Núcleo de Pesquisa em Eletroanalítica
Instituto de Química-UFU

3D printing for electroanalysis: From electrochemical cells to sensors

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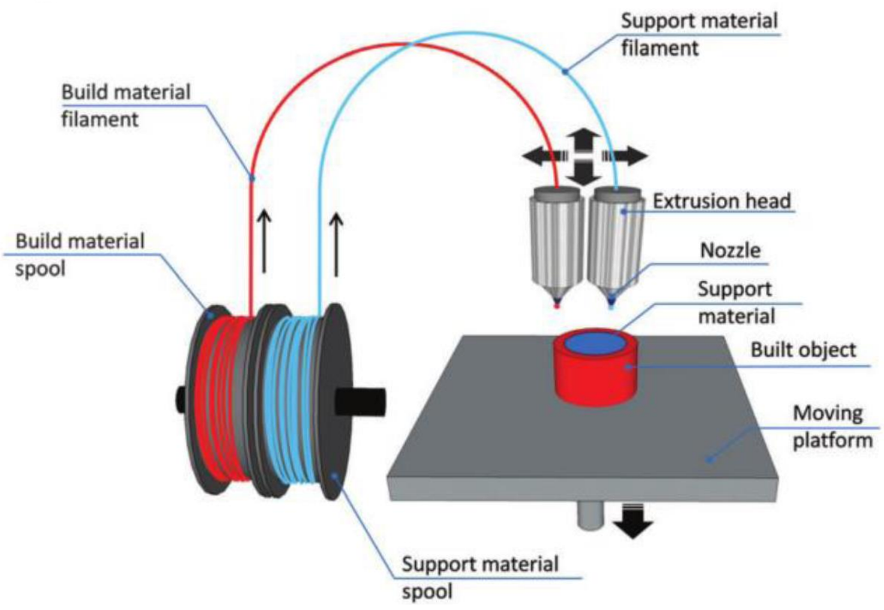
Summary

- **Introduction**
- **Fused deposition modelling 3D printing**
  - Electrochemical Cells
  - Electrochemical Sensors
- **Applications**
  - Forensics
    - TNT
  - Clinical analysis
    - Uric acid and nitrite
- **Perspectives**

Introduction: Fused deposition modeling

- Fused deposition modeling (FDM) or Fused Filament Fabrication (FFF)
- The cheapest 3D printing technology
- Scott Crum, 1989
- Layer-by-layer
- Hotend with different materials:
- ABS, PLA, Nylon, resin,

food! etc...

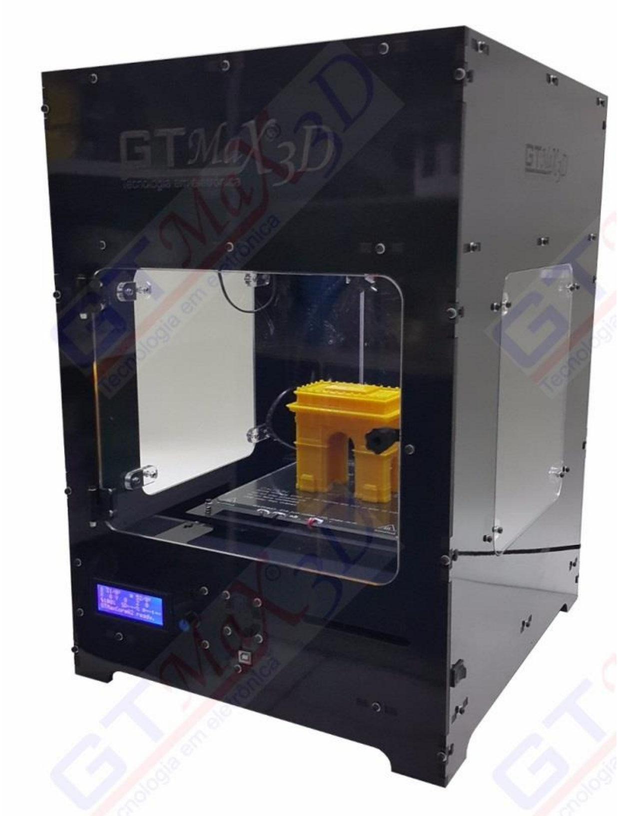


AMBROSI, A.; PUMERA, M. 3D-printing technologies for electrochemical applications. **Chem. Soc. Rev.**, v. 45, p. 2740–2755, 2016.

Introduction: Fused deposition modeling

Commercial available models used in this work

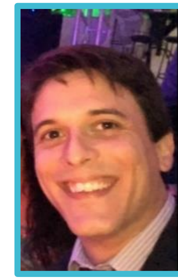
RepRap Prusa I3 printer
(Kit to build by yourself)



GTMax 3D® printer

Part 1: 3D printing technology for electroanalysis: Electrochemical Cells

Multiuse electrochem. cell (BIA, FIA and steady-state):



- Rep-Rap 3D printer (fused filament deposition)

  Layer-by-layer printing using ABS filament

R.M. Cardoso, at al. 3D printing for electroanalysis: From multiuse electrochemical cells to sensors, Anal. Chim. Acta. 1033 (**2018**) 49–57.

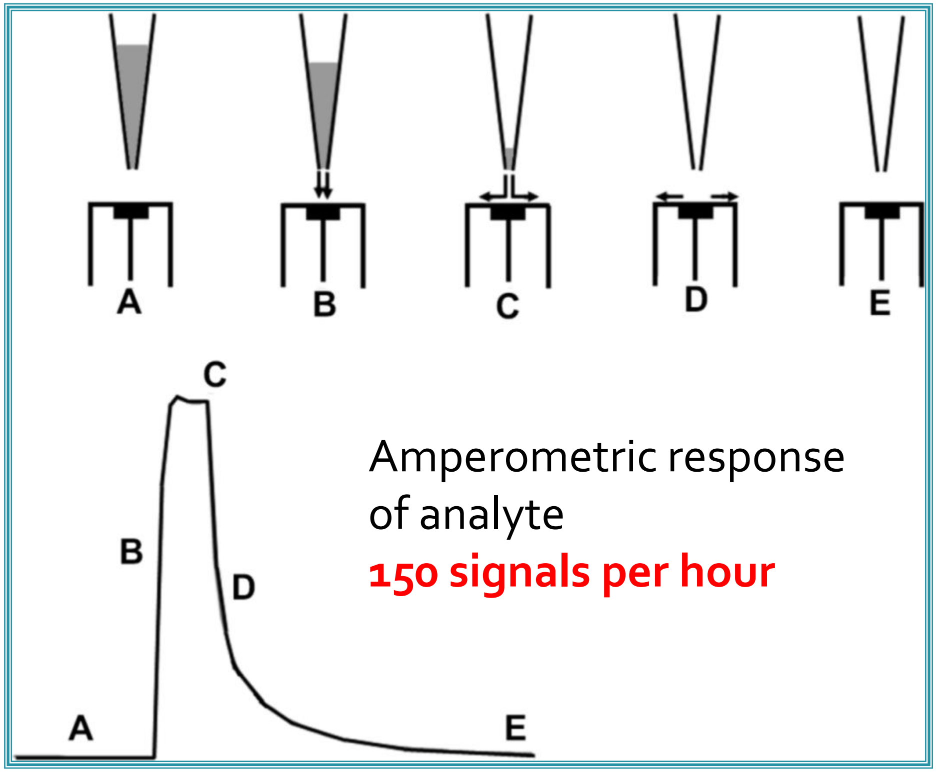
Batch-injection analysis (BIA)

Analogous to Flow-injection analysis (FIA)

Advantages: no need of pumps, tubing and injection valves.

Easy to adapt for on-site analysis

Stages of acquisition of the transient signal by BIA



(A) Before injection

(B) Transport during the injection

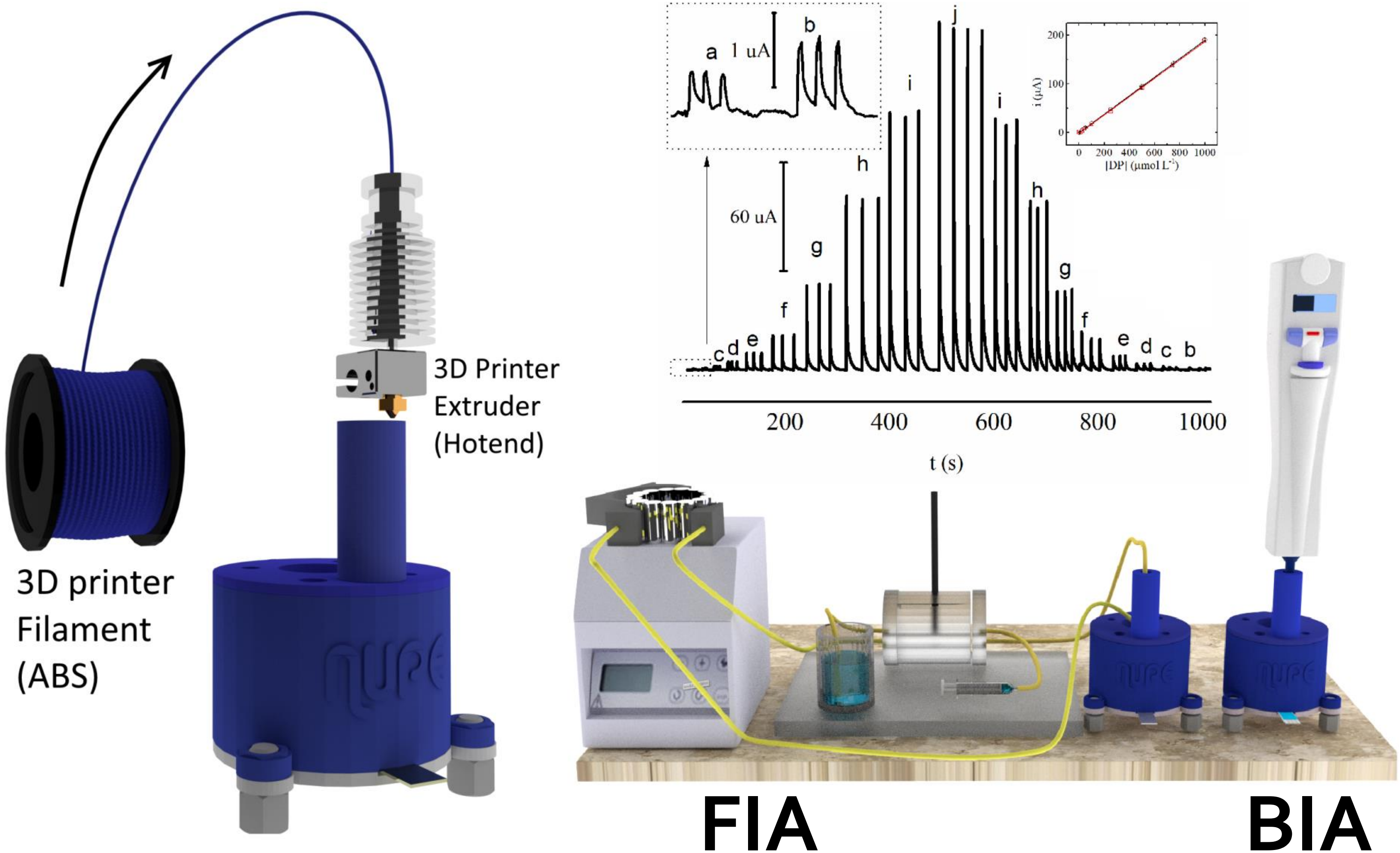
(C) End of the injection

(D) Washing out

(E) Final equilibrium

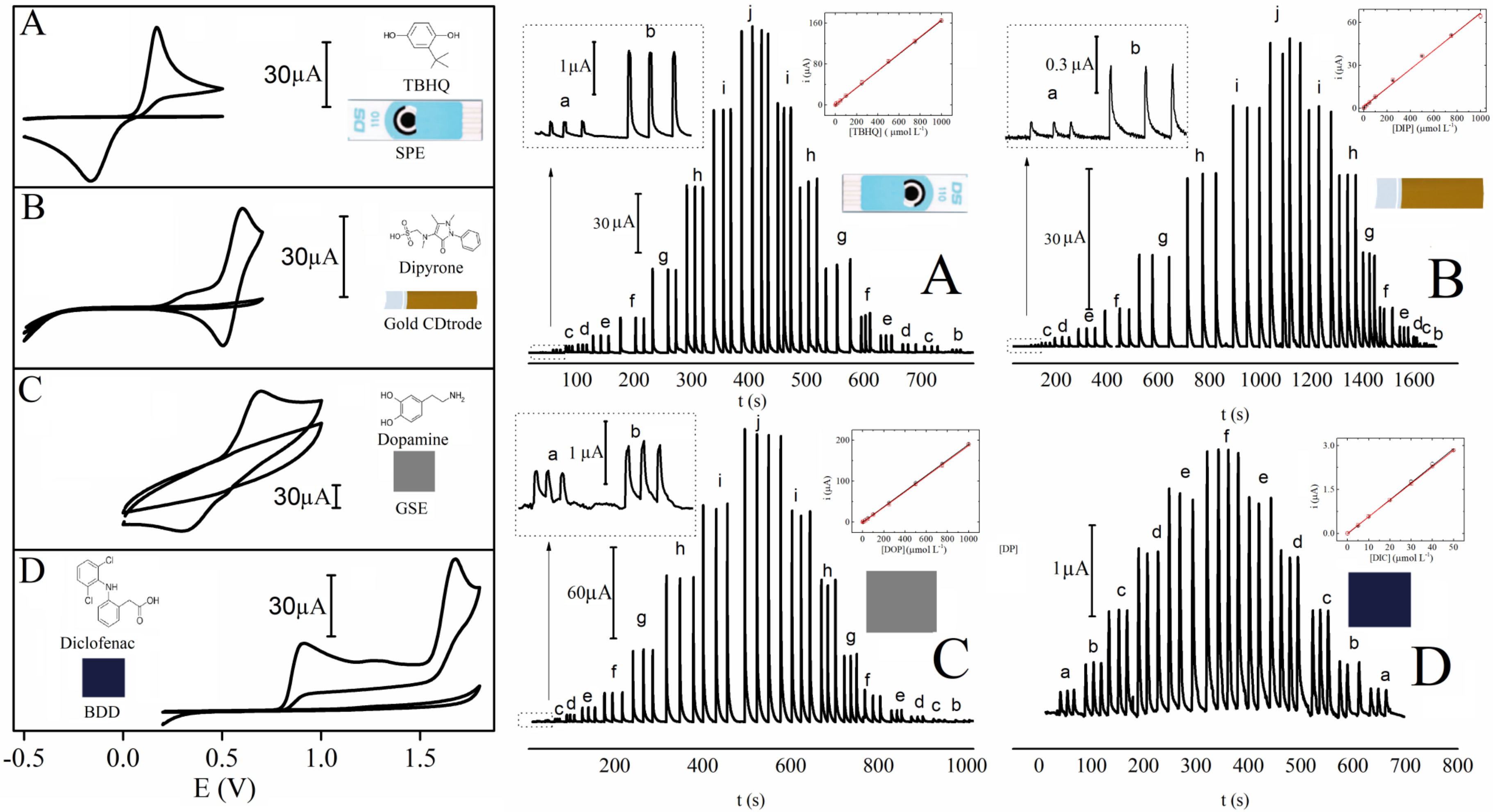
Quintino, M.S.M. and Angnes, L., *Batch injection analysis: An almost unexplored powerful tool.* Electroanalysis, 2004. **16**(7): p. 513-523.

Part 1: 3D printing technology for electroanalysis: Cells and sensors



R.M. Cardoso, et al., 3D printing for electroanalysis: From multiuse electrochemical cells to sensors, Anal. Chim. Acta. 1033 (**2018**) 49–57.

Part 1: 3D printing technology for electroanalysis: Cells and sensors



R.M. Cardoso, et al., 3D printing for electroanalysis: From multiuse electrochemical cells to sensors, Anal. Chim. Acta. 1033 (**2018**) 49–57.

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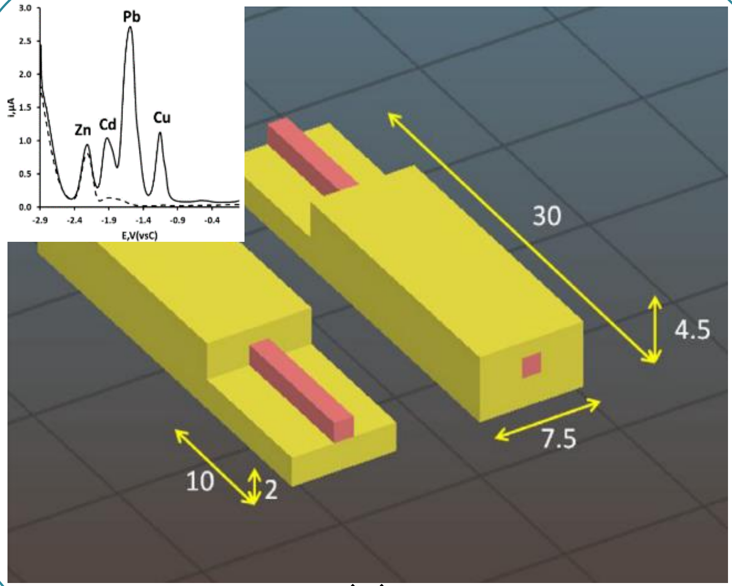
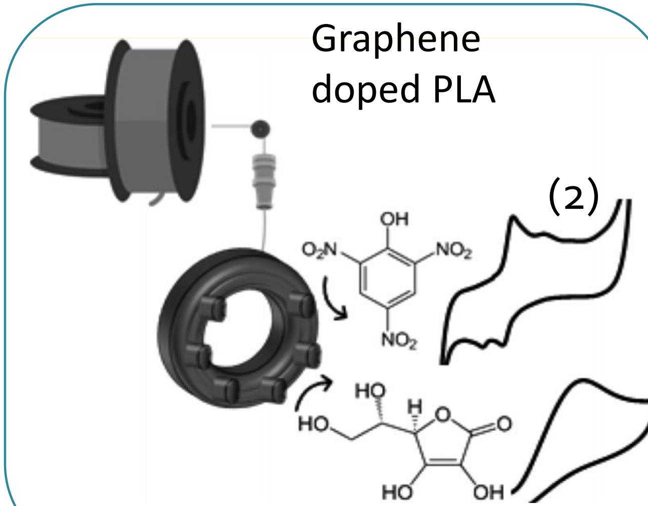
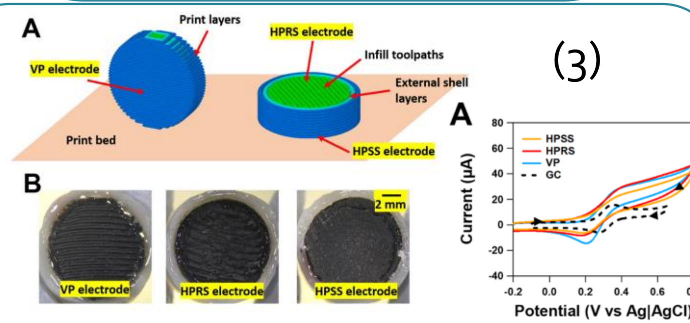
Sensing with 3D-printed electrodes



(1)



(2)



(3)

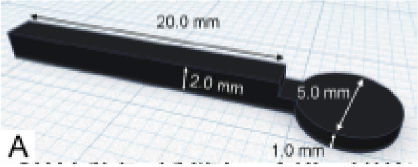
[1] K.C. Honeychurch, Z. Rymansaib, P. Iravani, Anodic stripping voltammetric determination of zinc at a 3-D printed carbon nanofiber–graphite–polystyrene electrode using a carbon pseudo-reference electrode, Sens. Actuators, B: Chem. 267 (**2018**) 476–482.

[2] C. Tan, M.Z.M. Nasir, A. Ambrosi, M. Pumera, 3D Printed Electrodes for Detection of Nitroaromatic Explosives and Nerve Agents, Anal. Chem. 89 (**2017**) 8995–9001.

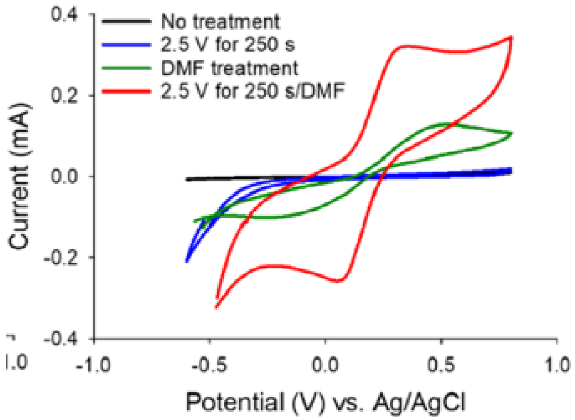
[3] H.H. Bin Hamzah, O. Keattch, D. Covill, B.A. Patel, The effects of printing orientation on the electrochemical behaviour of 3D printed acrylonitrile butadiene styrene (ABS)/carbon black electrodes, Sci. Rep. 8 (**2018**) 1–8.

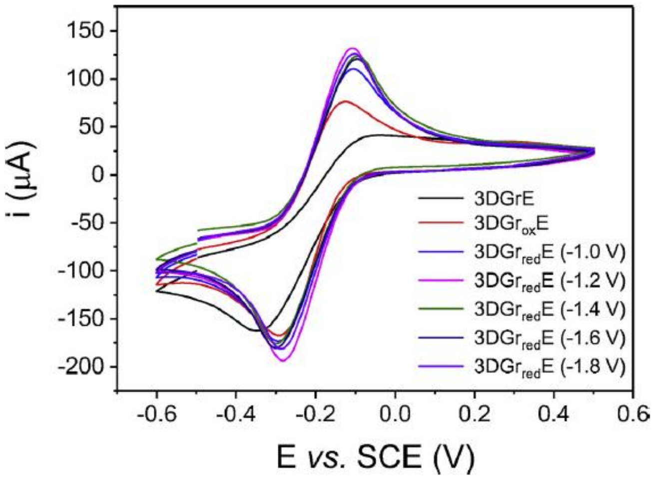
Sensing with 3D-printed electrodes

Surface treatment (chemical or electrochem) of 3D printed sensors



Soaked in DMF for 10 min
Washed with ethanol
24 h drying
EC treatment:
+2.5 V for 250 s
PBS (pH 7.2)





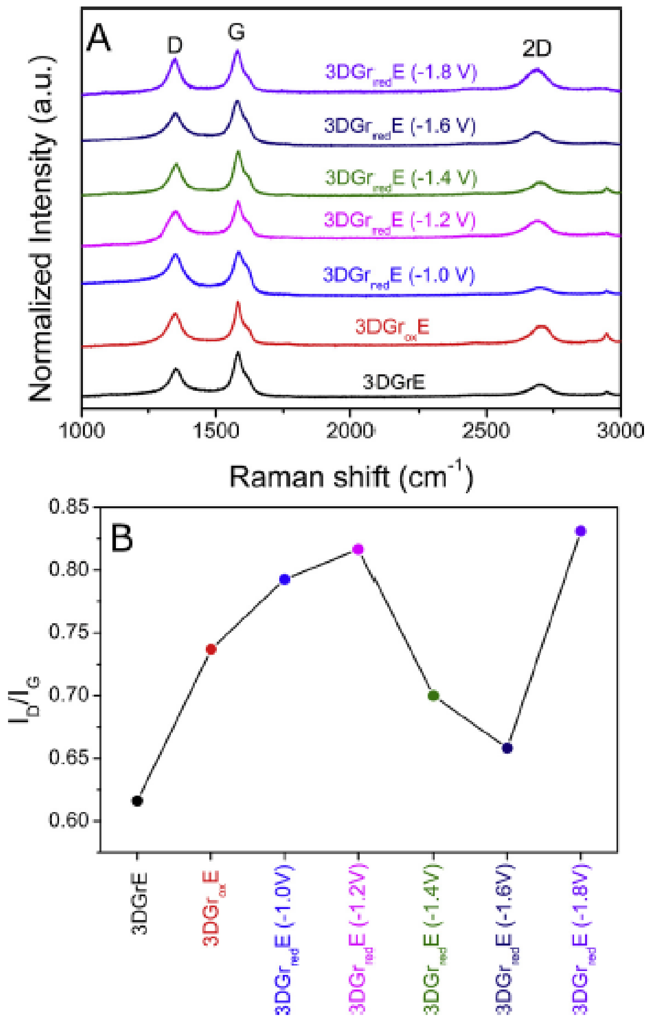
No solvent treatment
EC treatment:
+1.8 V for 900 s followed by a cycle from 0 to -1.8 V
PBS (pH 7.4)

[4] M. P. Browne, F. Novotny, Z. Sofer, M. Pumera, 3D Printed Graphene Electrodes' Electrochemical Activation, ACS Appl. Mater. Chem. 10 (**2018**) 40294–40301.

[5] P. L. Dos Santos, V. Katic, H.C. Loureiro, M.F. Dos Santos, D.P. Dos Santos, A.L.B. Formiga, J.A. Bonacin , Enhanced performance of 3D printed graphene electrodes after electrochemical treatment: Role of exposed graphene sheets , Sens. Actuat. B 281 (**2019**) 837–848.

Sensing with 3D-printed electrodes

Electrochemical Surface treatment of 3D printed sensors



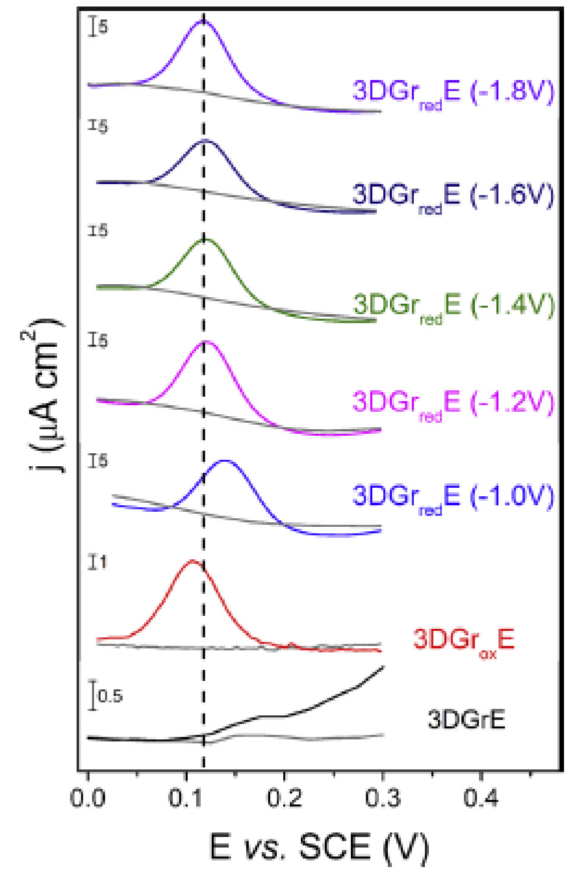


Fig. 9. Comparison between the differential pulse voltammograms of the 3D printed graphene electrodes in the absence (gray line) and the presence of 0.01 mmol L^{-1} of dopamine. Supporting electrolyte: 0.1 mol L-1 KCl in 0.1 mol L^{-1} PBS (pH 7.4).

[5] P. L. Dos Santos, V. Katic, H.C. Loureiro, M.F. Dos Santos, D.P. Dos Santos, A.L.B. Formiga, J.A. Bonacin , Enhanced performance of 3D printed graphene electrodes after electrochemical treatment: Role of exposed graphene sheets , Sens. Actuat. B 281 (**2019**) 837–848.

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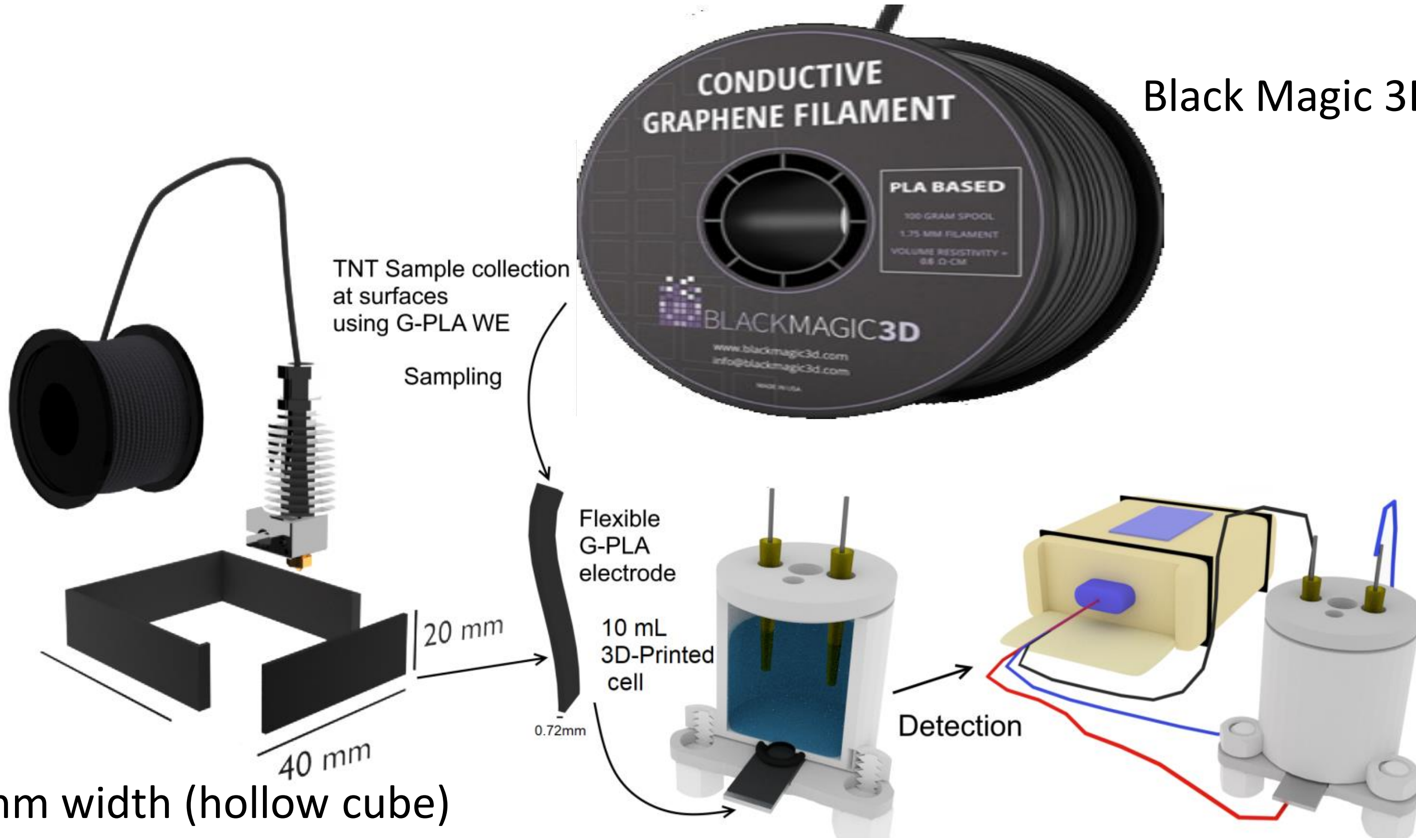
Part 2: 3D printing technology for electroanalysis: Electrochemical sensors

Electrochemical sensors: graphene-doped polylactic acid (PLA)



Black Magic 3D (USA)

0.76 mm width (hollow cube)
0.5 mm hotend nozzle
Bed temperature at 220ºC
0% infill

BIA cell scheme
(transversal cut)

Assembled BIA cell
+ potentiostat

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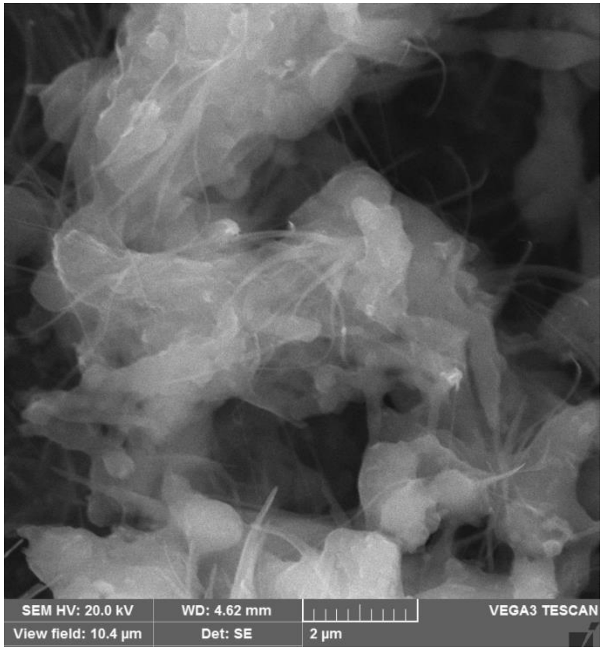
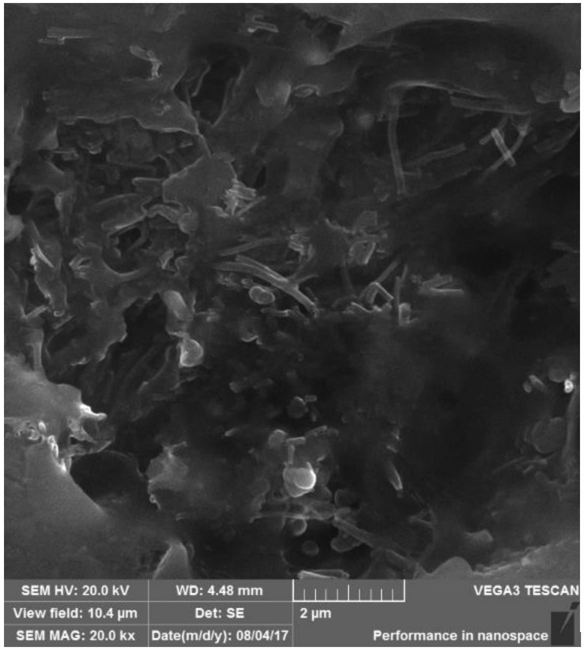
Part 2: 3D printing technology for electroanalysis: Electrochemical sensors

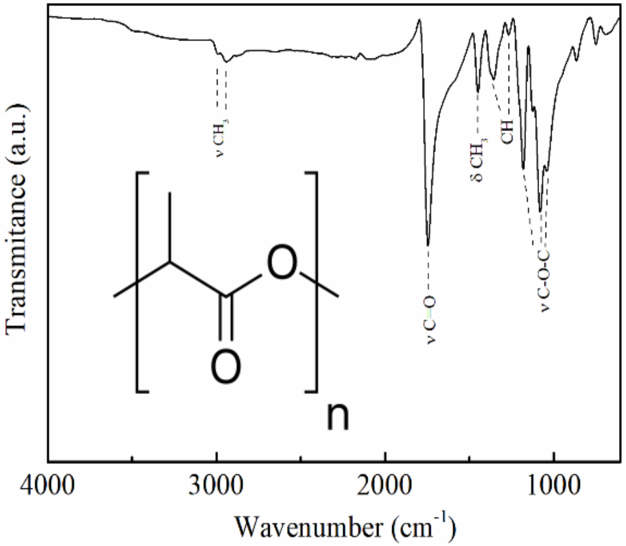
Electrochemical sensors: graphene-doped polylactic acid (PLA)

Mechanical polishing for 30 s (on sandpaper wet with deionized water)





SEM image of unpolished and polished 3D-printed surfaces



InfraRed spectroscopy

R.M. Cardoso, et al., submitted.

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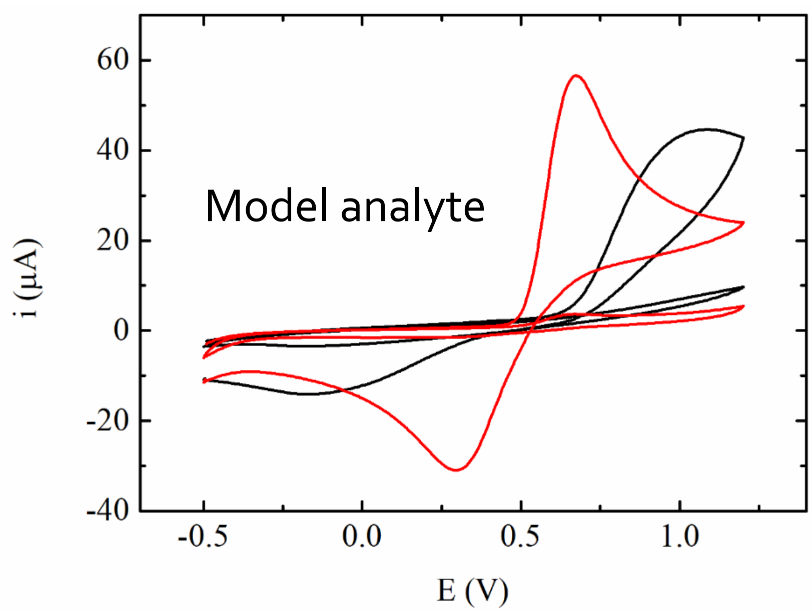
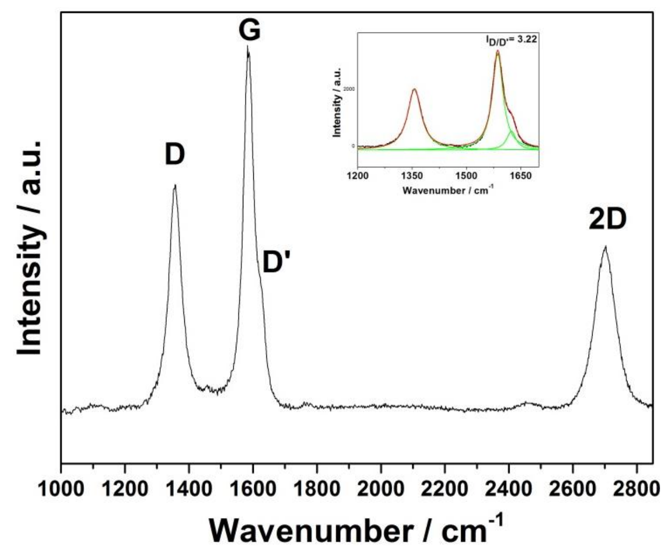
Part 2: 3D printing technology for electroanalysis: Electrochemical sensors

Electrochemical sensors: graphene-doped polylactic acid (PLA)

Mechanical polishing for 30 s (on sandpaper wet with deionized water)



CV of 1 mmol L^{-1} catechol on unpolished (black) and polished (red) 3D-printed surfaces and respective blanks



Raman spectroscopy (I_D/I_G) shows higher density of defects indicative of higher electron transfer)

R.M. Cardoso, et al., submitted.

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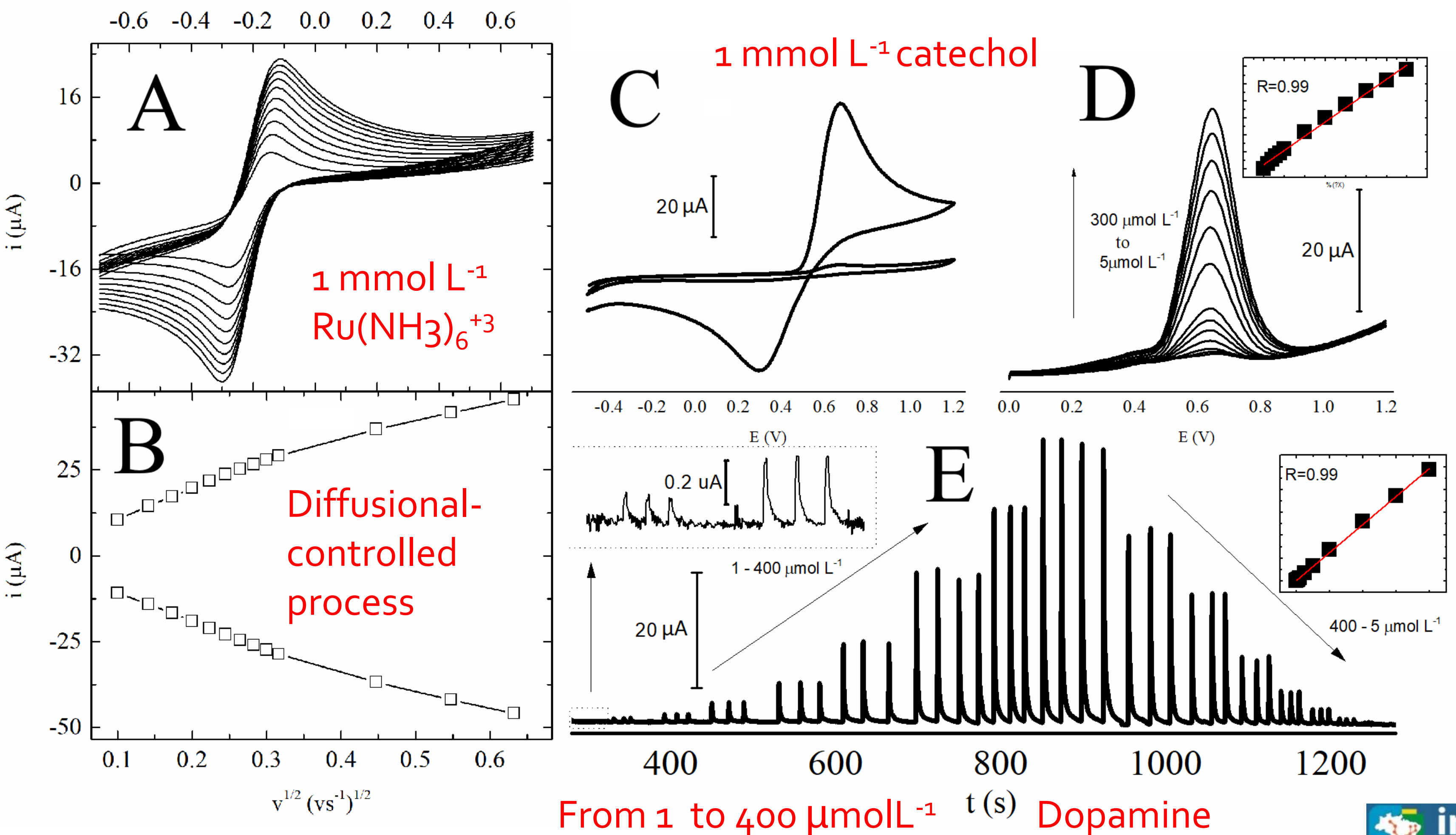
Part 2: 3D printing technology for electroanalysis: Electrochemical sensors

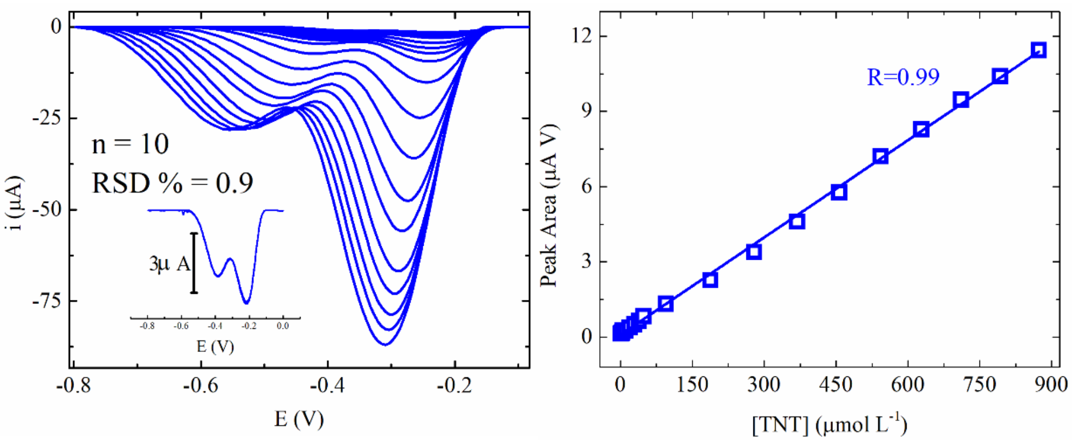
Electrochemical sensors: graphene-doped polylactic acid (PLA)

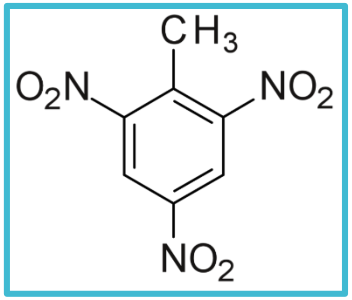


Part 3: 3D printing technology for electroanalysis: Sensors for forensics

Electrochemical sensors: graphene-doped polylactic acid (PLA)

TNT detection by fast square-wave voltammetry (SWV)





2,4,6-trinitrotoluene (TNT)

collaboration with Federal Police

(A) Curve: 1 – 870 µmol L^{-1} ; (B) Repeatability: 10 scans of 100 µmol L^{-1}

Conditions: Step: 6 mV; Amplitude: 40 mV; Frequency: 40 Hz;

Electrolyte: 0.1 mol L^{-1} HCl.

R.M. Cardoso, et al., submitted.

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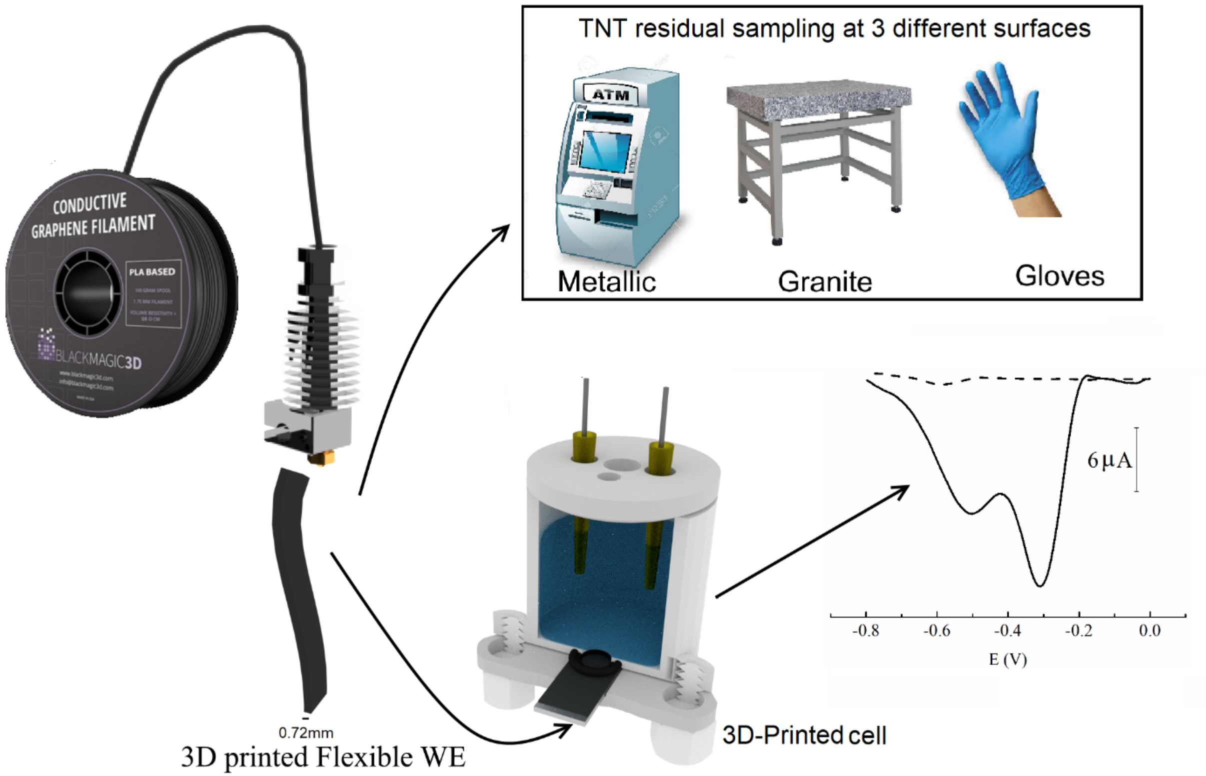
Part 3: 3D printing technology for electroanalysis: Sensors for forensics

Electrochemical sensors: graphene-doped polylactic acid (PLA)

Integrated device for sensing and detection of TNT (**Flexible !**)



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Part 3: 3D printing technology for electroanalysis: Sensors for forensics

Electrochemical sensors: graphene-doped polylactic acid (PLA)

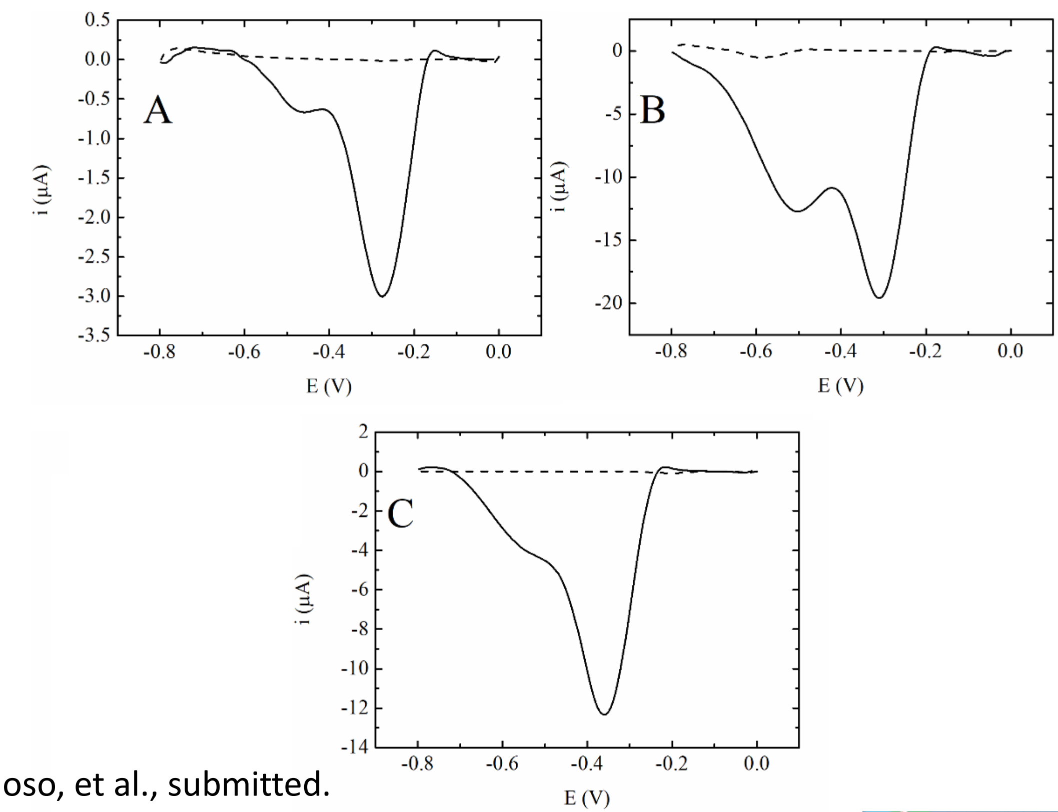
Integrated device for sensing and detection of TNT (**Flexible !**)

Quantification of TNT based on the calculated charge of SWVs

(A) Granite (3.2 ng);
(B) Metallic (20 ng);
(C) Gloves (15 ng).

Conditions: Step: 6 mV; Amplitude: 40 mV; Frequency: 40 Hz;

Electrolyte: 0.1 mol L^{-1} HCl.

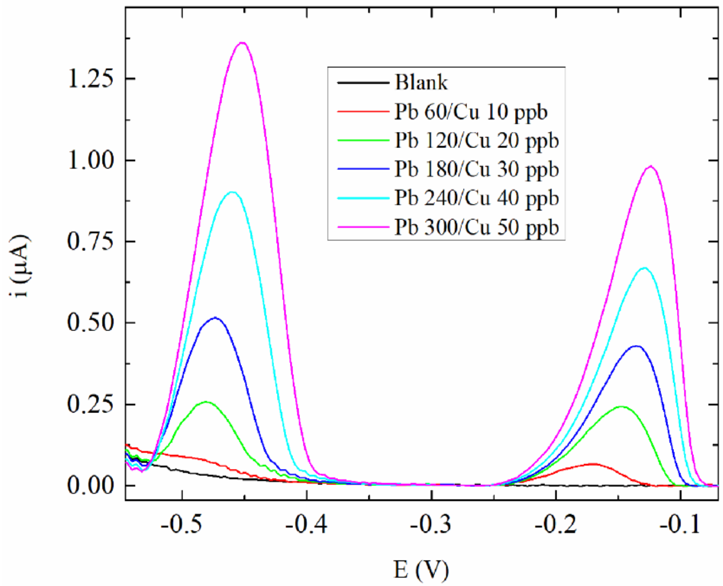


R.M. Cardoso, et al., submitted.

Part 3: 3D printing technology for electroanalysis: Sensors for forensics

Electrochemical sensors: graphene-doped polylactic acid (PLA)

SWASV: Pb and Cu (Gunshot residues ??) etc.

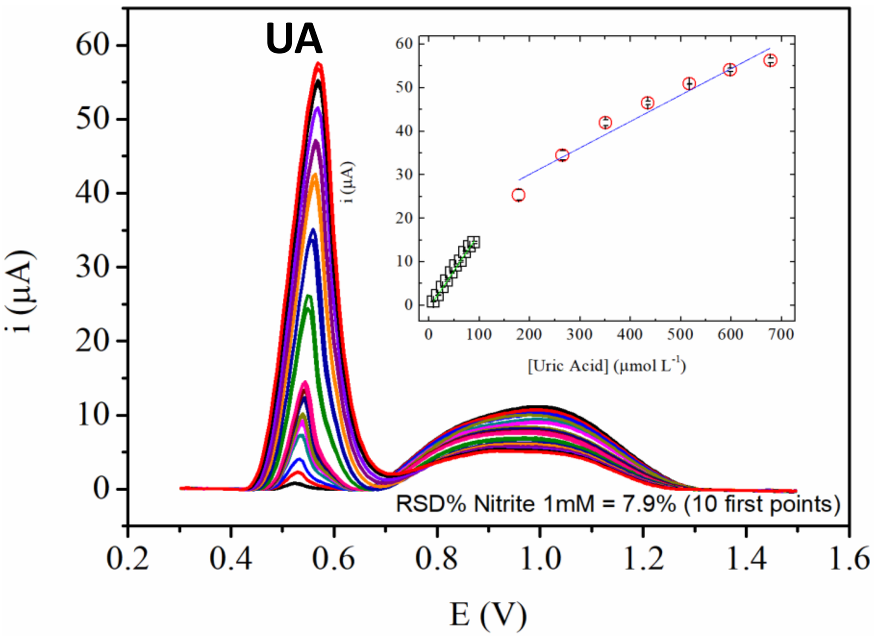


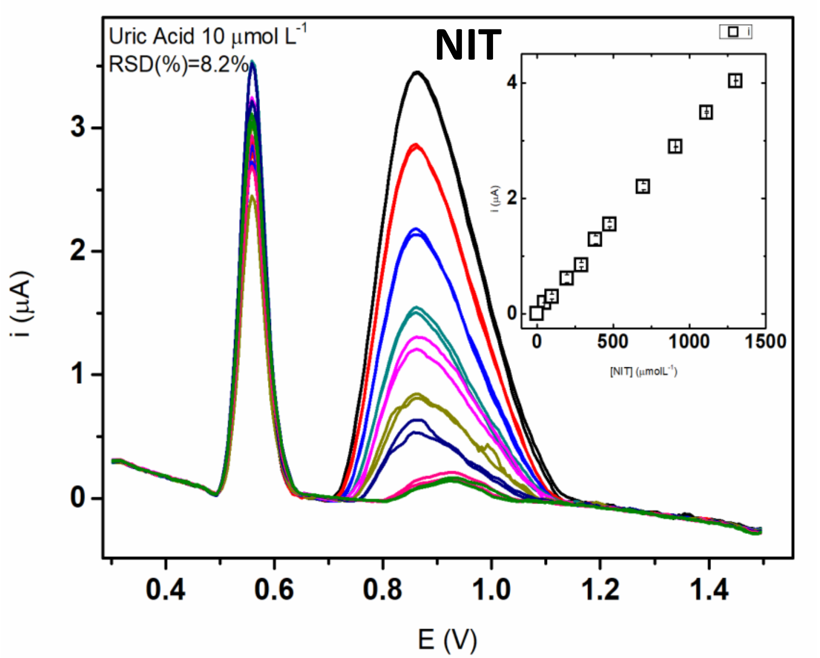
Metals	Slope µA L µg^{-1}	Linear range µg L^{-1}	R	LOD µg L^{-1}
Pb(II)	0.00037	60-300	0.987	36.2
Cu(II)	0.00153	10-60	0.995	8.8

Electrolyte: 0.1 mol L^{-1} HCl
Edep: -0.30 V; tdep: 90 s
Step: 4mV; Amplitude: 40mV; Frequency: 10 Hz

Part 4: 3D printing technology for electroanalysis: Sensors for clinical analysis

Nitrite (NIT) and Uric Acid (UA) are involved in various physiological processes. **Differential-pulse voltammetry (DPV):**





AU: 10 – 90 µmol L^{-1} (NIT=1 mmol L^{-1}) **NIT: 50 – 1300 µmol L^{-1}** (UA = 10 µmol L^{-1})

R^2 = 0.998 (UA) RSD (%) = 7.9 (NIT) R^2 = 0.998 (NIT) RSD (%) = 8.2 (UA)

0.1 mol L^{-1} BR buffer (pH 2); Step: 5mV; Ampl.: 100mV; Modulation time: 20 ms

Part 4: 3D printing technology for electroanalysis: Sensors for clinical analysis

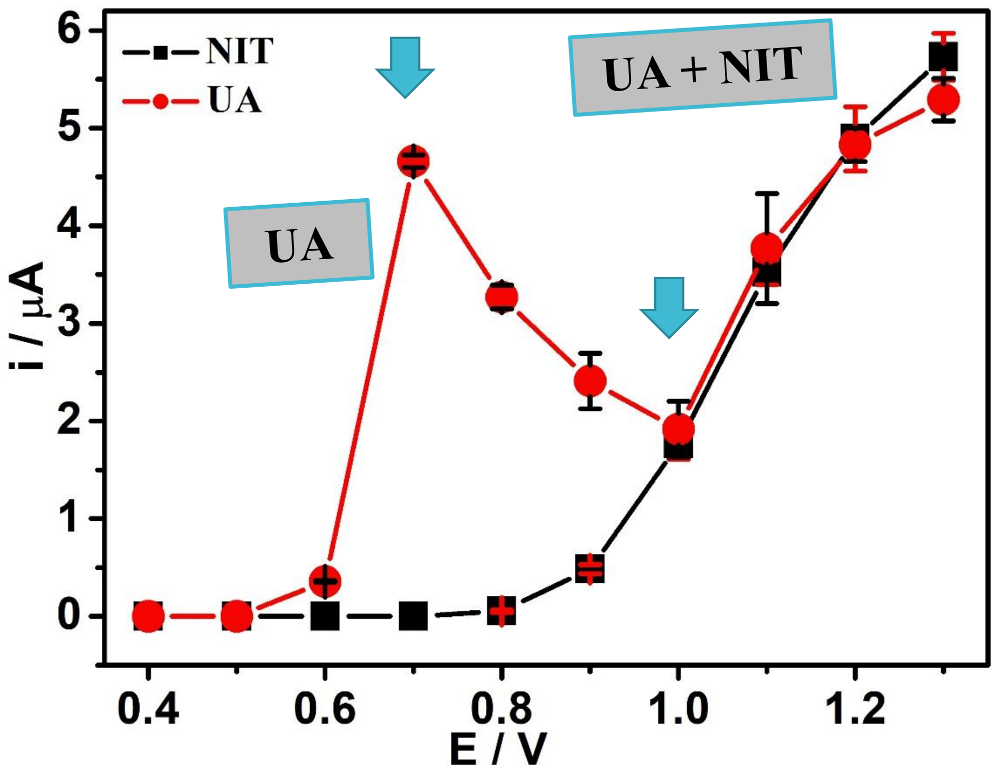
Nitrite (NIT) and Uric Acid (UA) are involved in various physiological processes.

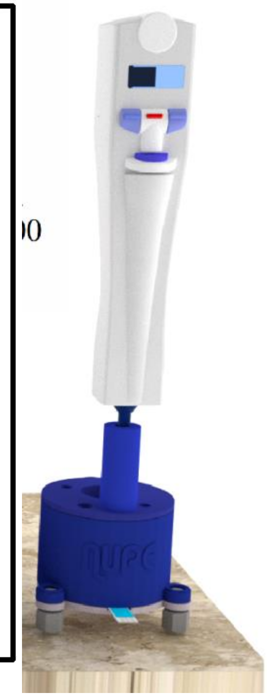
Amperometric detection:

FIRST STUDY: SELECTION OF APPLIED POTENTIALS
HYDRODYNAMIC VOLTAMMETRY

AMPEROMETRIC RECORDINGS FOR TRIPLICATE INJECTIONS AT DIFFERENT POTENTIALS

MULTIPLE (DUAL) PULSE AMPEROMETRY





100 μmol L^{-1} UA or NIT
0.1 mol L^{-1} BR buffer (pH 2)
Injection rate: 277 $\mu L s^{-1}$
injection volume: 100 μL

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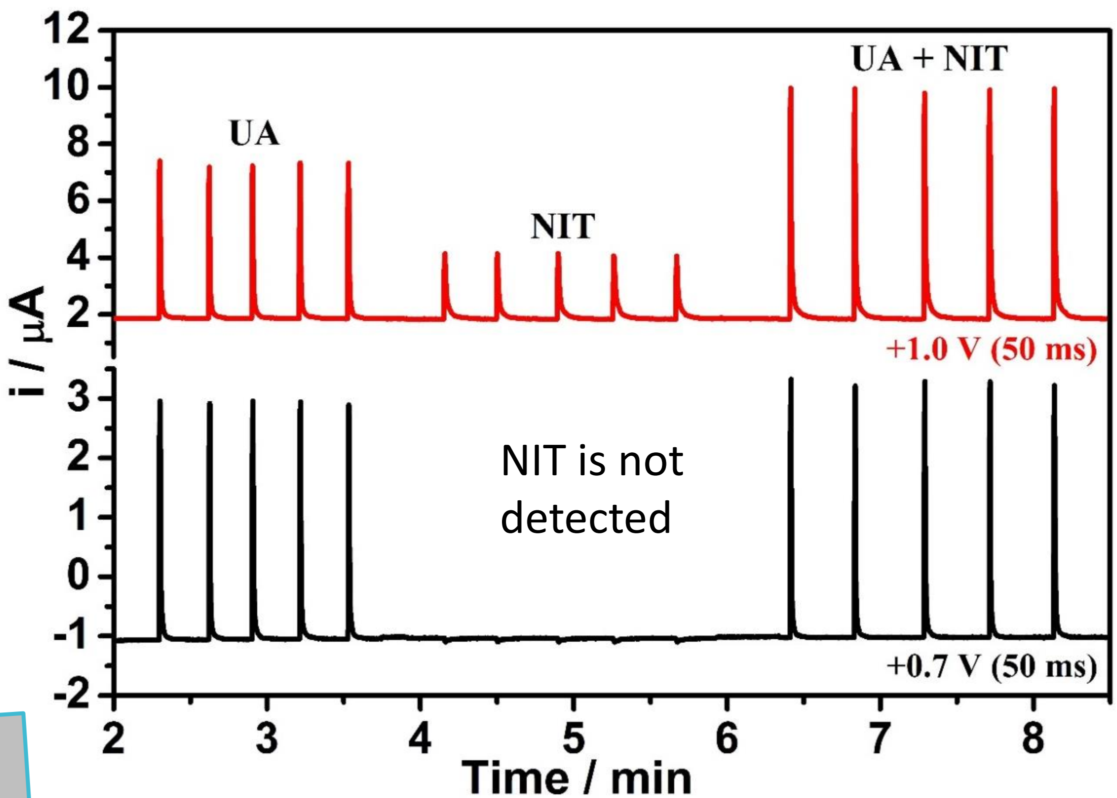
Part 4: 3D printing technology for electroanalysis: Sensors for clinical analysis

MULTIPLE PULSE AMPEROMETRIC DETECTION

SELECTIVITY IS VERIFIED – NO INTERFERENCE FROM NIT ON AU DETECTION

E_2 = 1.00 V
E_1 = 0.70 V
50 ms (each)

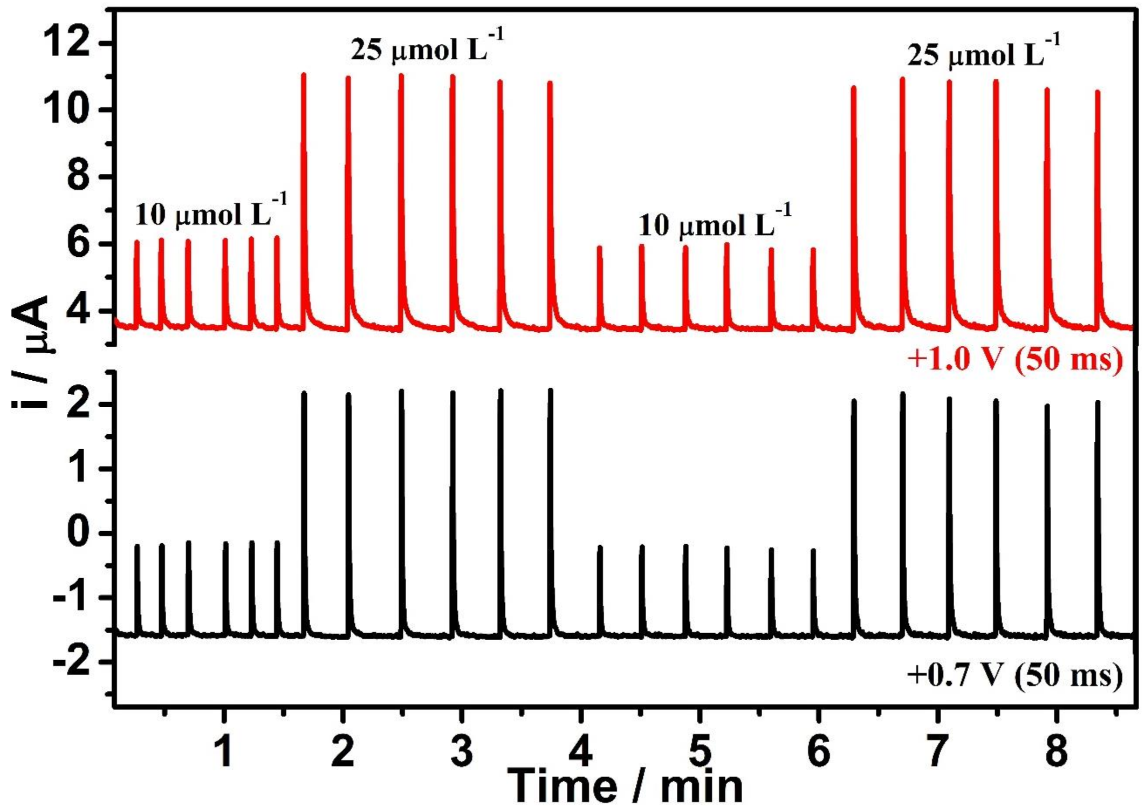


[UA] = 20 µmol L^{-1}
[NIT] = 20 µmol L^{-1}

Part 4: 3D printing technology for electroanalysis: Sensors for clinical analysis

MULTIPLE PULSE AMPEROMETRIC DETECTION

REPEATABILITY CONFIRMED – LOW RSD VALUES FOR CONTINUOUS INJECTIONS



RSD (%) < 4.0 (10 μmol L^{-1}) / RSD (%) < 2.6 (25 μmol L^{-1})

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Part 4: 3D printing technology for electroanalysis: Sensors for clinical analysis

Linear range :

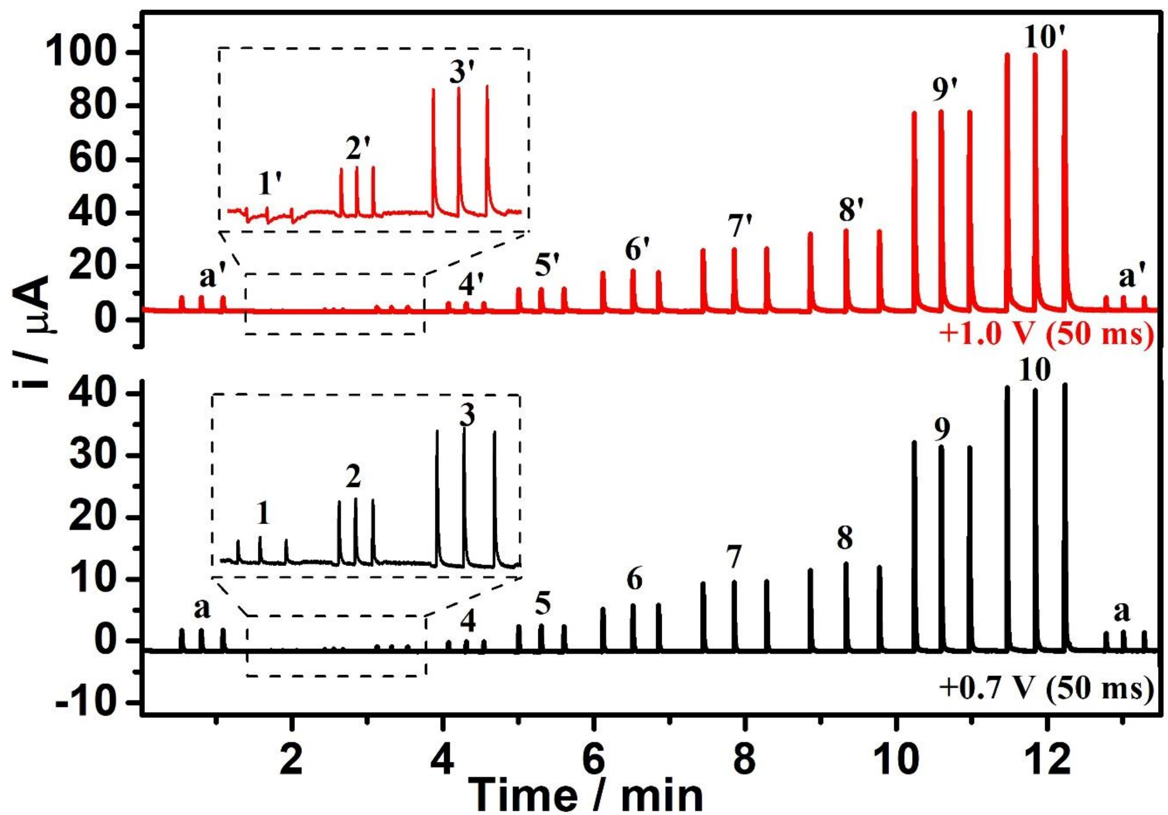
0.5 to 250 µmol L^{-1}

0.70 V: R = 0.999

1.00 V: R = 0.999

$$CF = \frac{i_{UA}\,(1.00\ V)}{i_{UA}\,(0.70\ V)}$$

$CF_{average}$ = 1.5



$$i_{NIT} = i_{(1.00\ V)} - (\, CF_{aver} \times i_{0.70\ V} \,)$$

Part 4: 3D printing technology for electroanalysis: Sensors for clinical analysis

- The results indicate that the **BIA method with MPA detection** enabled the simultaneous detection of uric acid and nitrite;
- 3D-printed graphene-PLA sensor responds similarly to a conventional carbon electrodes;
- Future work: application to biological fluids (urine, saliva, and plasma samples)

PERSPECTIVES / COLLABORATIONS

- 3D-priting of the complete electrochemical sensor;
- Modification of the filaments with chemical modifiers to fabricate improved sensors in large-scale production;
- Incorporation of biomolecules to obtain biosensors;
- Association with miniaturized separation techniques.

Acknowledgements

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Thiago Paixão (USP) **Wendell Coltro (UFG)**
Craig Banks (Manchester Metrop.Univ, UK)
Carlos Garcia (Clemson Univ, USA)

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Conselho Nacional de Desenvolvimento Científico e Tecnológico

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Rodrigo A. A. Muñoz - munoz@ufu.br

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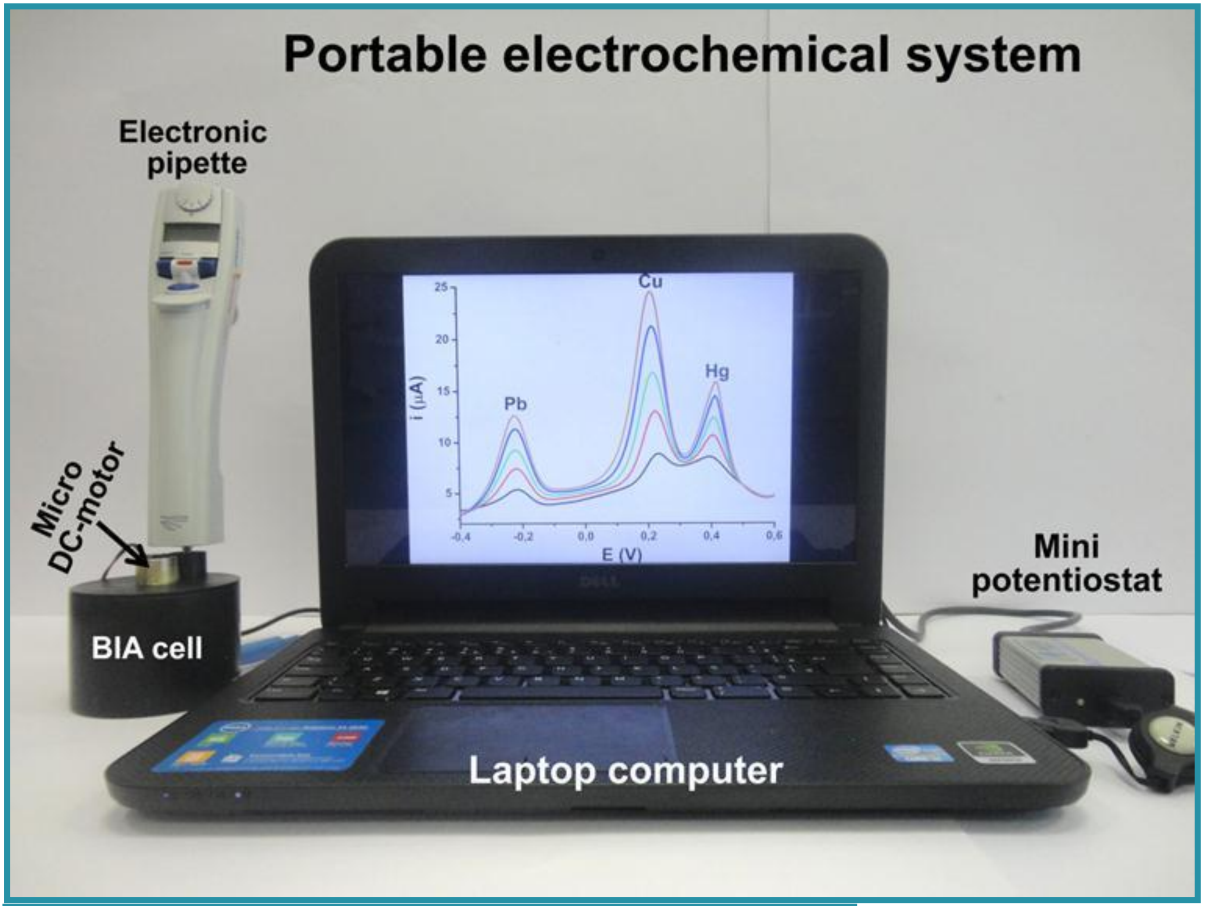
Portable and low-cost analytical system



Combination of screen-printed electrodes and batch injection analysis: A simple, robust, high-throughput, and portable electrochemical system

Sensors and Actuators B 202 (2014) 93–98

BIA – SPE cell

Dropsens

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Part 4: 3D printing technology for electroanalysis: Sensors for clinical analysis

Multiple-pulse amperometry (MPA): e.g. electrochemistry of RNO2