CARBON-BASED NANODOTS AS EFFECTIVE ELECTROCHEMICAL SENSING TOOLS TOWARDS THE SIMULTANEOUS DETECTION OF BIOACTIVES COMPOUNDS IN COMPLEX MATRIX

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INTRODUCTION

This work pretends to give a deep comparative insight about the electrochemical behavior of GQDs, CQDs and CNDs containing similar functionalized surface (oxygenated groups), but different crystallinity, core hybridization, morphology, and quantum confinement. As the first step, three families were synthesized following the top-down methodology and later thoroughly characterized both structural and electrochemically by means of well-known redox probes, surface sensitive in different degree to its chemistry and microstructure. The electroanalytical capabilities of these carbon nanodots-electrodes as sensing electrochemical modifiers are also evaluated versus a set of significant bioactive target analytes, namely vitamins (Vitamin B2, Vitamin B6 and Vitamin C) and amino acids (*L*-tyrosine). Primary interactions responsible for their shifts in peak potentials and their increase in peak currents were also elucidated. Finally, attending to its valuable electrochemical features, modified GQD-SPEs were selected to carry out the simultaneous detection of these bioactives in commercial nutritional supplements by differential pulse voltammetry (DPV). The present research tries to open new possibilities for the design and tailoring of sensing systems attending the specific chemistry of the sought analyte.

REFERENCES

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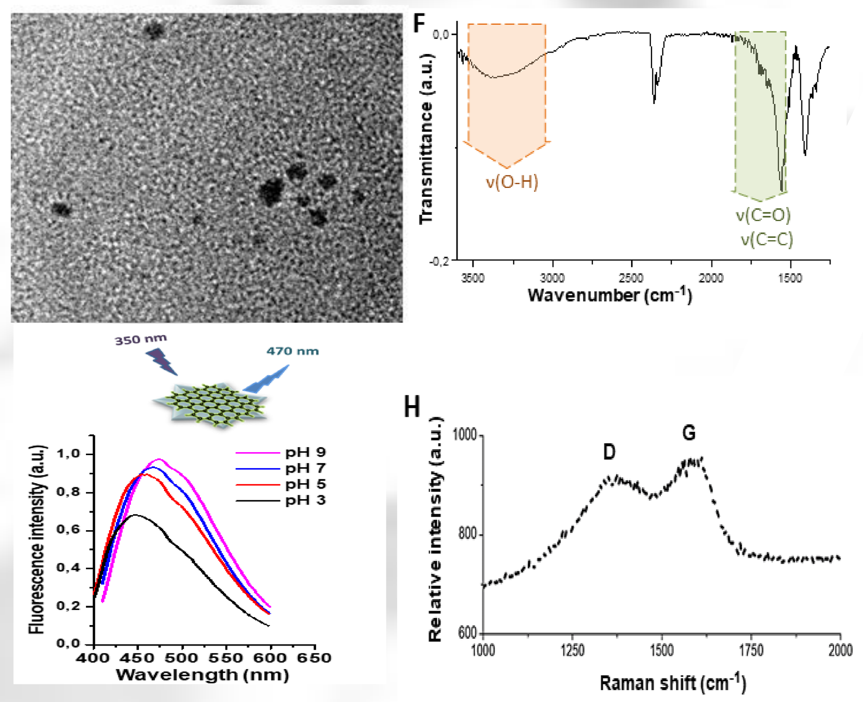
STRUCTURAL CHARACTERIZATION OF GQD



The size by TEM was 9 nm± 0.27. By FTIR, bands found at ca. 3500 and 1700 cm^{-1} are typically ascribed to the stretching vibrational modes of the hydroxyl (O-H) and carbonyl (C=O) bonds, which likely involve the presence of carboxyl groups. Raman profile is alike in appearance and characteristic of graphenic structures with their typical features including both G (≈1585 cm^{-1}, crystalline) and D (≈1380 cm^{-1}, disorder) modes, which confirmed the sp^2 hybrids carbons at basal planes and the symmetry breaking at edges and defects with existence of sp^3 carbons.

ELECTROCHEMICAL CHARACTERIZATION OF SENSOR

Probe	Electrode	ΔEp (mV)	$k^{0'}$ (cm/s)	A (cm^2)
$[Ru(NH_3)_6]^{3+}$	Bare	115	$1.68·10^{-3}$	0.110
	GQDs/ Nf	172	$5.33·10^{-4}$	0.089
$[Fe(CN)_6]^{3-}$	Bare	235	$1.11·10^{-3}$	0.135
	GQDs/ Nf	84	$3.80·10^{-3}$	0.021
Dopamine	Bare	518	$1.60·10^{-4}$	0.010
	GQDs/ Nf	389	$6.85·10^{-4}$	0.019

ELECTROANALYTICAL PERFORMANCE CHARACTERISTICS

Firstly, precision of GQD-Nf electrode was evaluated by means of repeatability and reproducibility studies of both current and potential peak values for the electrochemical sensing of riboflavin and tyrosine as target analytes. These results evidenced the good precision of the electrode considering a potential manufacturing process (batch-to-batch evaluation).

	Riboflavin		Tyrosine	
	Current	Potential	Current	Potential
Repeatability (n = 9)	2.8	1.3	8.8	0.4
Reproducibility (n = 4)	0.9	0.7	3.3	1.0

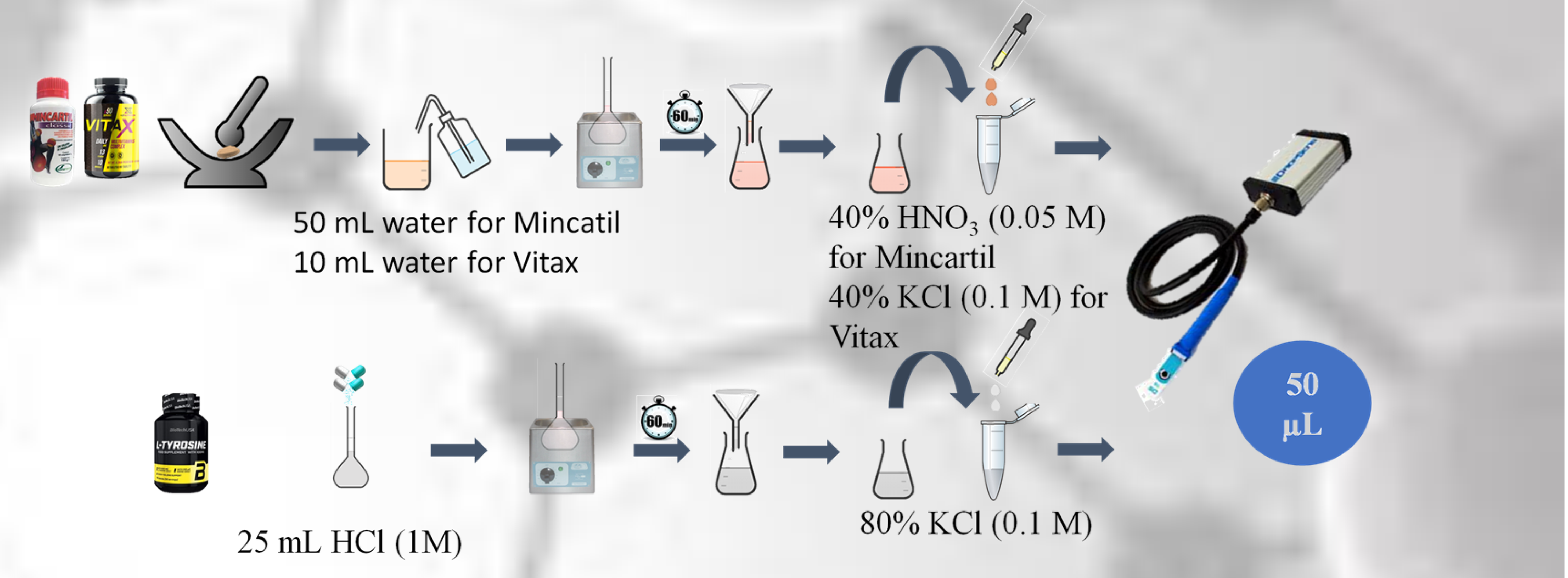
The linear behavior was checked for the electrochemical sensing of riboflavin, ascorbic acid, and tyrosine in KCl 0.1 M using the GQD-Nf screen printed electrode, achieving the following results:

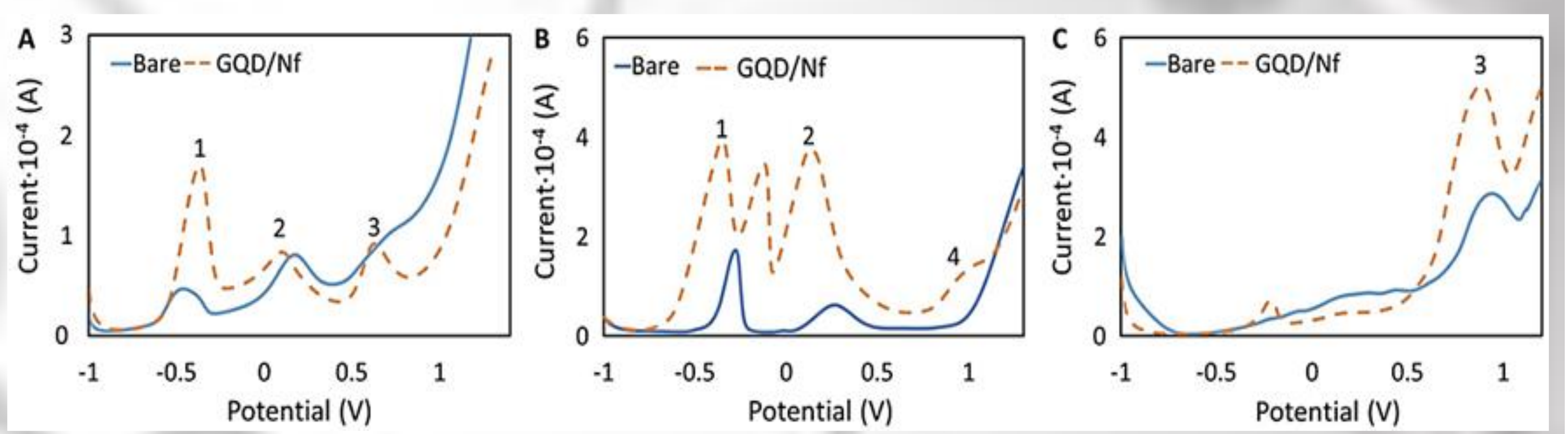
Analyte	Linear fit	r^2	LOD	LOQ
Riboflavin	$I_p = [1.94·10^{-5} \pm 4.47·10^{6}]+[3.96·10^{-3} \pm 8.93·10^{-5}]·C$ (mM)	0.997	0.83 µM	2.50 µM
Ascorbic acid	$I_p = [1.39·10^{-5} \pm 1.78·10^{-7}]+[9.90·10^{-6} \pm 2.31·10^{-7}]·C$ (mM)	0.997	0.1 mM	0.30 mM
Tyrosine	$I_p = [-1.23·10^{-5} \pm 8.44·10^{-7}]+[6.30·10^{-5} \pm 1.04·10^{-6}]·C$ (mM)	0.999	0.12 mM	0.35 mM

It is important to highlight that reached LOD values were significantly lower than other previously reported [1, 2] using similar carbon nano-based sensing materials.

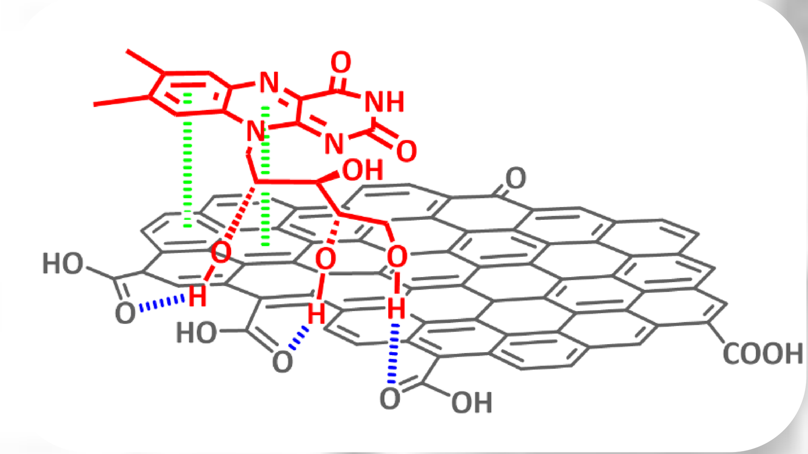
APPLICATION TO COMMERCIAL NUTRITIONAL SUPPLEMENTS

Attending to the electrocatalytic behavior displayed GQD/Nf was selected to attain the simultaneous detection in three commercial sport supplements: Mincartil (Vit. B2, Vit. C and Tyr) Vitax (C, B2 and B6 vitamins) and L-Tyrosine BioTech (Tyr). In all cases, the working samples were prepared upon advices of their recommended daily amounts.





Voltammograms for Mincartil in 0.1 M KCl (A), Vitax in 0.05 M HNO_3 (B) and L-tyrosine BioTech (C) in 0.1 M KCl using the GQD/Nf electrodes. Peaks marked as 1,2,3 and 4 refer to the analytical signal of riboflavin, ascorbic acid, tyrosine, and pyridoxine, respectively.



Interactions of GQD on the electrode surface and riboflavin as the target analyte.

The results indicate the importance of hydrogens bonding (caused by surfaced oxygenated functionalities) and the π-π interactions (from graphenic nanosheets) as main contributions to enhance the detection of various targeted molecules.

CONCLUSION

This work offers then a rational survey about the electrocatalytic activity of grpahene quantum dots (GQDs) affording advantages in the electrode preparation (by simple drop-casting modification of the SPCEs) with a good batch-to-batch reproducibility, which is of great consideration for their further potential manufacturing. With that research, we try to search new possibilities for the design of electrochemical sensors based on functionalized GQDs depending on the specific chemistry of various target analytes to find also an effective resolution of the mixtures in complex samples with an improved sensitivity.