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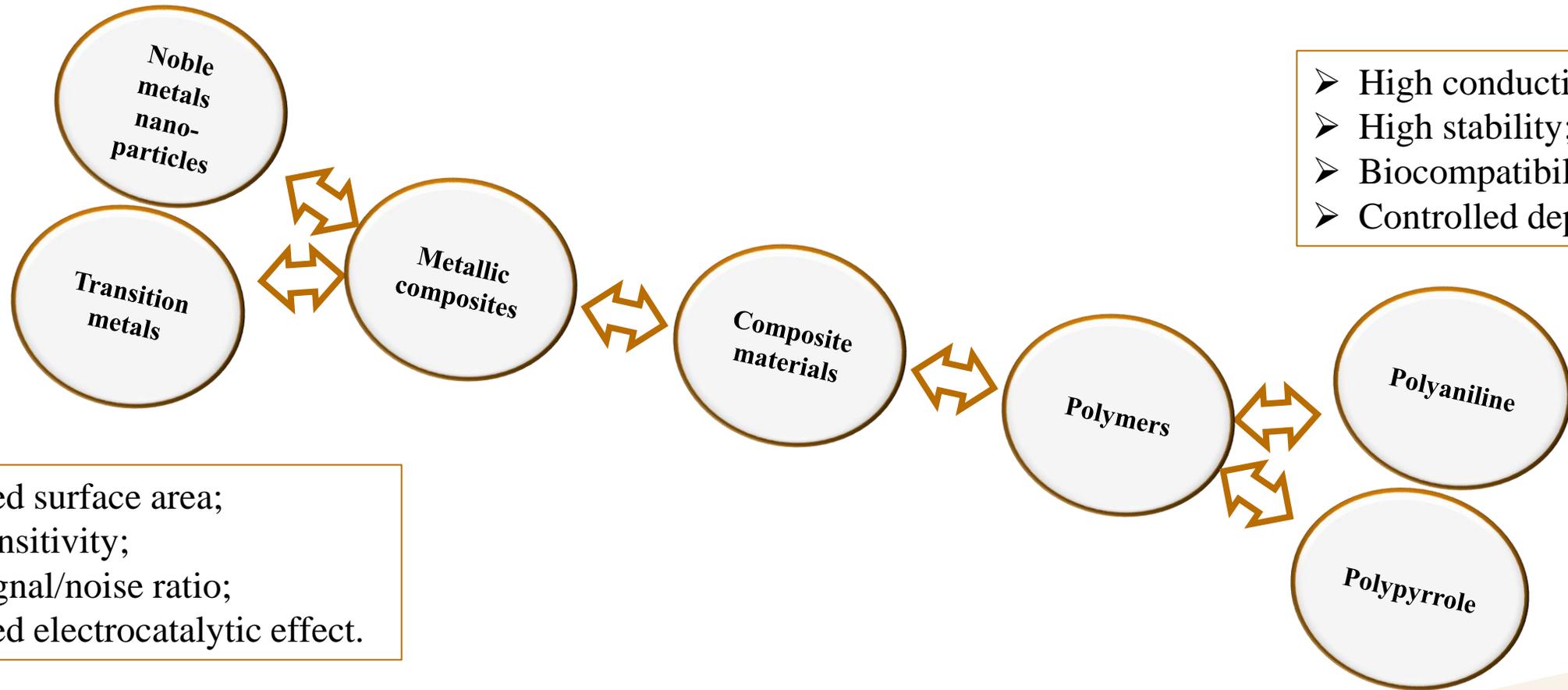
Nanocomposite-based electrochemical platforms for pharmaceutical and environmental applications

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Introduction



- Increased surface area;
- High sensitivity;
- High signal/noise ratio;
- Increased electrocatalytic effect.

- High conductivity;
- High stability;
- Biocompatibility;
- Controlled deposition.

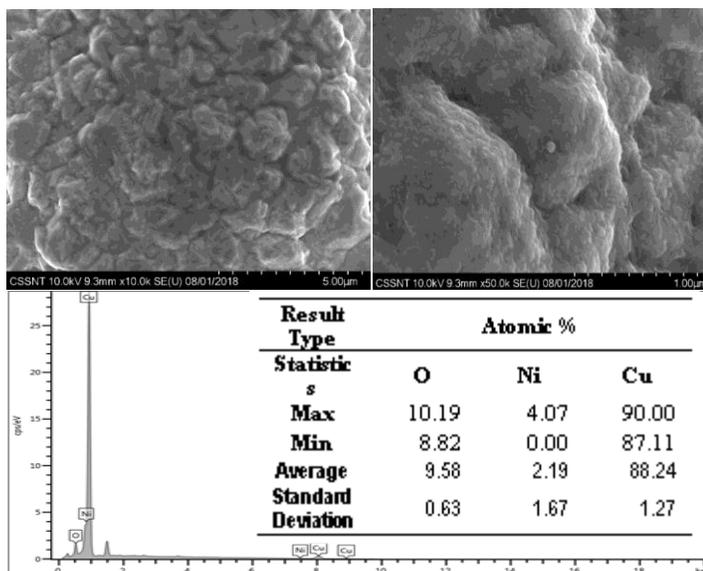
❖ Preparation and characterization of 3D Cu nanoporous electrodes

Preparation

Coating system	Electrolyte composition	Operating conditions
Cu/Ni _f (denoted Cu/Ni _f)	(i) 0.1 M NiCl ₂ *6H ₂ O + 2M NH ₄ Cl	pH = 4-4.5 T = 25°C i = 1 A cm ⁻² time = 3 min.
	(ii) 0.8 M CuSO ₄ *5H ₂ O + 0.6 M H ₂ SO ₄	T = 25-30°C i = 28-35 mA cm ⁻² time = 15-20 min.

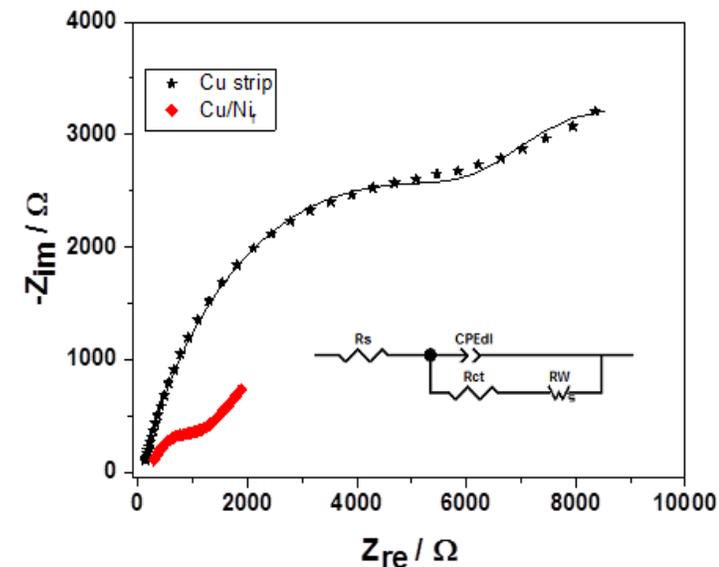
Electrolytes composition and operating conditions for electrochemical preparation of the 3D Cu nanoporous electrodes

Surface characterisation



SEM images at different magnifications (X10000, X50000 and corresponding EDX analysis of Cu electrodeposited onto Ni_f at 35 mA cm⁻² for 15 min

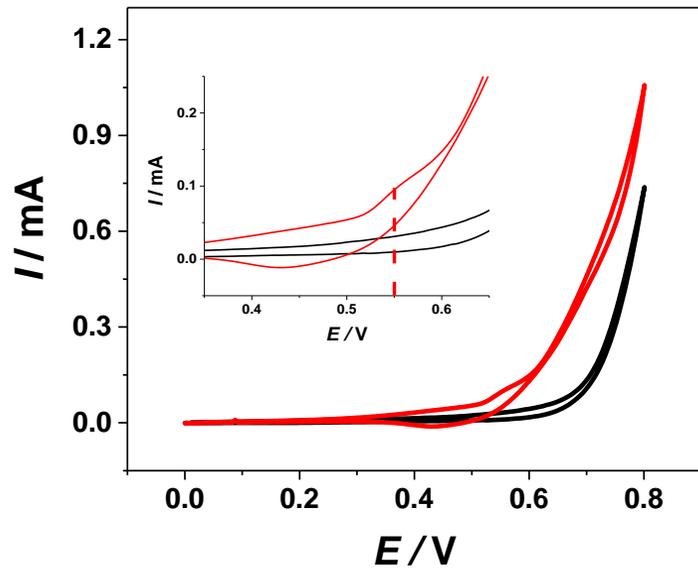
Electrochemical characterisation



EIS data recorded in 5 mM [Fe(CN)₆]^{3-/4-} in 0.1 M KCl solution for Cu strip and Cu/Ni_f electrodes as Nyquist plots (inset: the proposed equivalent circuit to fit the measured points)

❖ Glucose detection

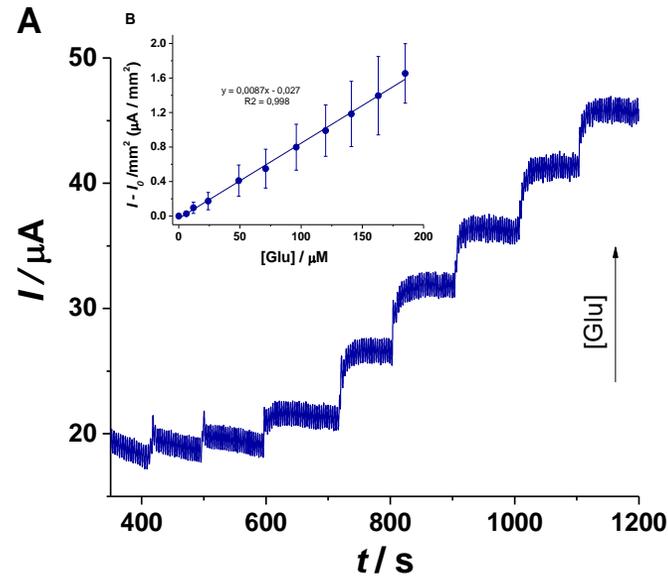
Peak potential identification



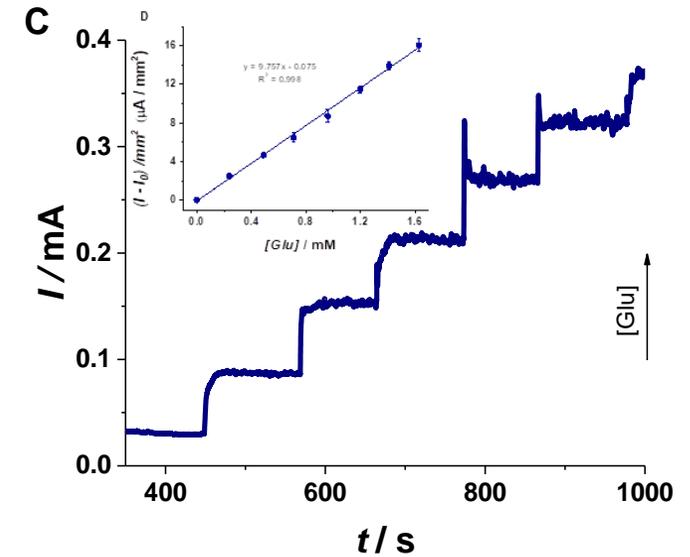
CVs of the Cu/Ni_f working electrode:

- in the absence of 0.225 mM Glu
- and in the presence of 0.225 mM Glu in 0.1 M NaOH (10 mV/s)

Calibration curves



- A. CA of CuNi_f electrodes in 0.1M NaOH with standard additions of 2.5 mM of Glu, under continuous stirring at 500 rpm (0.55 V, 0.1 s step potential);
- B. The calibration curve in the range of 6 - 185 μM Glu



- C. CA of CuNi_f electrodes in 0.1M NaOH with standard additions of 25 mM Glu, under continuous stirring at 500 rpm (0.55 V, 0.1 s step potential);
- D. The calibration curve in the range of 0.24 - 1.63 mM Glu.

LR

6 - 185 μM
0.24 - 1.63 mM

LOD

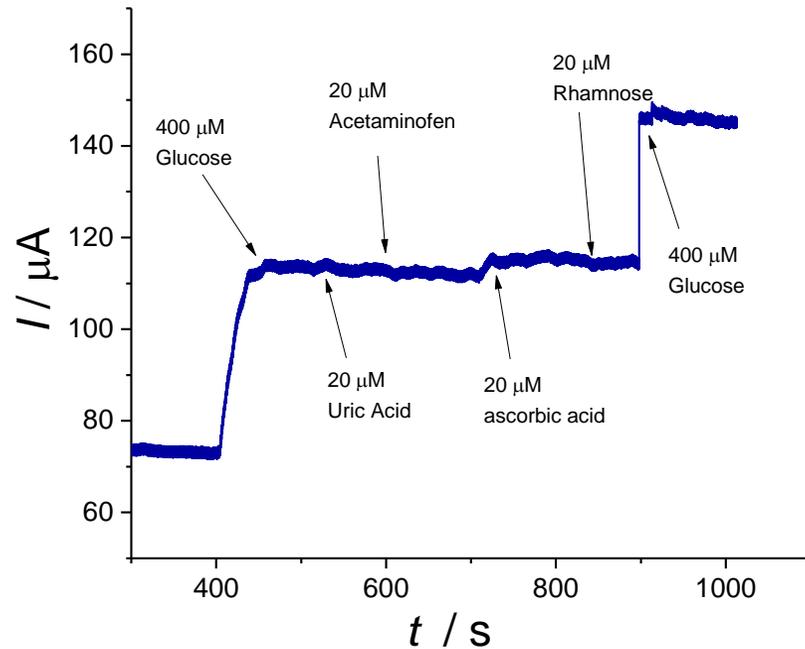
2 μM

LOQ

6 μM

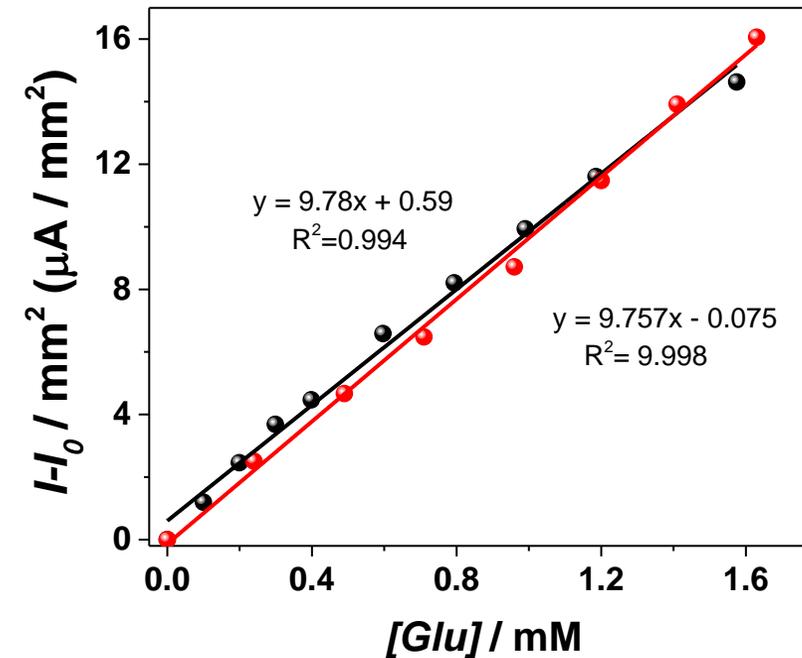
❖ Interference studies and applications

Interferences



CA in 0.1 M NaOH with standard additions every 100 s of 400 μM Glu, 20 μM UA, P, AA, R and 400 μM Glu ($E_p = +0.55$ V, 1100 s) for the Cu/Ni_f electrode

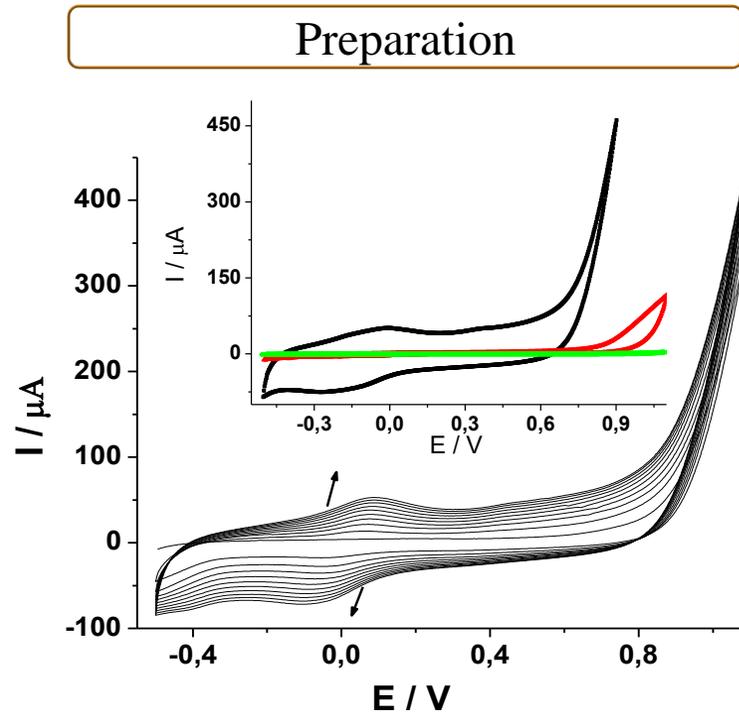
Serum analysis



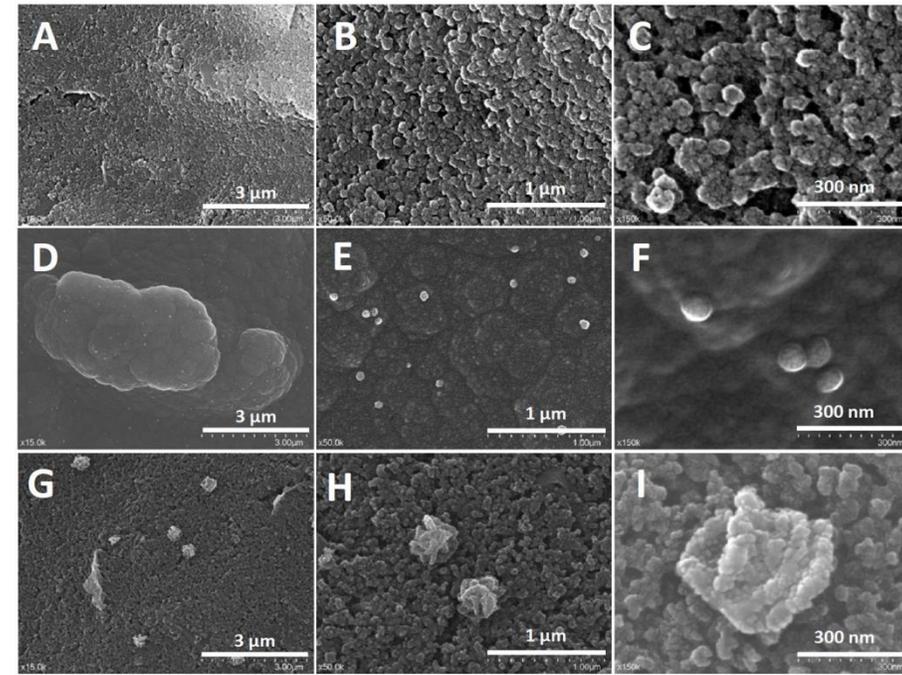
Calibration curve for the Cu/Ni_f on Cu electrode in the range of 0.24 - 1.63 mM Glu

- on standard solutions
- on commercial human serum spiked with 0.1 M Glu

❖ Preparation and characterization of polypyrrole modified electrodes



Surface characterisation



Electrochemical deposition of 3-carboxylic PPy in 0.1 M LiClO₄ and 9 mg/ml PVP.

Inset: 10th cycle for the electrochemical polymerization of:

- 3-carboxylic Py with PVP in 0.1 M LiClO₄,
- 0.1 M LiClO₄ in the absence of the monomer and PVP
- 0.1 M LiClO₄ with 9 mg/ml PVP in the absence of Py

SEM images performed on the carbon-based working surface at different magnifications (x15K, x50K, x150K):

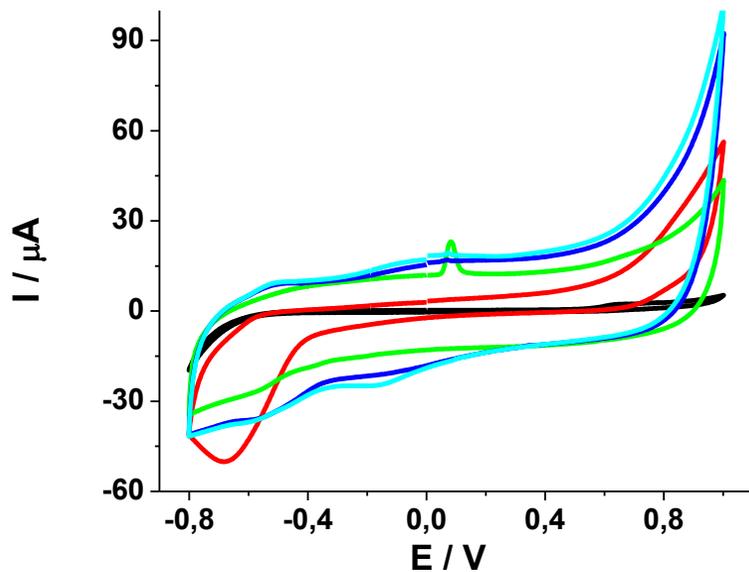
(A, B, C) unmodified graphite-based electrode

(D, E, F) 3-carboxylic pyrrole (0.05 M) in 0.1 M LiClO₄ with 9 mg/ml PVP,

(G, H, I) 3-carboxylic pyrrole (0.25 M) in 0.1 M LiClO₄ with 9 mg/ml PVP

❖ Folic Acid detection

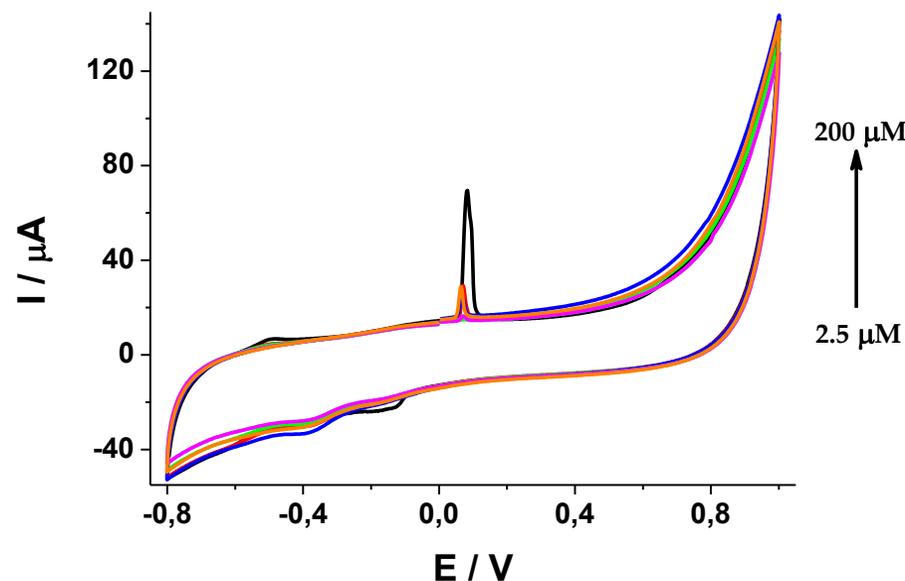
FA on different platforms



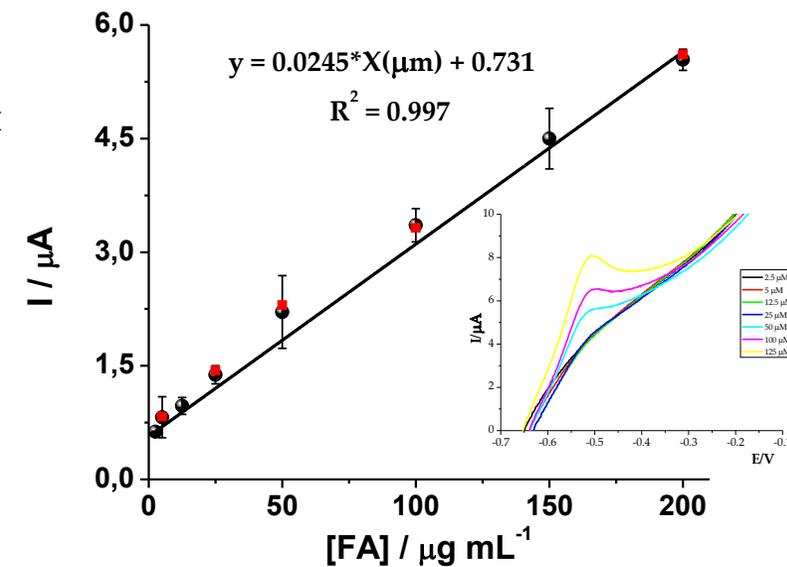
CVs in 100 μM FA:

- on the unmodified electrode;
- **3-carboxylic Py in 0.1 M LiClO₄ in the absence of PVP;**
- **0.1 M LiClO₄ and PVP in the absence of Py;**
- **3-carboxylic Py in 0.1 M LiClO₄ and PVP;**
- **3-carboxylic Py in 0.1 M LiClO₄ and PVP kept 5 minutes under nitrogen prior the analysis**

Calibration curve



CVs for FA standard solutions in 20 mM PBS pH 7.4 (2.5 μM, 5 μM, 12.5 μM, 25 μM, 50 μM, 100 μM, 150 μM) on the modified surface.



Calibration curve for different concentrations of FA in PBS pH 7.4;

FA standard solutions in 1:100 commercial human serum in 20 mM PBS pH 7.4 (5 μM, 25 μM, 50 μM, 100 μM, 200 μM);

Inset: magnification of the anodic peak at -0.5 V/Ag.

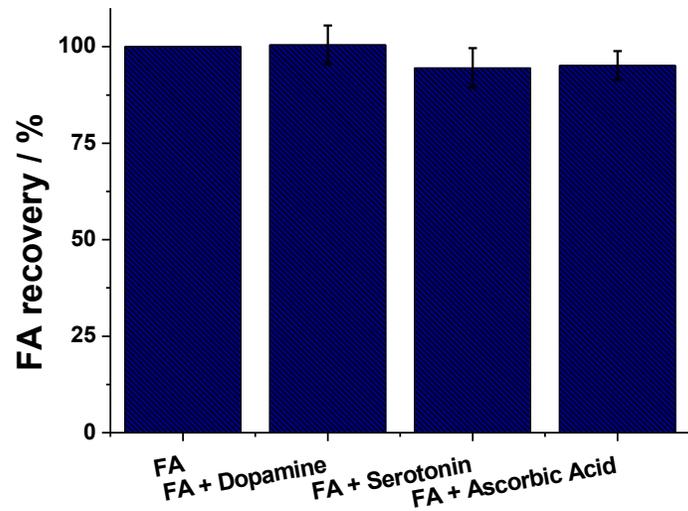
LR 2.5 – 200 μM

LOQ 2.5 μM

LOD 0.8 μM

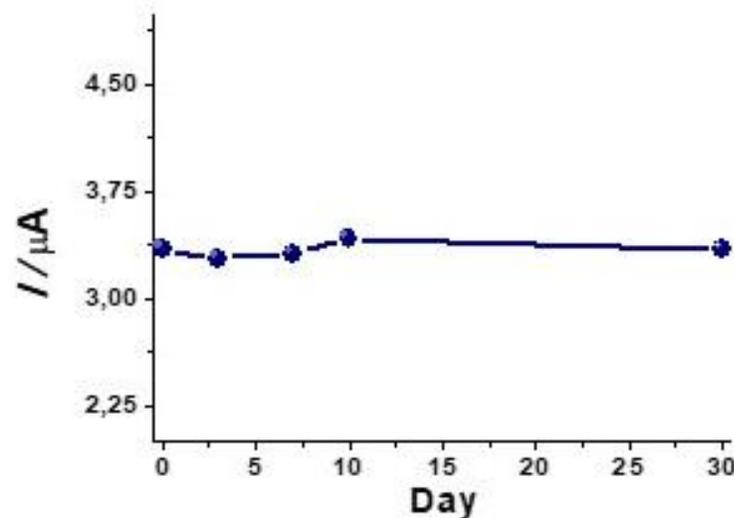
❖ Interference studies and applications

Interferences



Recoveries for the current intensity (μA) of the anodic peak correlated with the electrochemical oxidation of 5, 8-dihydrofolic acid in the presence of 100 μM FA and of 25 μM interfering agents: dopamine, serotonin and ascorbic acid

Stability



Current intensity (μA) of the anodic peak correlated with the electrochemical oxidation of 5, 8-dihydrofolic acid after 1, 3, 7, 10 and 30 days in the presence of 100 μM FA;

Real samples

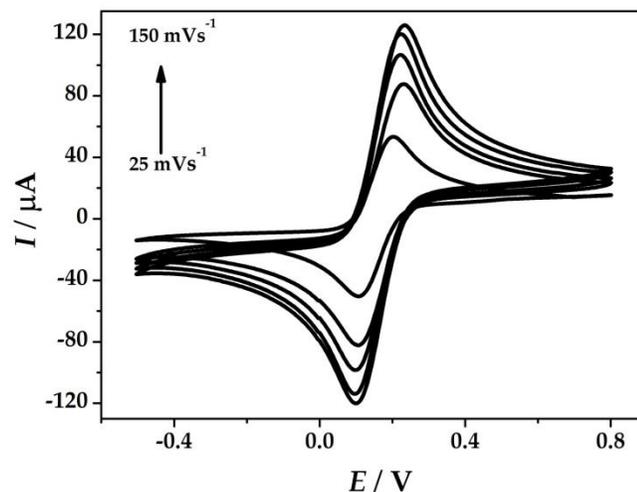
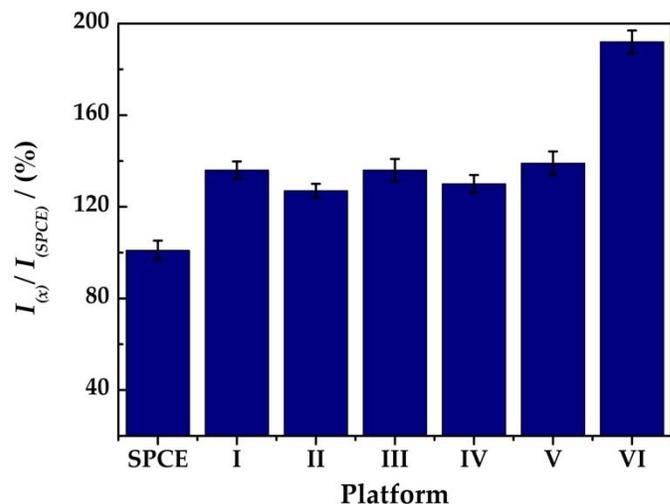
Commercial serum spiked with FA				
	[FA] (μM)	Recovery (%)		
		Current intensity	Calculated [FA]	
	25	104.1%	115%	
	50	104.07%	128%	
	100	98.96%	105.67%	
Pharmaceutical tablets (5 mg)				
Extraction solvent	[FA] (μM)	Recovery (%)		Amount of FA in tablets
		Current intensity	Calculated [FA]	
Deionized water	25	96.37%	97.79%	96%
	25	96.37%	97.79%	96%
	50	88.23%	99.5%	101.94%
20 mM PBS pH 7.4	100	98.36%	104.44%	102.42%

❖ Platforms development

Platform design		Experimental conditions	
		Solution concentration	Electrodeposition parameters
(I)	AuNPs/SPCE	2 mM HAuCl ₄ in 0.5 M H ₂ SO ₄	– 0.20V for 130 s
(II)	PtNPs ⁱ /SPCE	4 μM H ₂ PtCl ₆ in 0.5 M H ₂ SO ₄	– 0.20V for 130 s
(III)	PtNPs ⁱⁱ /SPCE	1 mM H ₂ PtCl ₆ in 0.5 M H ₂ SO ₄	– 0.20V for 130 s
(IV)	Au-PtNPs/SPCE	Mixture of 2 mM HAuCl ₄ and 4 μM H ₂ PtCl ₆ in 0.5 M H ₂ SO ₄	– 0.20 V for 130 s
(V)	PANI/SPCE	2.5 mM C ₆ H ₅ NH ₂ in 50 mM HClO ₄ ;	CV: -0.40– 0.80 V vs Ag/AgCl, 10 scans, 50 mV s ⁻¹ at SPCE
(VI)	Au-PtNPs/PANI/SPCE	2.5 mM C ₆ H ₅ NH ₂ in 50 mM HClO ₄ ; Mixture of 2 mM HAuCl ₄ and 4 μM H ₂ PtCl ₆ in 0.5 M H ₂ SO ₄	CV: -0.40– 0.80 V vs Ag/AgCl, 10 scans, 50 mV s ⁻¹ at SPCE – 0.20 V for 130 s at PANI/SPCE

❖ Platforms characterisation

Electroactive area



Electroactive surface area % versus geometric area of a bare SPCE compared to SPCE modified with:

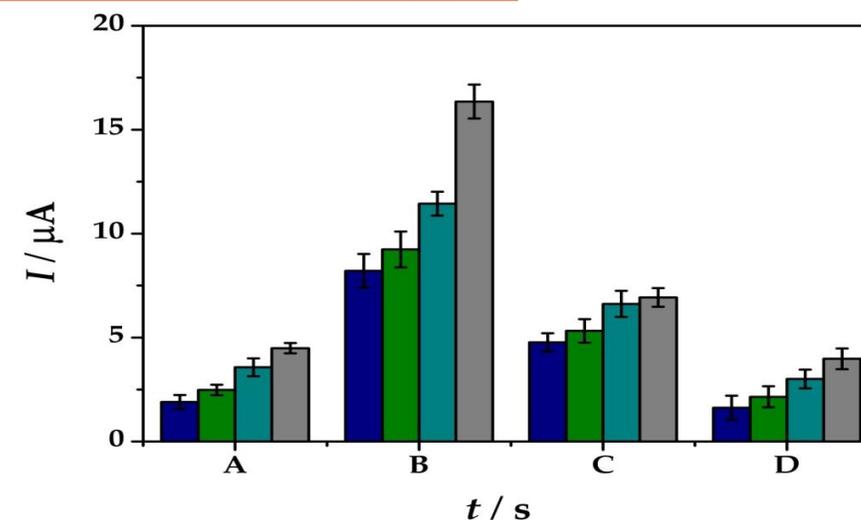
- (I) AuNPs,
- (II) PtNPsⁱ,
- (III) PtNPsⁱⁱ,
- (IV) Au-PtNPs,
- (V) PANI,
- (VI) Au-PtNPs/PANI

CVs in 5 mM $[Fe(CN)_6]^{4-/3-}$ in 0.1 M KCl solution at (IV)Au-PtNPs/SPCE at rates 25–150 mV s⁻¹

- Tested electrolytes:
- 6M LiClO₄ in 0.5M H₂SO₄
- 0.1M KCl in 0.1M HCl
- 0.1M HCl

Optimised parameters:

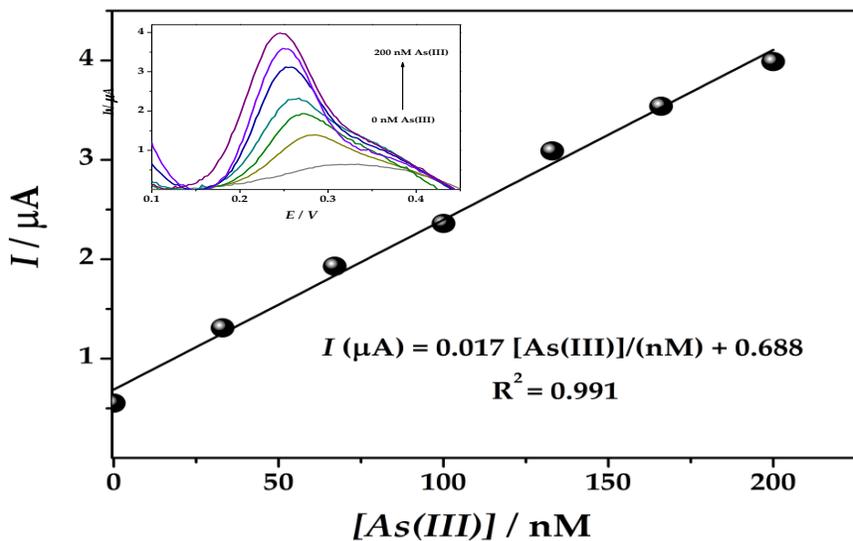
- Deposition time : 60s, 120s, 180s, 240s
- Deposition potential: -0.35V; -0.5V



Peak current intensities obtained by means of SWASV measurements at platform IV from solutions containing As(III) of 0.033 μM (blue), 0.067 μM (green), 0.133 μM (cyan), 0.2 μM (grey) in 0.1 M HCl by applying a cathodic pre-concentration time (t_{dep}) of 60 s (A), 120 s (B), 180 s (C), 240 s (D) at $E_{dep} = -0.50$ V

❖ Detection and interference studies

Calibration curve



Calibration plot for As detection.

Inset: SWASV obtained at (IV) Au-PtNPs/SPCE platform ($E_{dep} = -0.5 \text{ V}$; $t_{dep} = 60 \text{ s}$) with As(III) solution concentrations of 33, 67, 100, 133, 166, 200 nM in 0.1 M HCl solution;

Sensors performances

- Platforms (IV) and (VI) were evaluated for arsenic detection in 0.1M HCl electrolyte;
- Platform (IV) Au-PtNPs/SPCE presented a linear range in the domain 33-200 nM with a sensitivity of $0.017 \mu\text{A nM}^{-1}$ and a LOD of 19.7 nM;
- Platform (VI) Au-PtNPs/PANI/SPCE presented a dose response curve in the range of 0.1 - 1.25mM As(III) with a sensitivity of $6.116 \mu\text{A mM}^{-1}$

Interferences

Metal	E / V	I / μA
As(III)	0.2	8.93
Cu(II)	0.26	0.96
Pb(II)	0.47	5.67
Hg(II)	0.25	1.87

SWASV signal for As(III), Cu(II), Pb(II), Hg(II) solution in 0.1 M HCl in the potential range from 0 to +0.6 V; $t_{dep} = 60\text{s}$, $E_{dep} = -0.50 \text{ V}$.

Conclusions

Nanomaterials have been extensively used in biosensors design to enhance their electrochemical performance in terms of sensitivity, reproducibility and oftentimes selectivity;

**Cu /
Ni_f**

Cu electrodes have been doped with Ni_{foam} in order to increase its catalytic activity and selectivity towards Glucose; the analyte was detected with a LOD of 2 μM;

PPy

3D polymeric 3-Carboxylic Pyrrole modified electrodes have been used for selective folic acid detection, with a LOD of 0.8 μM, and successfully applied in serum and commercial folic acid tablets samples;

**Au-
PtNP/
PANI**

Gold-platinum nanoparticles have been used to increase the catalytic effect of a Polyaniline platform and successfully applied for Arsenic detection obtaining 2 calibration curves, in the absence and presence of Polyaniline, with the minimum LOD of 19.7 nM.

THANK YOU FOR YOUR ATTENTION!



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