SUSNANO SPRING SCHOOL

# Scalable Manufacturing Of Electrochemical Sensors Based On Tailor-made Metal Nanoparticle Carbon Materials Applied To The Detection Of Water Pollutants

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gtq silicon technologies for sensing

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tecnio catalonia Fins a 31/12/2023 ACCIÓ Generalitat de Catalunya

15th April, 2024

# OUTLINE

- Electrochemical sensors for measuring water pollutants
- Sol-gel production of functional materials
- Thick- film sensors by screen-printing
- Thin-film sensors by microfabrication
- Alternative materials for sustainable sensors

# Water strategy: Opportunities


**100 000**

surface water bodies, including streams, rivers, lakes, wetlands, and reservoirs

**Only 40%**

of surfaces waters are in good status

**EU Directive** 2000/60/EC (2013/39/EU) – Environmental Quality Standards

**Contaminants in surface waters**

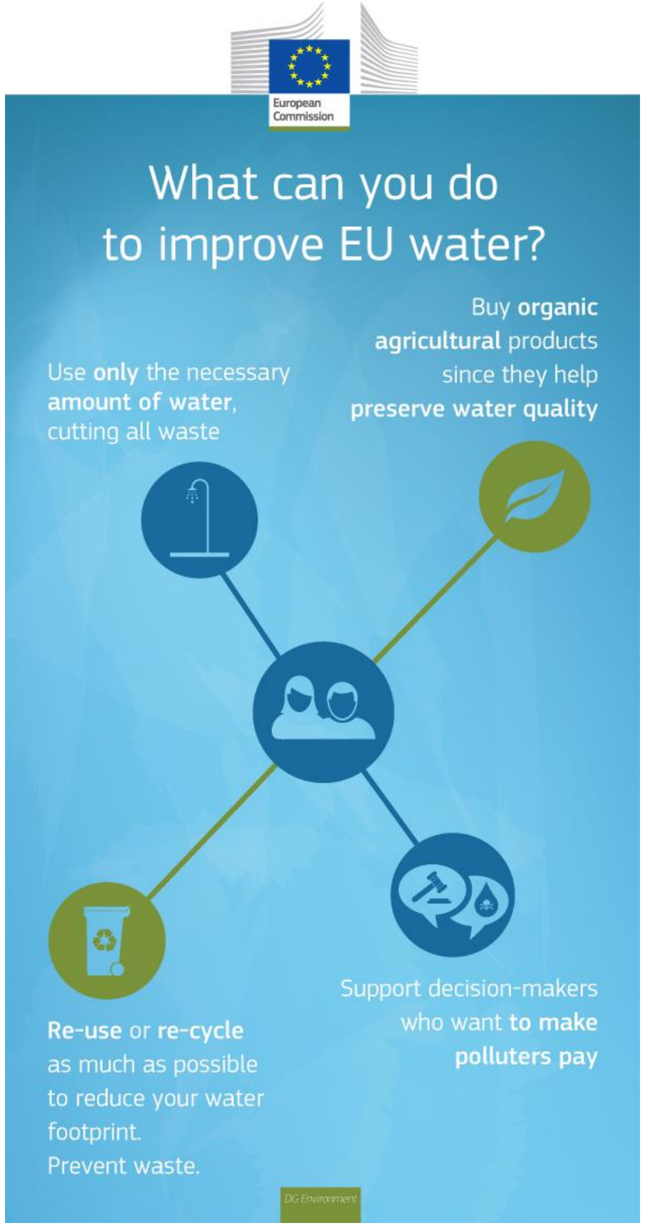
- **Priority substances** (regulated): **45 (2013) – 70 (2022)**
- **Watch list substances**: 23 (2022)
- **Contaminants of emerging concern** (non-regulated): **> 700**

**Analyses currently comprise:**

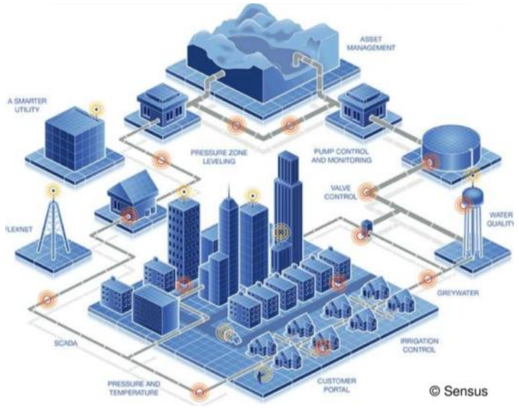
1. Sample uptake
2. Sample stabilisation
3. Sample transport
4. Sample storage
5. Use of bulky and expensive equipment (HPLC-MS, GC-MS,…)
6. Highly skilled personnel

*Source: Guidance Document No. 19: Guidance on surface water chemical monitoring under the water framework directive; https://sensus.com/internet-of-things/smart-water/*

# Electrochemical sensors for measuring water pollutants




## IoT: Smart Water

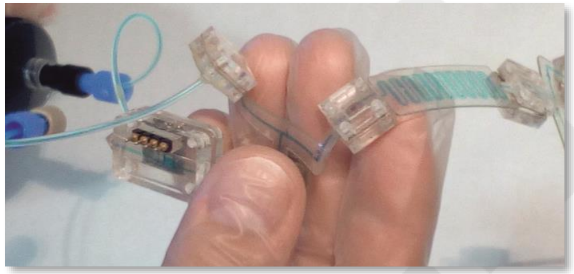



## Electrochemical sensors - Microfluidics

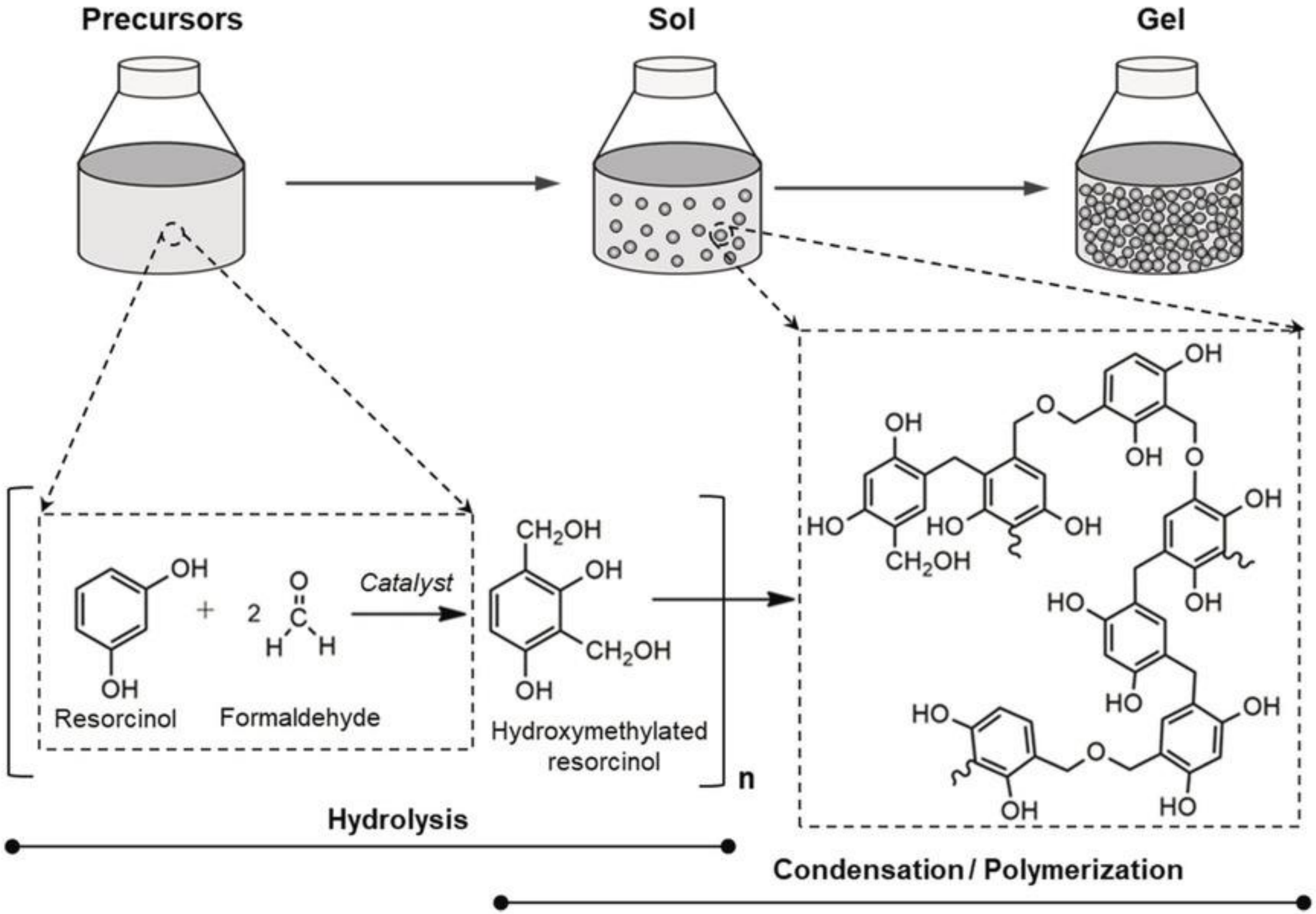
- Compact
- Low Cost
- Low power electronics
- Low maintenance
- Decentralized
- Wireless communication and cloud data storage

- Analytical devices applied on-site for timely detection of **contamination outbreaks** and **periodic analyses**

- Deployable analytical platforms to continuously monitor **water quality** and assess **water reuse**

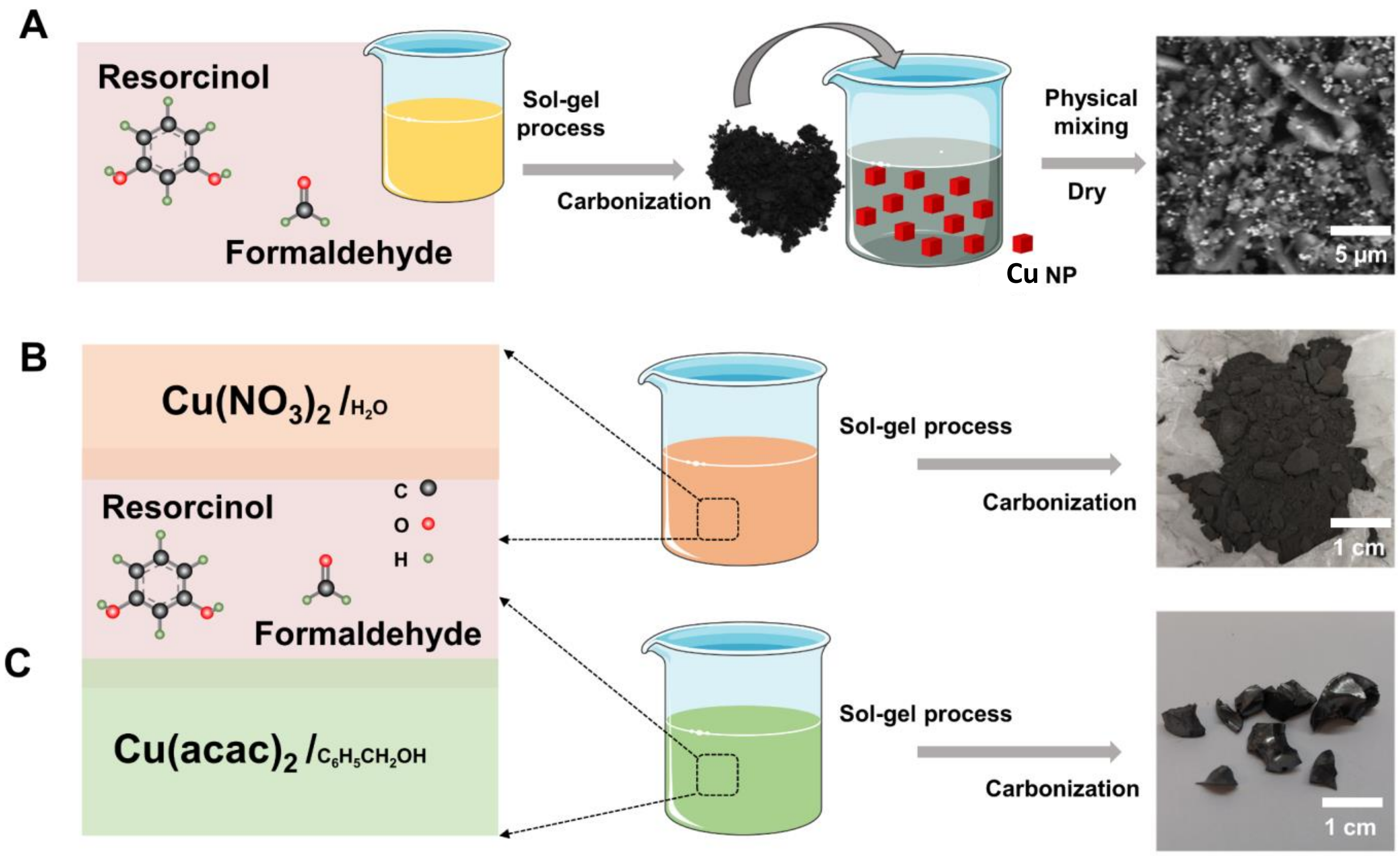


# Sol-gel production of functional materials



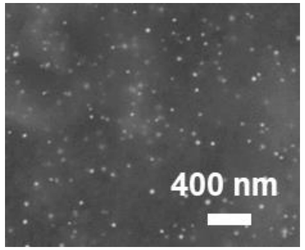

P. Niu, M. Gich, A. Roig, C. Fernández-Sánchez, Metal Nanoparticle Carbon Gel Composites in Environmental Water Sensing Applications, Chem Record 2018,18, 749 – 758.
DOI: 10.1002/tcr.201800011

## Carbon and metal nanoparticles




W. Duan, et al., Composites of porous carbon and copper-based nanoparticles for the electrochemical analysis of chemical oxygen demand, Mat. Today Chem 24 (2022) 100899.
DOI: 10.1016/j.mtchem.2022.1008997

# Fabrication process

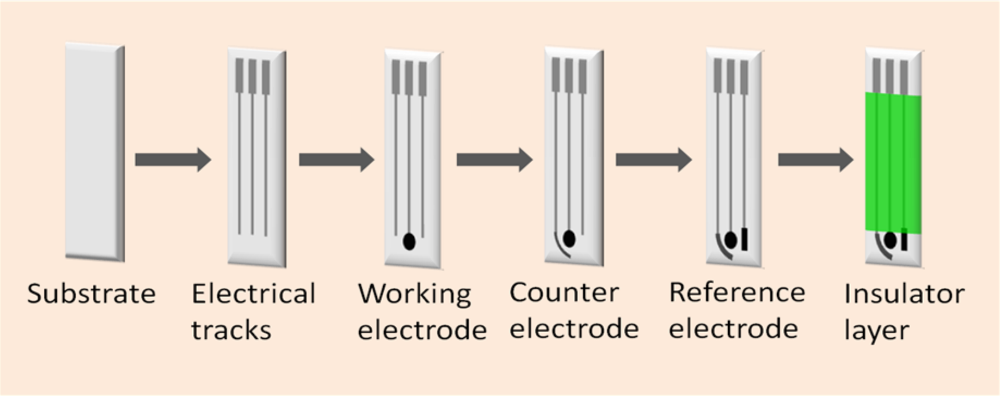



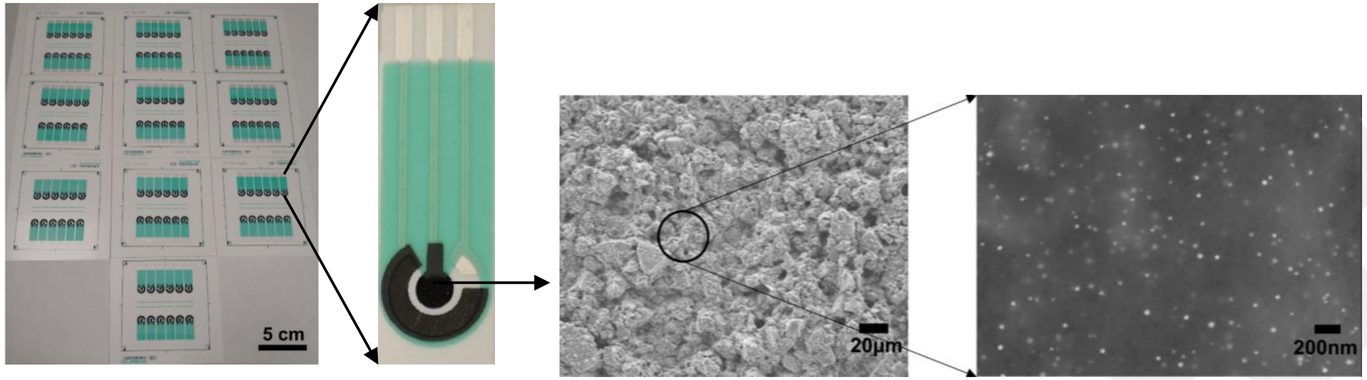

*Pyrolized material*

*C composite ink*

*Home-made and industrial screen printing machine*

## Fabrication sequence



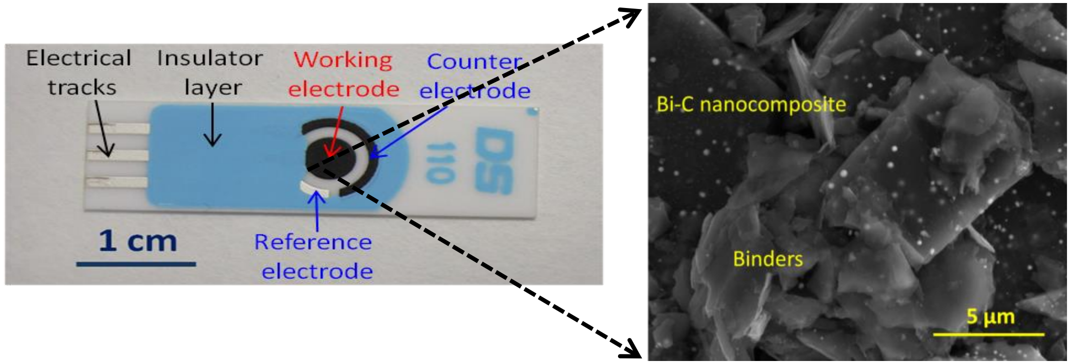




6 g material to produce ~120 electrodes

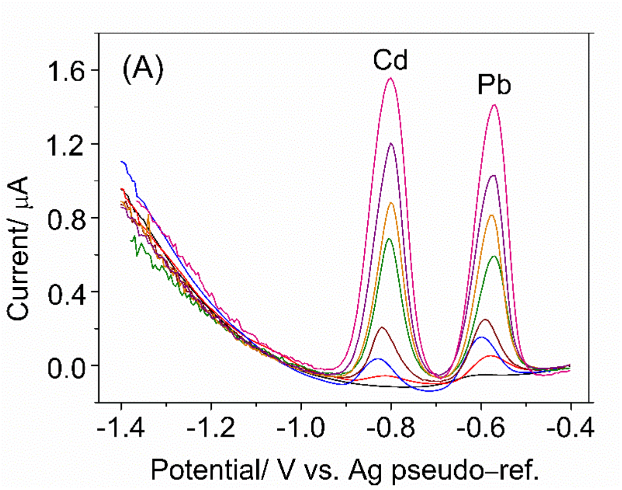
W. Duan, F. J. del Campo, M. Gich, C. Fernández-Sánchez, In-field one-step measurement of dissolved chemical oxygen demand with an integrated screen-printed electrochemical sensor, Sensors and Actuators B 369, 2022, 132304. DOI: 10.1016/j.snb.2022.132304

# Thick- film sensors by screen-printing

## Electrochemical sensor for measuring Pb(II) and Cd(II)




20g nanocomposite material to manufacture ~ 450 electrodes




- Square-wave anodic stripping voltammetry
- Response time: 6 min
- Linear ranges: 1-50 ppb
- LOD: 2.3 (Cd), 1.5 (Pb) ppb

### Water sample analysis

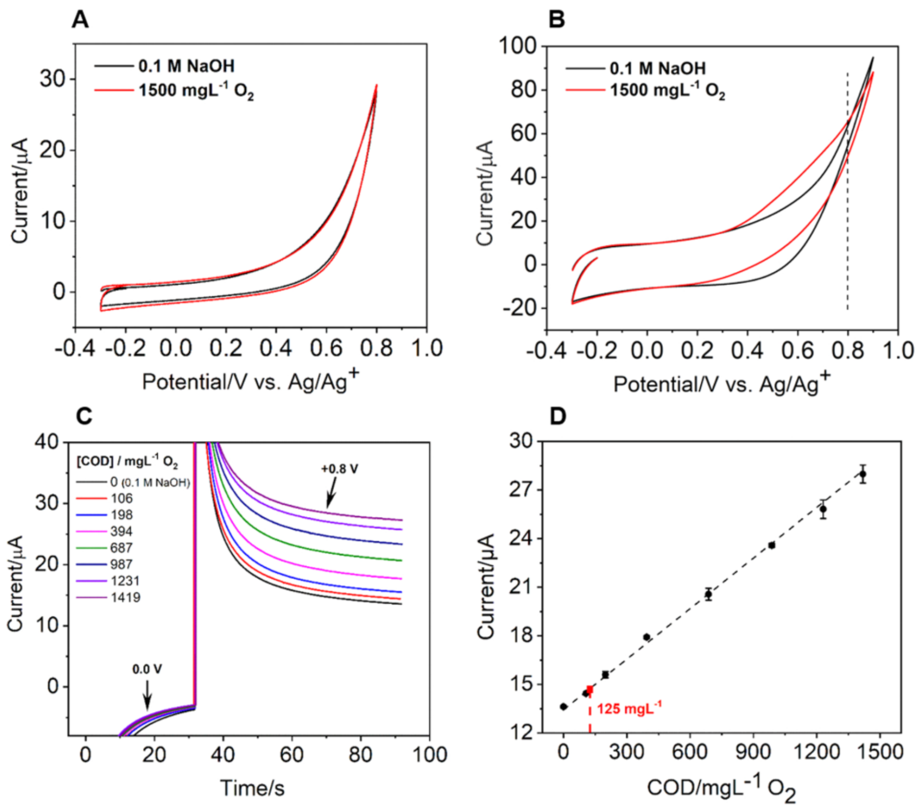
| Water Samples | Heavy Metals Elements | Added Concentration (ppb) | Analyzed Concentration (ppb)[1] | Recovery (%) |
|---|---|---|---|---|
| Tap Water | Pb(II) | 20.0 | 23±2 | 115 |
| | | 50.0 | 58±5 | 117 |
| | Cd(II) | 20.0 | 18±4 | 89 |
| | | 50.0 | 44±5 | 90 |
| Waste Water | Pb(II) | 5.0 | 5.3±0.3 | 106 |
| | Cd(II) | 5.0 | 6.0±0.9 | 120 |

[1]Mean value ± standard deviation of three replicates


P. Niu *et al.* Electrochim. Acta **2015,** *165*, 155-161
P. Niu *et al.* Microchim. Acta **2016**, *183*, 617-623

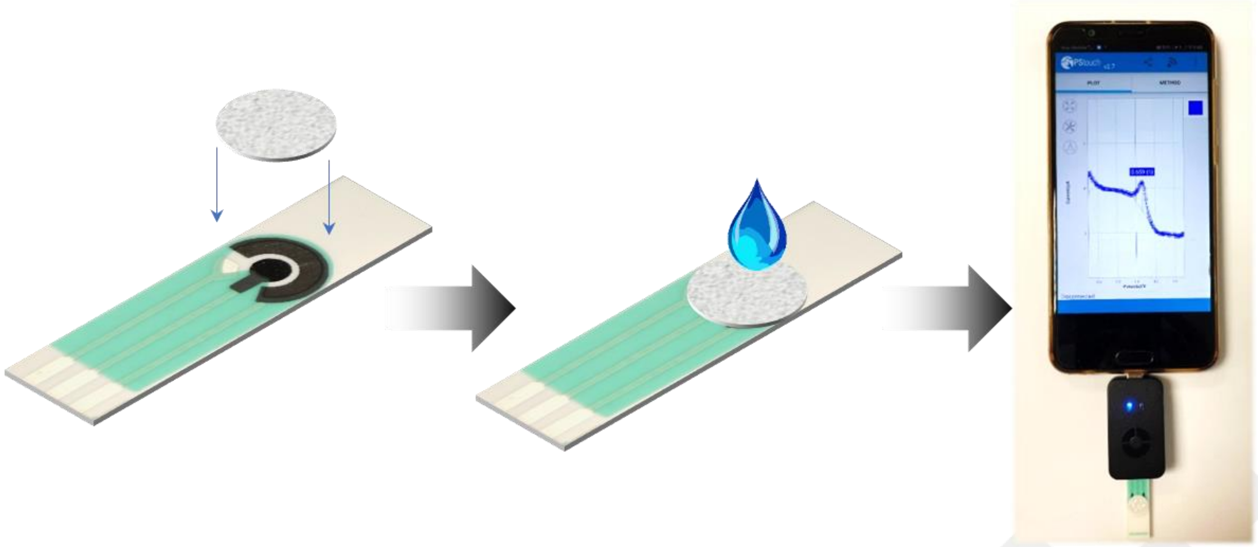
# Cu-NP C SPE sensor for Chemical Oxygen Demand (COD)

Produced using a **CuNP C nanocomposite ink**




- COD detection by chronoamperometry
- Linear range and LOD: 50 – 1400 mgL$^{-1}$ $O_2$ and 28 mgL$^{-1}$ $O_2$

**Sample-to-result** electrochemical sensor



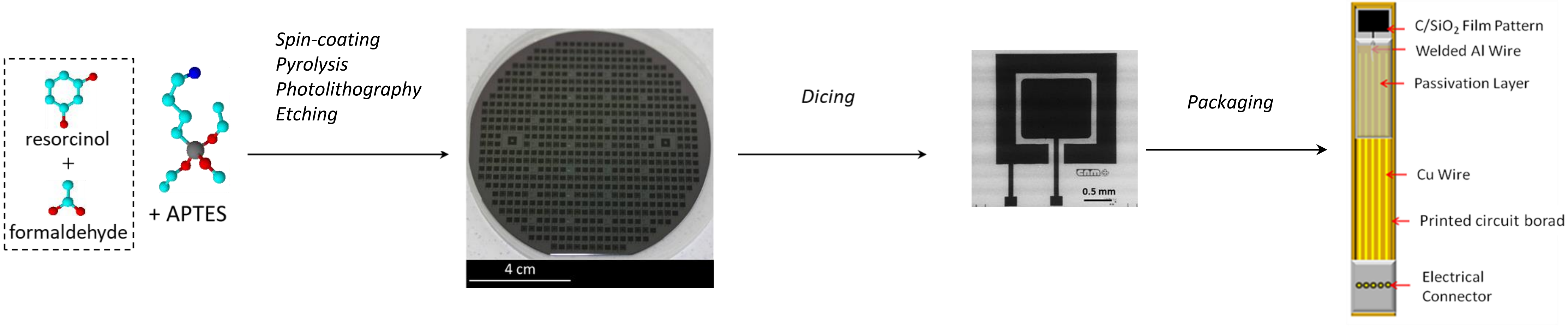
20 µL sample volume and 10 min analysis time

W. Duan *et al.* Sens. Actuat B **2022,** *369*, 132304
C. Fernández-Sánchez, et al. EU patent application: EP21383025.0.

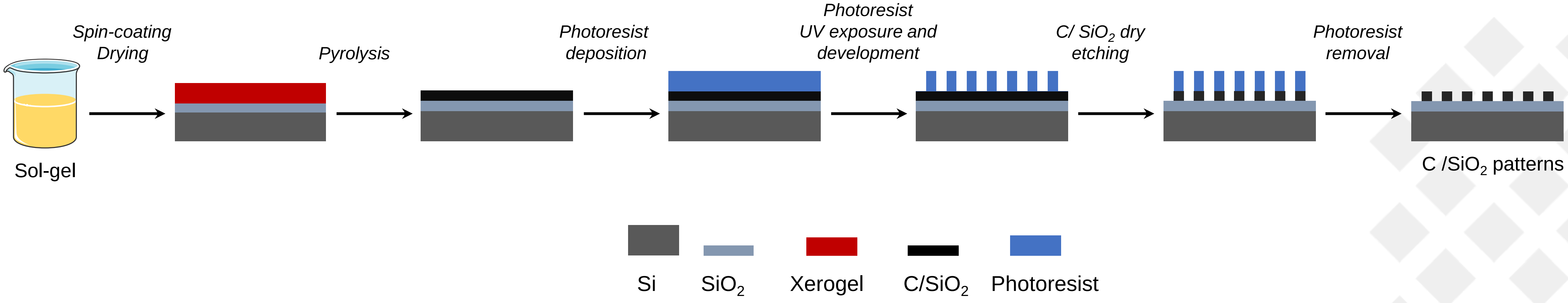
# COD sample analysis at an urban WWTP

| Technique | Effluent ($mgL^{-1}O_2$) | Clarifier ($mgL^{-1}O_2$) | Pretreatment ($mgL^{-1}O_2$) | Analysis time | Pre-filtered |
|---|---|---|---|---|---|
| Cu-NP C SPE | 42 ± 6 | 100 ± 2 | 228 ± 18 | 10 min | No |
| Dichromate method | 37 ± 8 | 85 ± 18 | 210 ± 25 | 2 h | Yes |

# Thin-film sensors by microfabrication



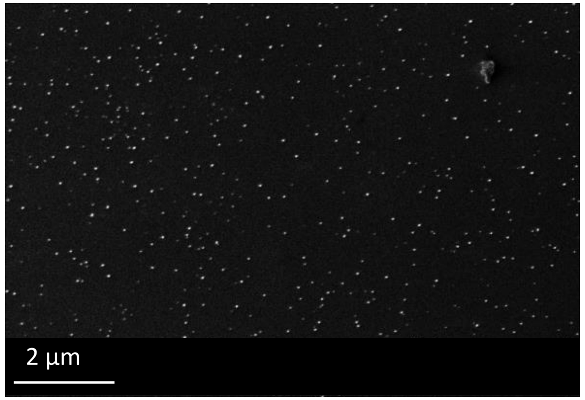

## Pyrolysis / Photolithography / Etching

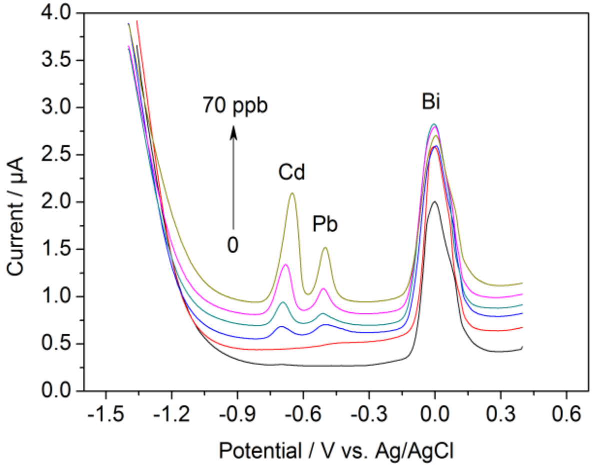


# Thin-film sensors by microfabrication

## Pb and Cd

Bi electrodeposition

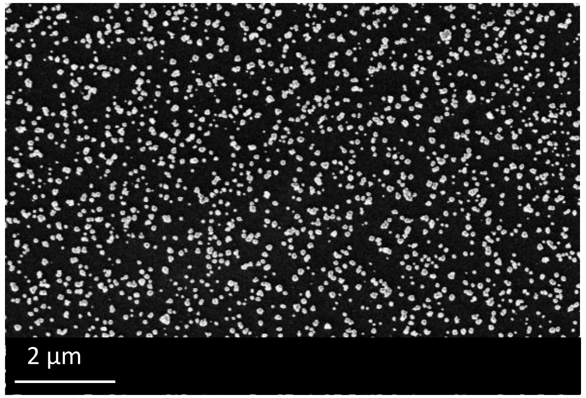


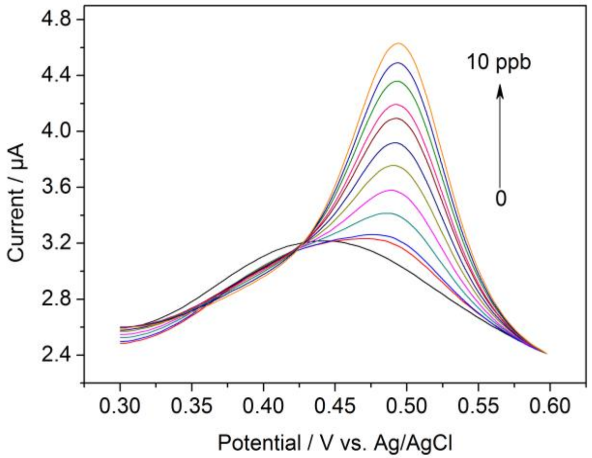




LODs: 1.2 (Cd); 4.3 (Pb) ppb

## Hg

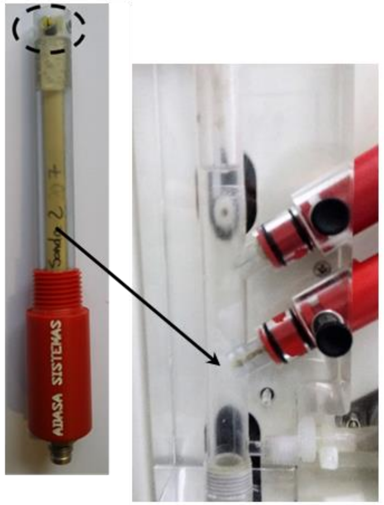
Au electrodeposition

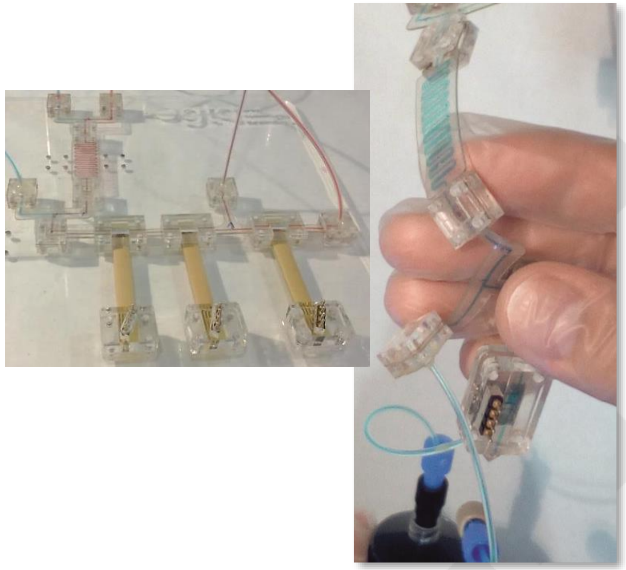



LOD: 0.45 ppb

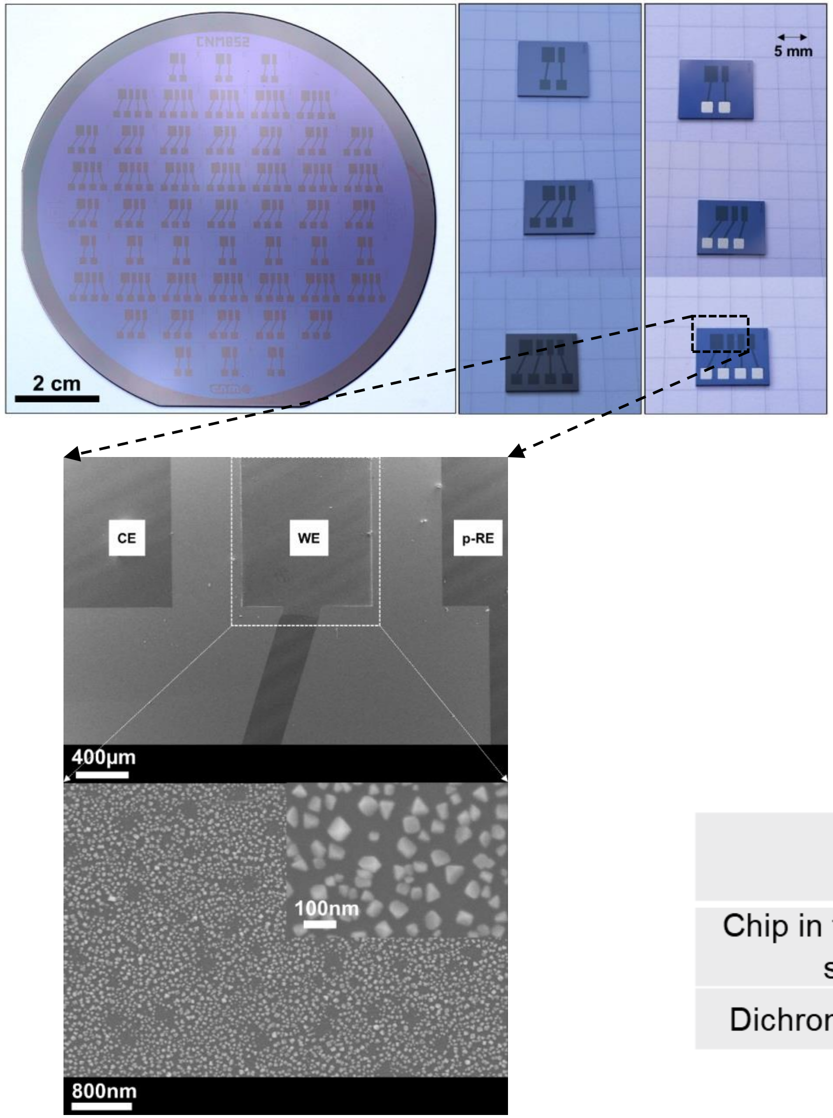
## Integration in a flow system

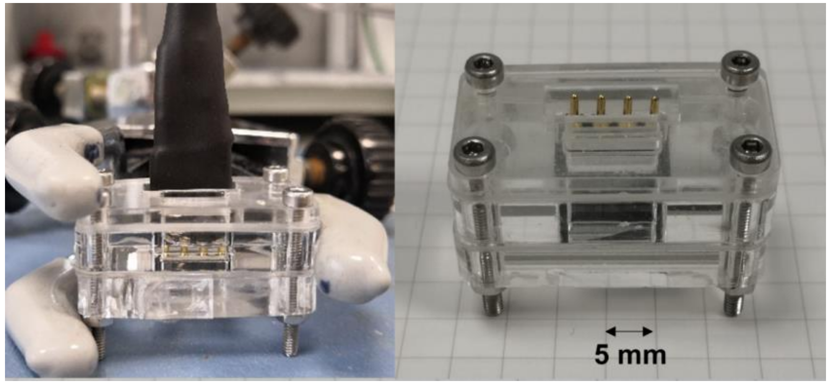


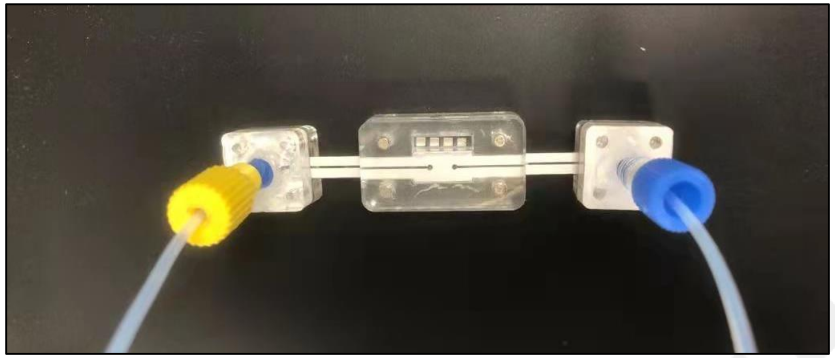



P. Niu *et al.* Adv. Mat. Tech. **2017**, *2*, 1700163 (11 pp.)

# Mass production of carbon thin-film electrodes



| Samples | 1_effluent | 2_ clarifier effluent | 3_ pretreatment effluent |
|---|---|---|---|
| Chip in the modular microfluidic system ($mgL^{-1}O_2$) | 45±5 | 67±8 | 191±14 |
| Dichromate method ($mgL^{-1}O_2$) | 37±8 | 85±18 | 210±25 |

W. Duan *et al.* Chem. Eng. J. **2022**, *449*, 137837

**Reducing the carbon footprint in the production of carbon inks:** Valorization of **bread waste** as the carbon source

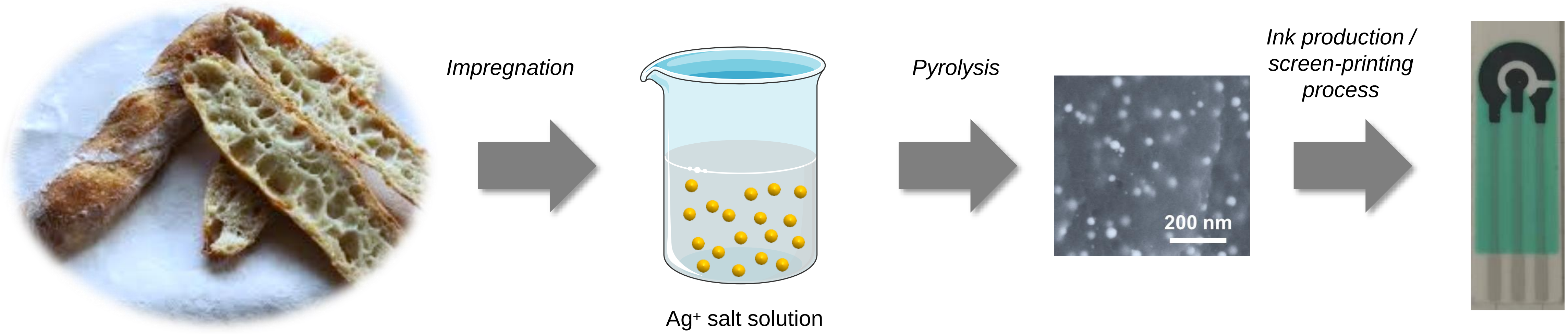
Bread composition

| | |
|---|---|
| Net amount | 210 g |
| Nutritional information | Mean / 100 g |
| Fats | 1 g |
| **Carbohydrates** | 68 g |
| Sugars | 0.68 g |
| Dietary fiber | 2.7 g |
| **Protein** | 8.6 g |
| Salt | 0.05 g |

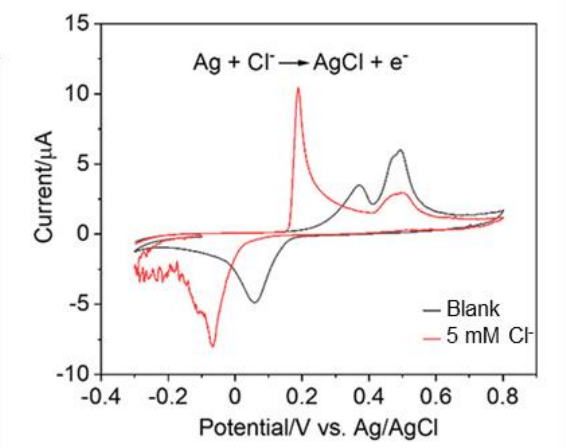
- Product with one of the highest waste generation in several parts of the supply chain, being between 10-30 % of the food waste generated everyday in many countries.
- 2.1 million tons of bread waste are annually generated in China
- 2nd most wasted food product in UK, totalling 20 million slices of bread per day

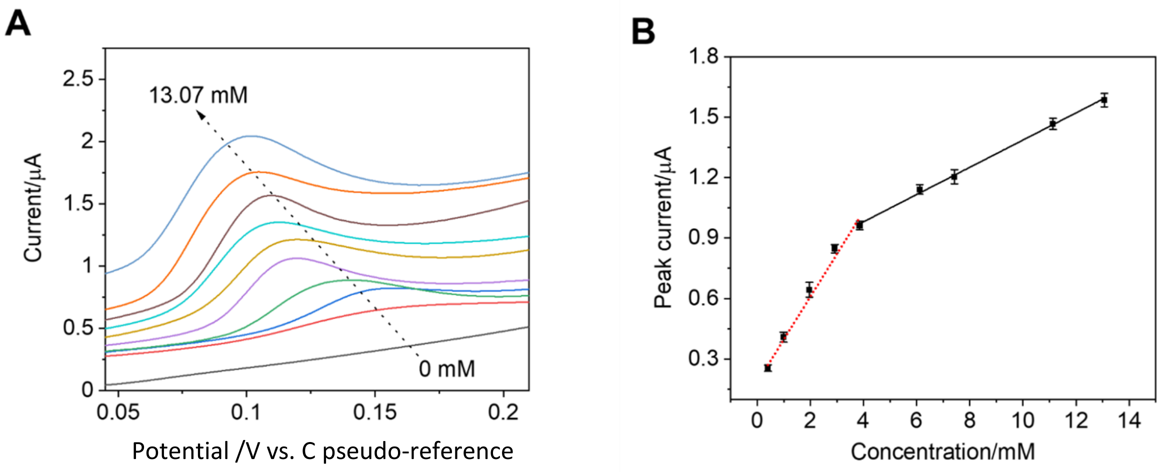
Source: V. Kumar et al. Bioresource Tech. 369 (2023): 128449; Han Wei, et al. J. Cleaner Prod. 141 (2017): 608-611.

# Alternative materials for sustainable sensors




## Detection of halogenated compounds: Sucralose



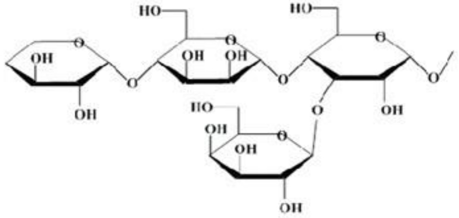




W. Duan *et al.* ACS Appl. Mat & Interf. **2022**, *14,* 40182−40190
W. Duan *et al.* Electrochim. Acta **2022**, *436*, 141459

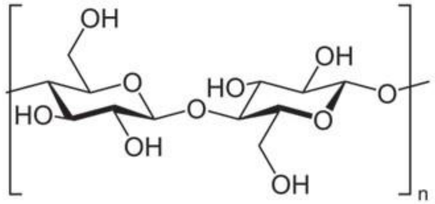
# Wood residues as the carbon source

~80 million ton of forestry residues are annually produced in the EU

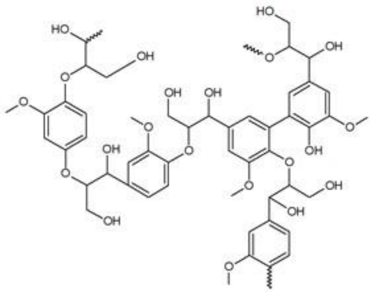
Hemicelullose



Celullose

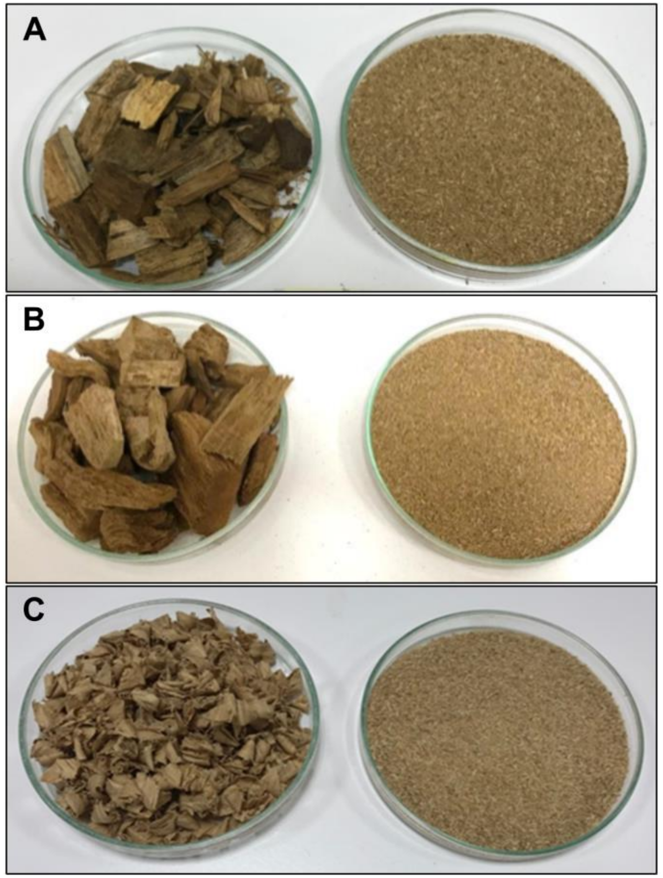



Lignin

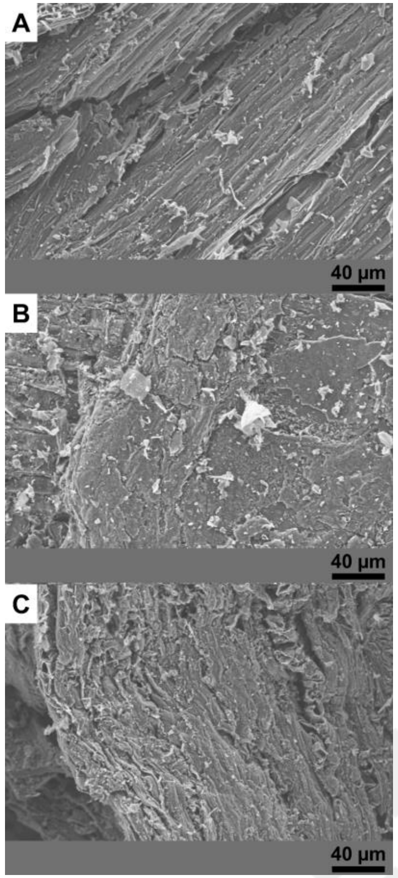


*Source: Lizundia, Erlantz, Francesca Luzi, and Debora Puglia. Green Chemistry (2022).*

**A- Pine; B- Chestnut; C- Oak**



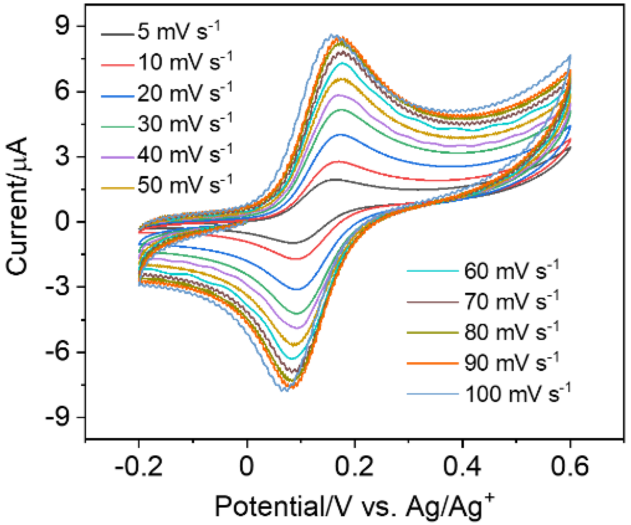

*Pyrolysis*

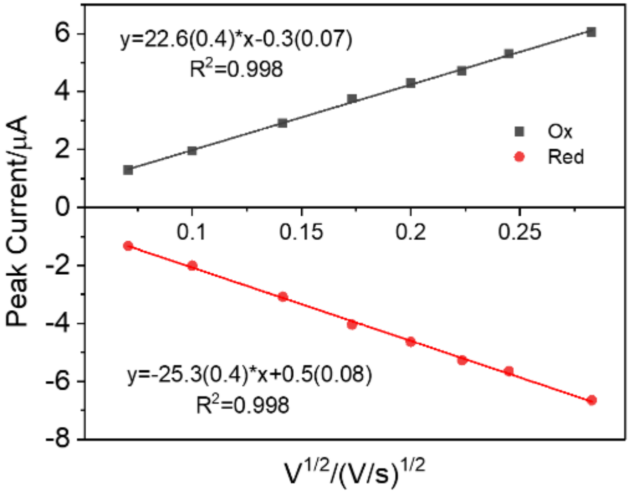




**Highest cellulose + Lignin content – Better electrochemical performance**

20 ml C ink produced from 60 g chestnut wood residues: 120 screen-printed electrodes

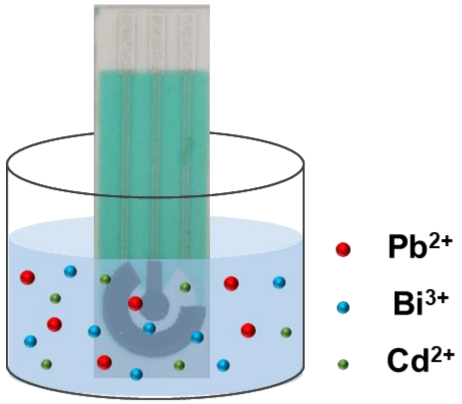
**Ferrocene-methanol**



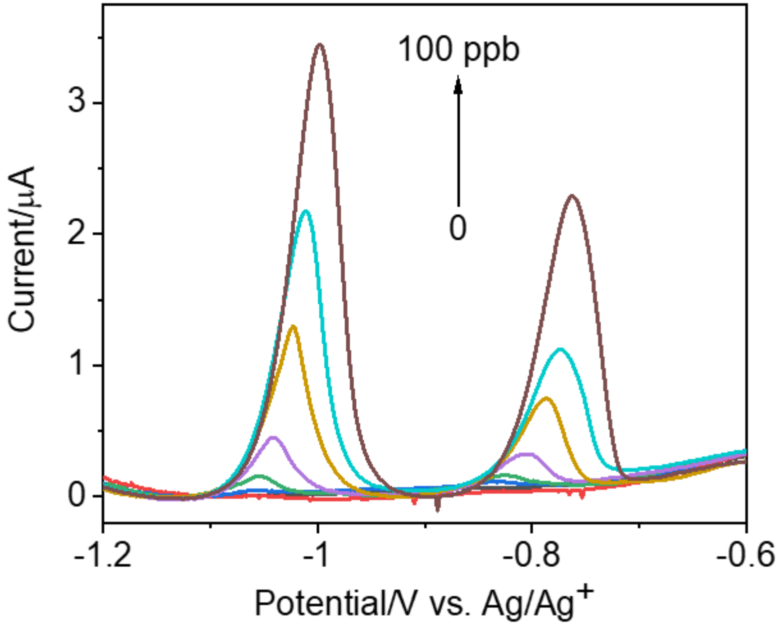



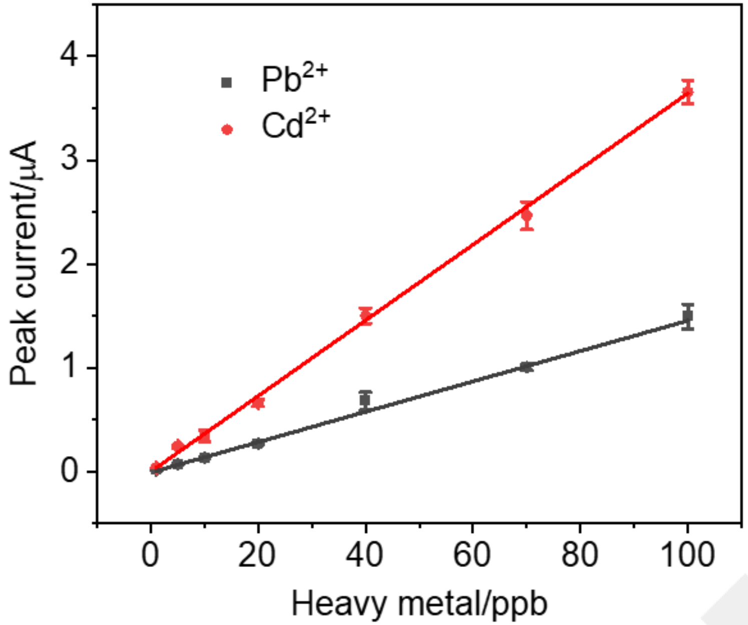

| | | $\Delta E_P$ (mV) | $K^0_{app}$[*$10^{-4}$ cm $s^{-1}$] |
|---|---|---|---|
| SPE | Ferrocene | 78 | 90±16 |
| SPE_$C_{comercial}$ | | 71 | 130±29 |

## Cd(II) and Pb(II) by Differential pulse Anodic Stripping Voltammetry




100 ppb Bi (III), -1.6 V applied DC potential and 5 min accumulation time




| | Linear range (ppb) | Sensitivity (μA/ppb) | LOD (ppb) | R |
|---|---|---|---|---|
| $Pb^{2+}$ | 1-100 | 0.015 ± 0.0005 | 0.37 | 0.994 |
| $Cd^{2+}$ | 1-100 | 0.036 ± 0.002 | 0.15 | 0.991 |

## Heavy metal detection

| Samples | Sensor (ppb) | | Reference values (ppb) | |
|---|---|---|---|---|
| | Pb (II) | Cd (II) | Pb (II) | Cd (II) |
| Tap water_IMB-CNM | 9.2 ± 0.6 | 10.8 ± 0.9 | 10 | 10 |
| WWTP Effluent | 9.1 ± 0.8 | 9.5 ± 0.7 | 10 | 10 |
| WWTP Pretreatment | 9.0 ± 0.7 | 9.4 ± 0.8 | 10 | 10 |
| Commercial sample_1 | 30 ± 2 | 19 ± 3 | 31.7 | 20.4 |
| Commercial sample_2 | 55 ± 3 | 36.4 ± 5 | 63.3 | 40.7 |

W. Duan *et al.* ACS Sust. Chem. & Eng. **2024**, *12*, 4386-4397

# Acknowledgements



gtq silicon technologies for sensing

cnm Centre Nacional de Microelectrònica IMB

MICRO nano FABS

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AGAUR

tecnio catalonia — ACCIÓ Generalitat de Catalunya

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# Thank you for your attention!

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