

- ✓ Semiconductor
- ✓ Band gap ~2.7 eV.
- ✓ Applications: electrochromic, gas sensor, electrocatalyst, thermochromic and photochromic





Redox reaction:

$$WO_3 + xM^+ + xe^- \rightleftarrows M_xWO_3$$

Hydrothermal synthesis WO_3

$NaWO_4 + HCl + NaCl$

Tungstic acid (H_2WO_4)

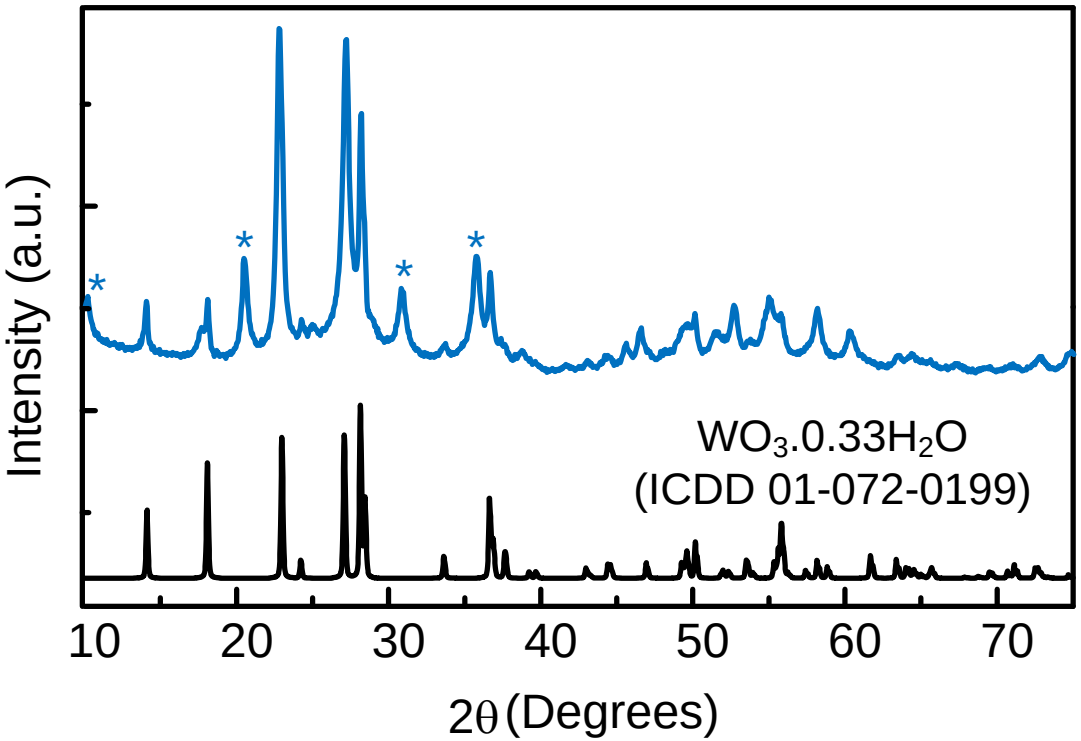
Nanostructured WO_3

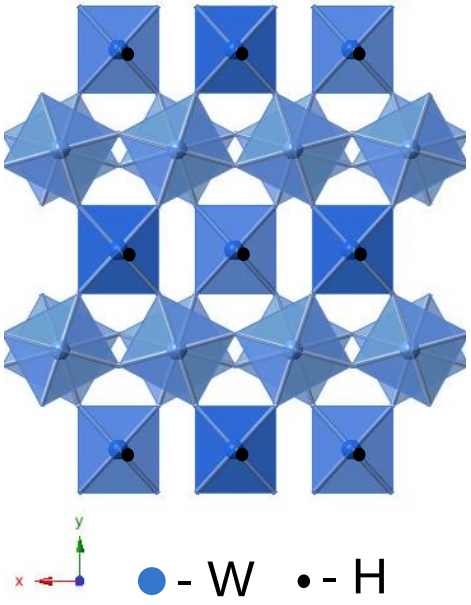
Synthesis:
1 hour
180 °C

WO_3 characterization

$WO_3.0.33H_2O$ orthorhombic
+
Non identified product (*)

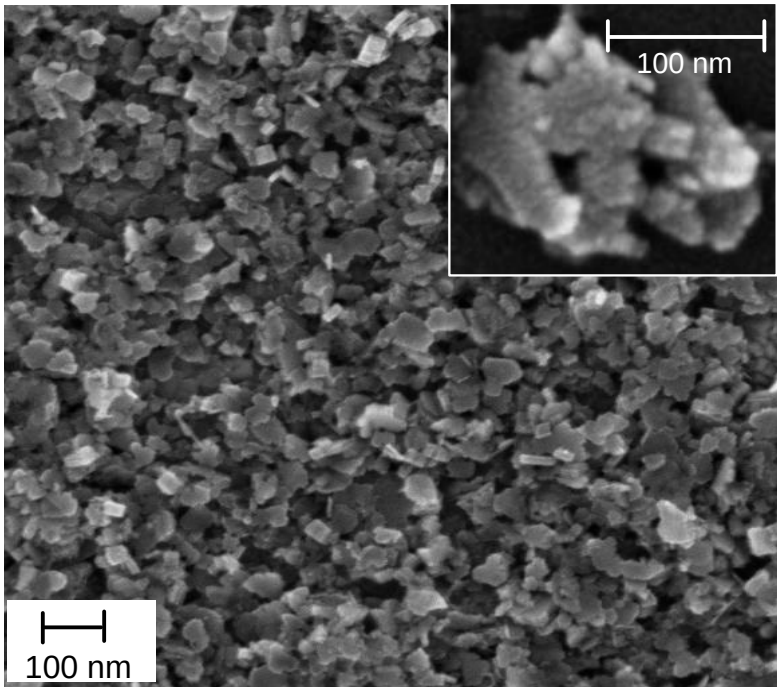
ReO_3-type structure with WO_6 octahedra

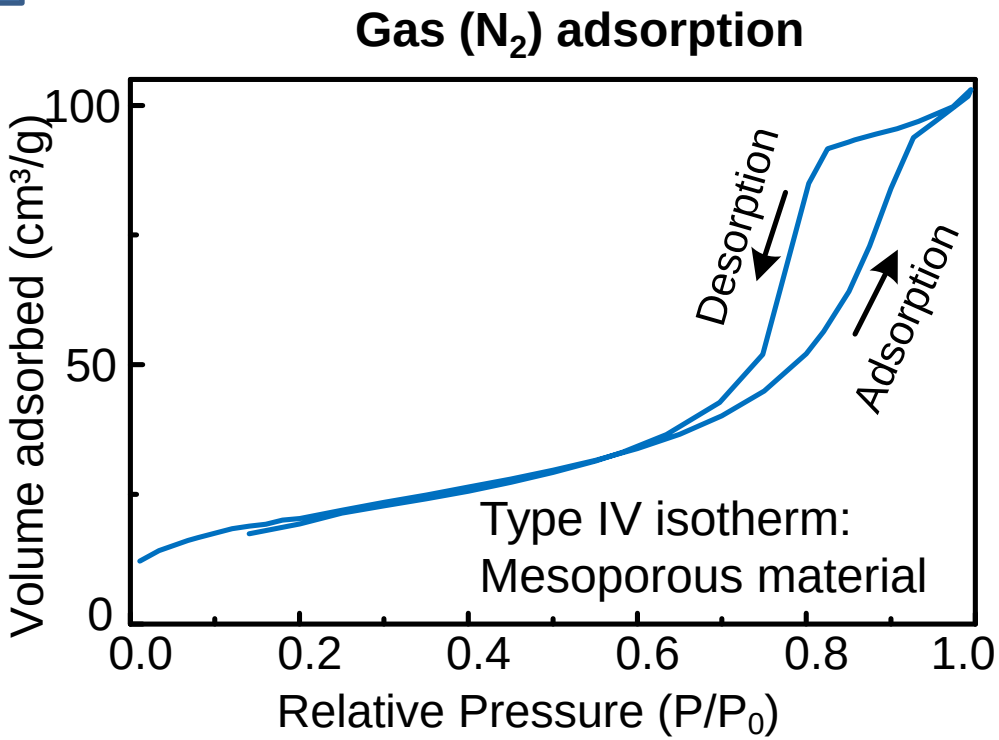




WO_3 characterization

Agglomerates of ~ 100 nm with
Nanoparticles of ~10 nm



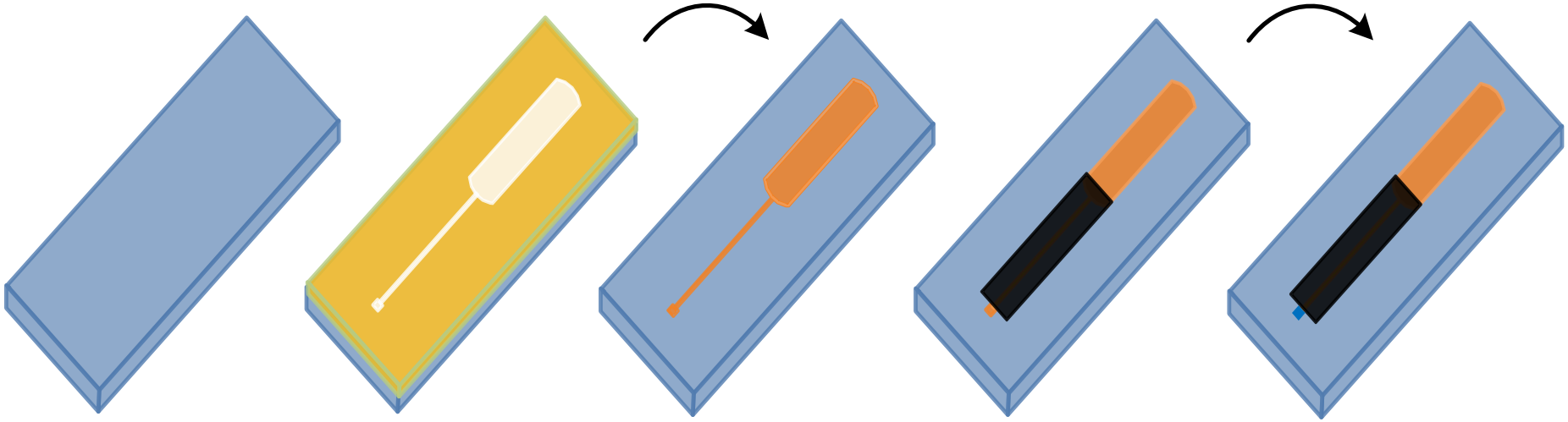


Sensor production

Polyimide substrate

2. E-beam evaporation of Ti/Au

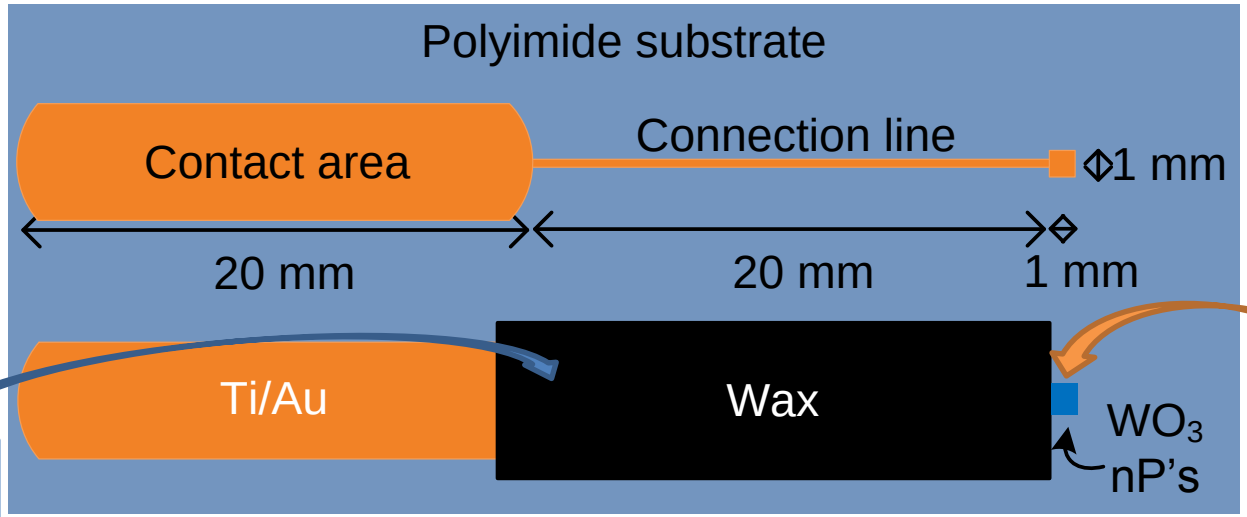
4. Electrodeposition of WO_3 nP's



1. Shadow mask with laser cut

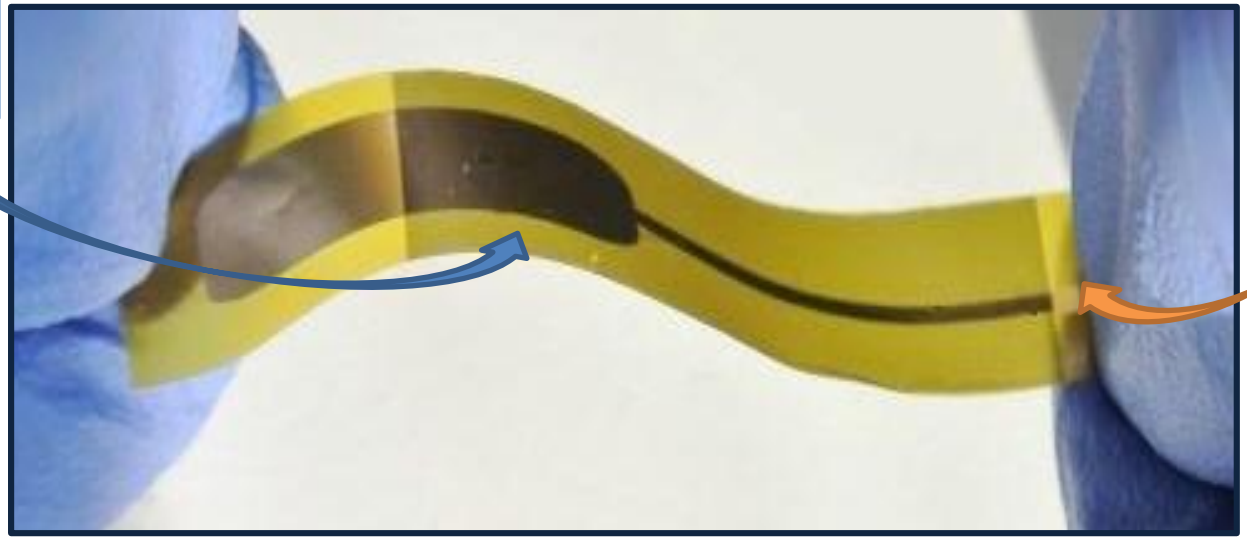
3. Wax printing

Sensor production



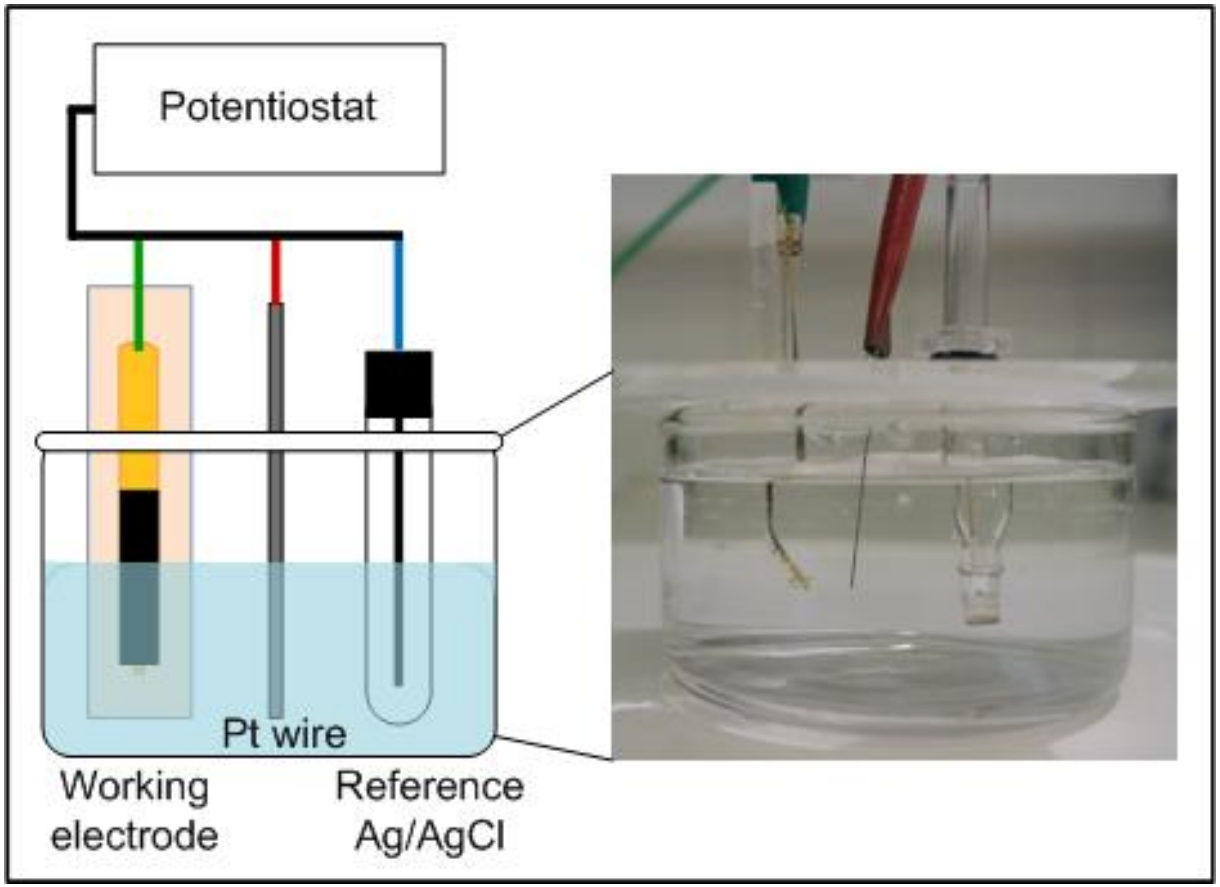
Printed wax as insulator is cytocompatible*

Sensing area 1 mm²



*International Standard (ISO 10993-5) – using extract method

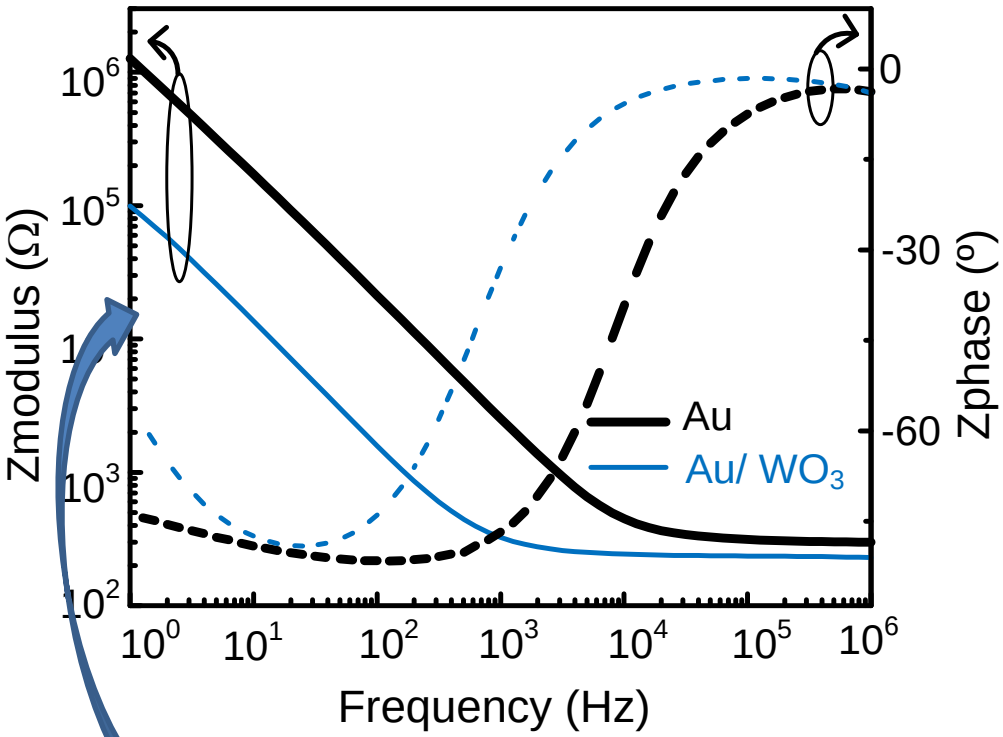
Electrodeposition of WO_3



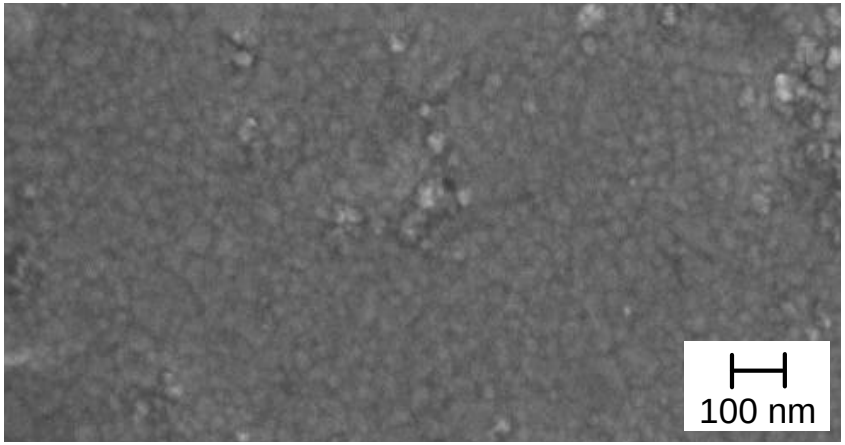
Constant current deposition:
20 µA for 900 s

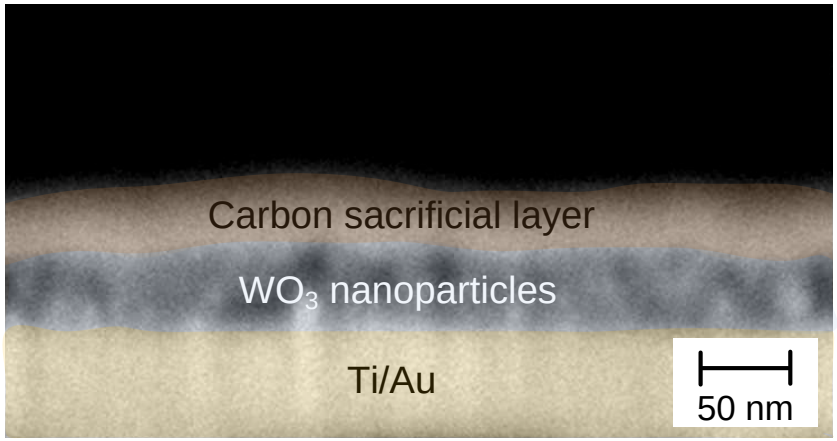
Drying:
60 °C for 1 H

Electrodeposition of WO_3



Increment of the electrochemical surface area

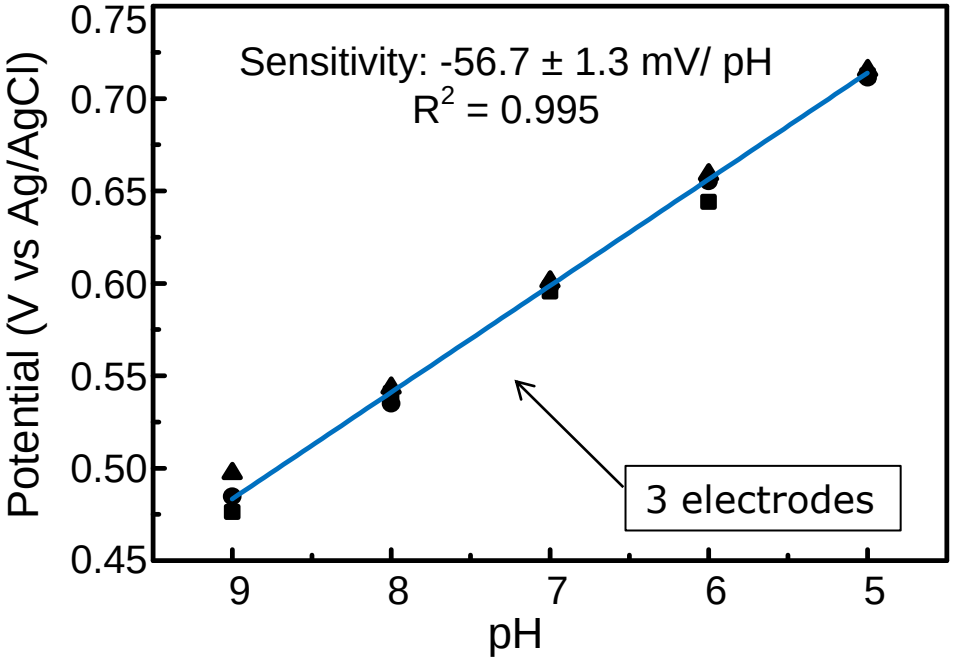




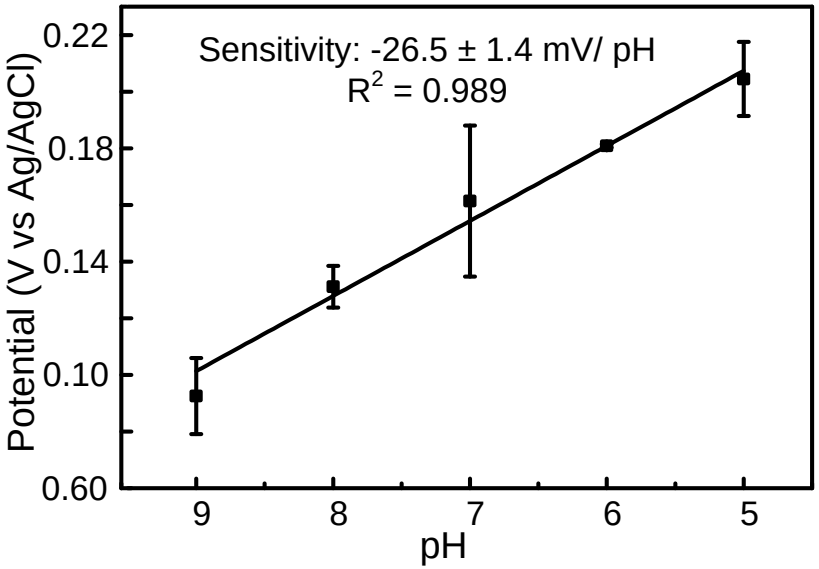
Sensor characterization

Reproducibility

Au/WO_3 Flexible Electrode



Au Flexible Electrode

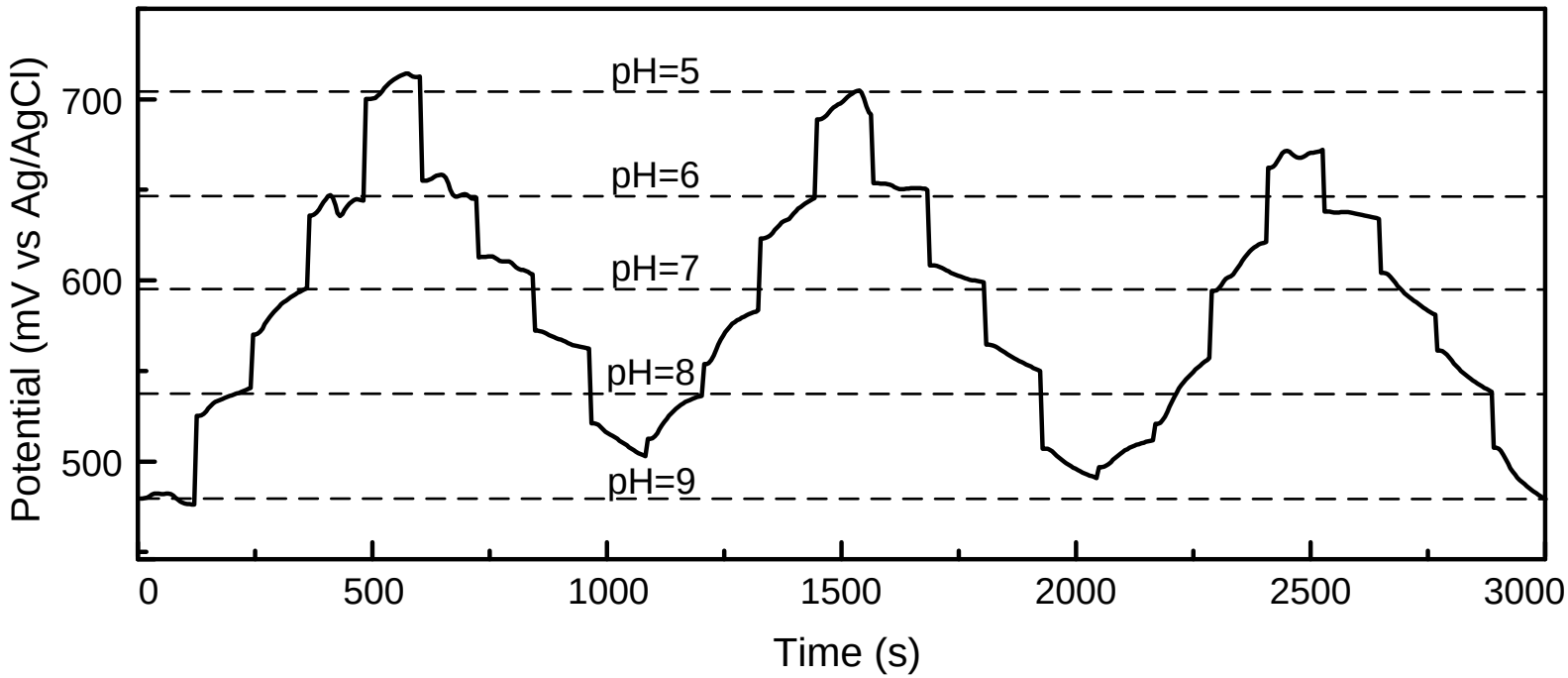


Theoretical sensitivity of -59 mV/pH according with Nernst equation:

$E = E^0 - (2.303\ RT/F)\cdot pH = E^0 - 0.05916\cdot pH$

Sensor characterization

Reversibility

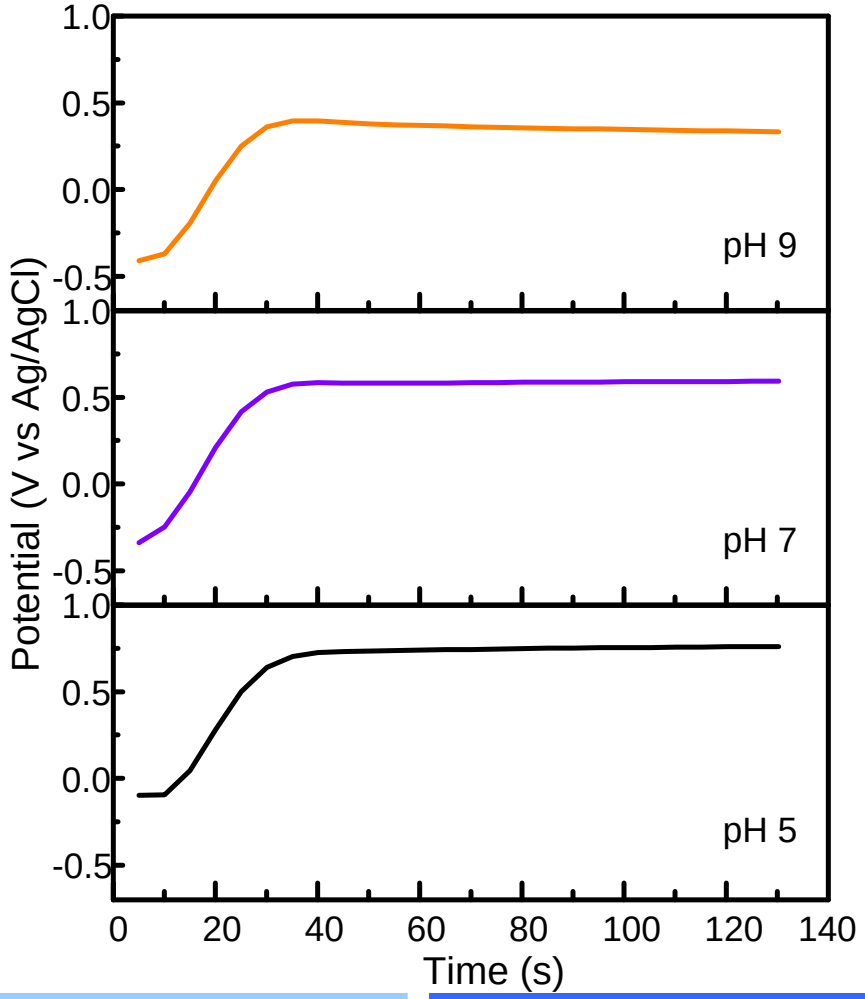


Some degradation of the interface due to deffects and/or charge trapping

Sensor characterization

Response Time

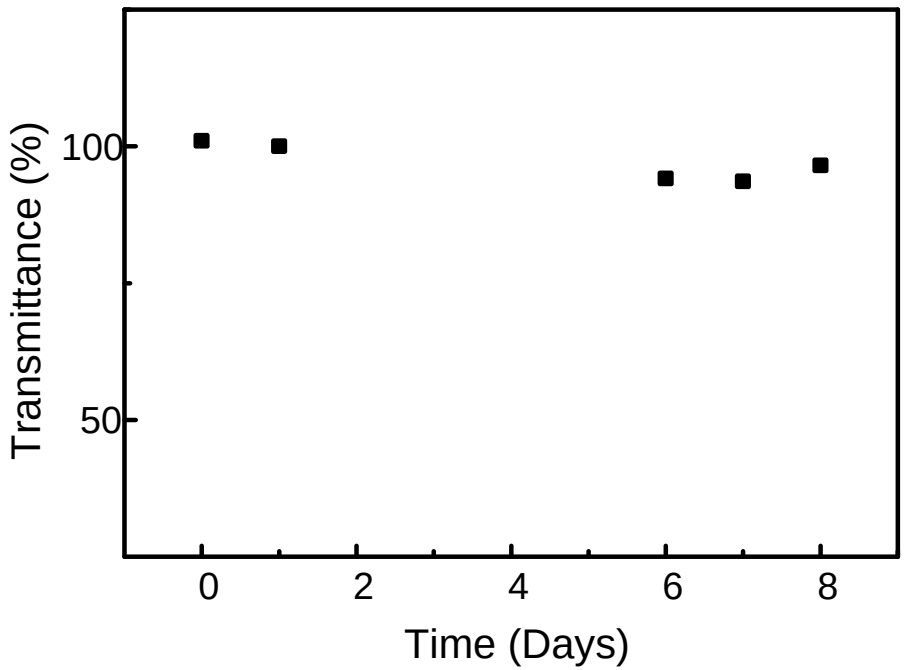
Time measured to reach 90% of the potential, starting in air: 23 to 28 seconds



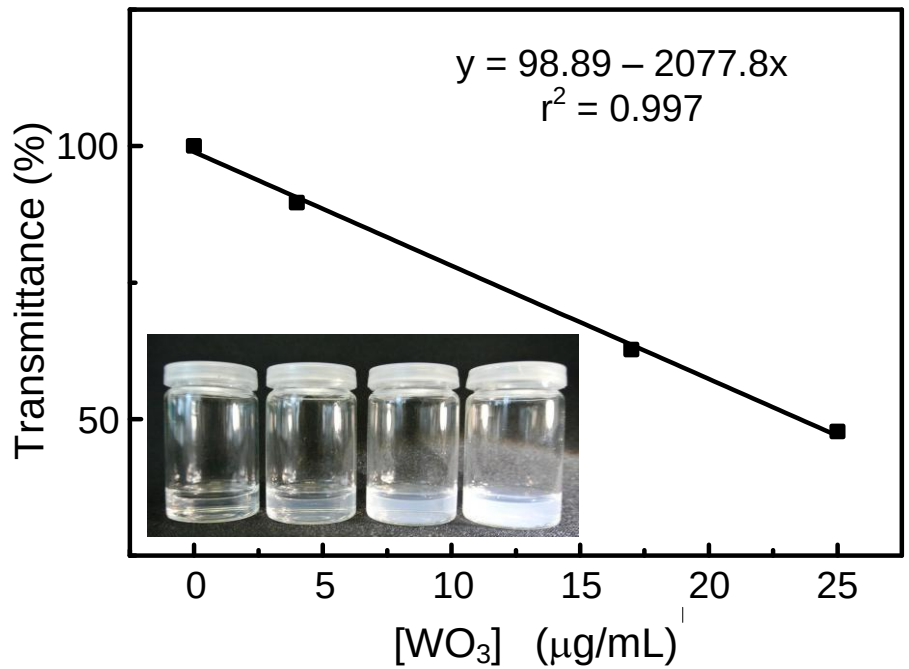
Sensor characterization

Adherence test

Transmittance measurements @ 280 nm



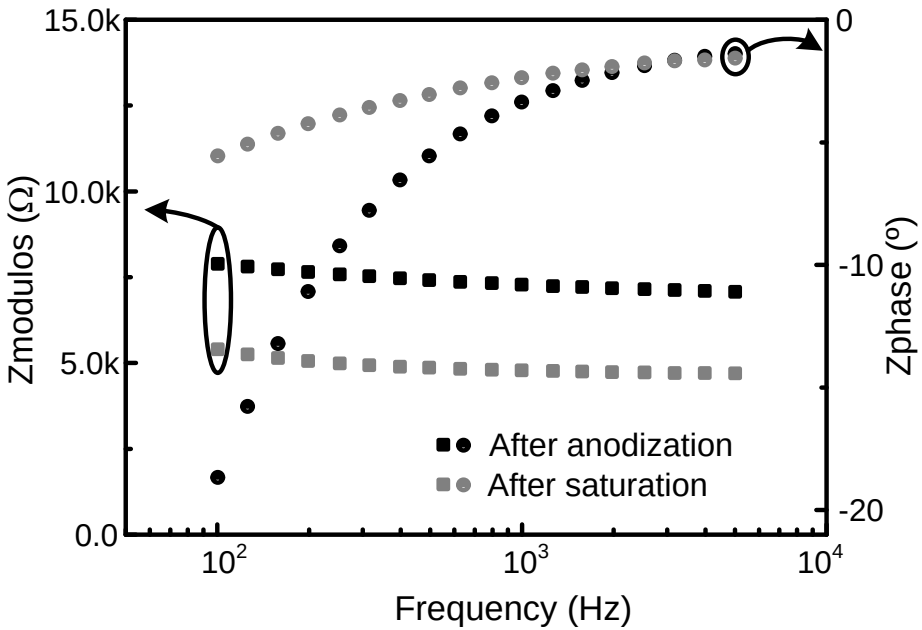
Calibration curve

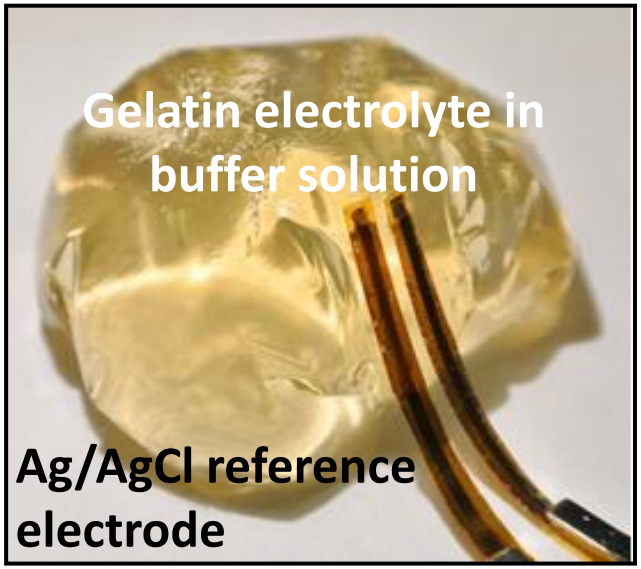


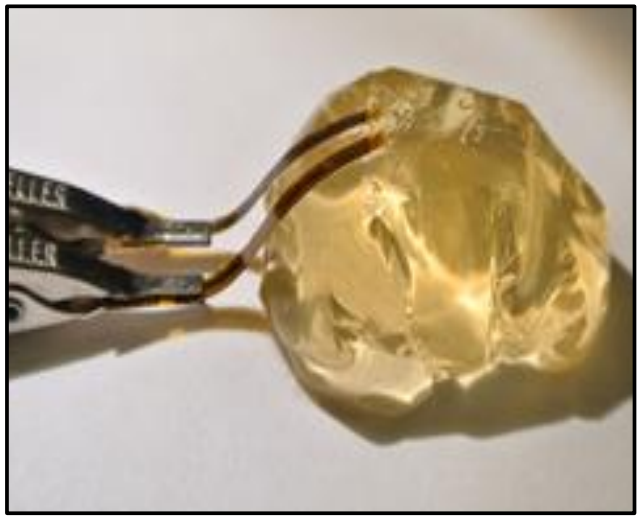
In UV-*vis* spectroscopy and SEM images:
No degradation after 8 days in PBS @ 37 °C

Proof of concept

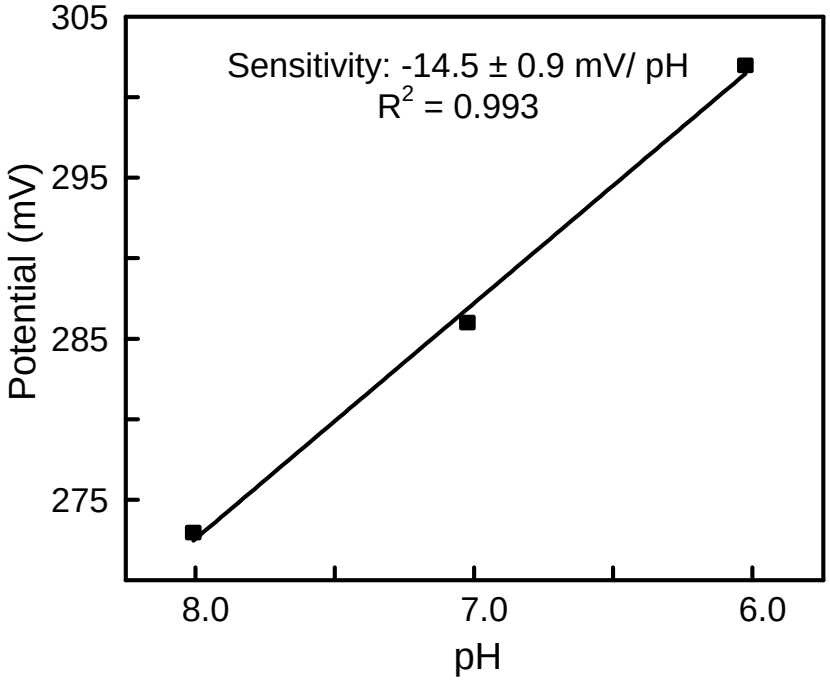
Reference electrode production:
1. E-beam Cr/Pt/Ag
2. Anodization in HCl
3. Saturation in KCl

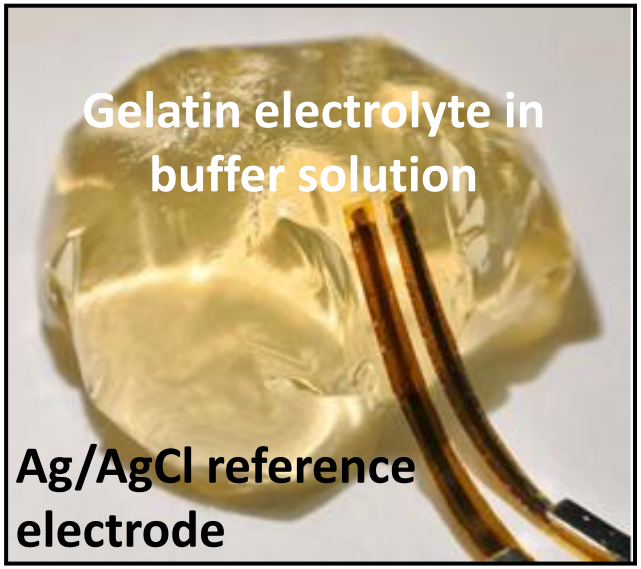


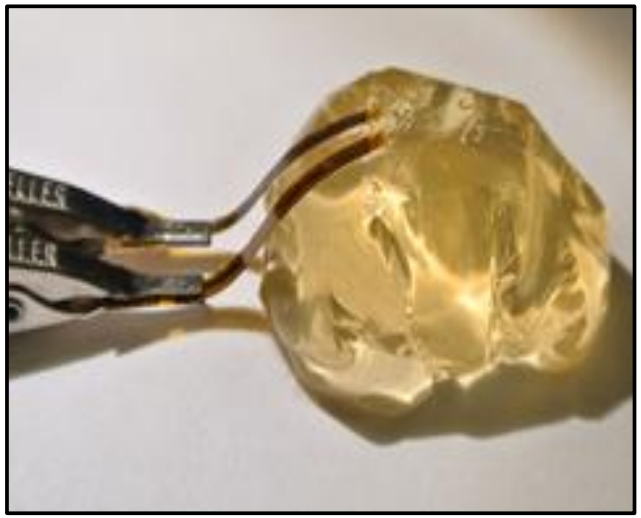




Proof of concept







Instability of the reference electrode
Low ion mobility of the solid electrolyte

Conclusions

- Sensitivity of the sensor close to the theoretical value (-59 mV/pH) – High reproducibility
- Good reversibility of the sensor after 3 complete cycles, from pH 9 to 5 and in reverse way
- Wax is cytocompatible and therefore a good option to insulate the sensor
- Sensor produced with low cost techniques and with good conformation to curve surfaces
- Applications from biomedical flexible devices but can also be adapted to other applications such as food packaging, soil monitoring in agriculture, erosion monitoring in construction or even lubricants.

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POINTS

Thank you
for your attention!

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