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Voltammetric sensors based on nanomaterials and electropolymerized coverages for bioadditive analysis

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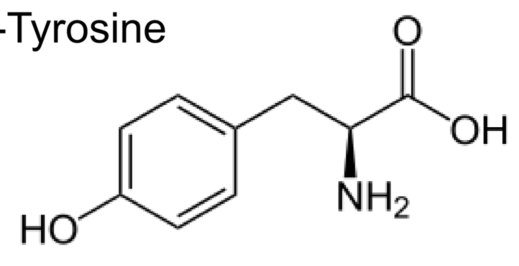
INTRODUCTION & AIM

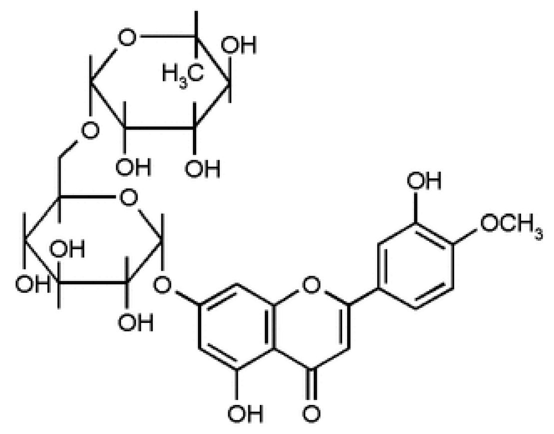
Bioadditives are often used around the world as a part of the daily human diet. Contrary to pharmaceuticals, bioadditives are not subject to rigorous quality control, and their full chemical composition is usually unknown. Therefore, the determination of active components in bioadditives is of high importance and can be achieved using voltammetry.

Novel voltammetric sensors were developed for the quantification of L-tyrosine and diosmin in bioadditives in current work.

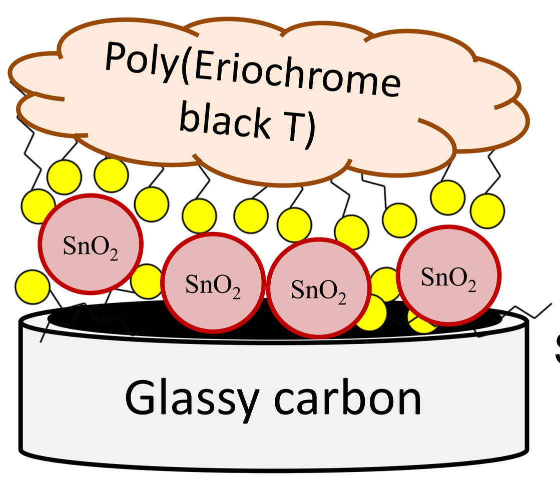
L-Tyrosine

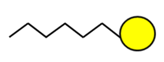


Diosmin

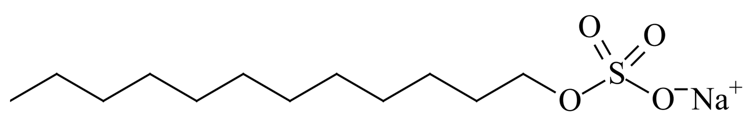


ELECTRODE SURFACE MODIFICATION

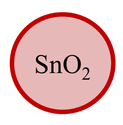




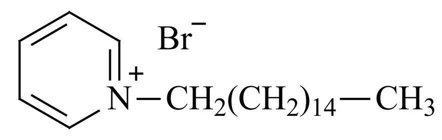
Surfactant



Sodium dodecyl sulfate(SDS)

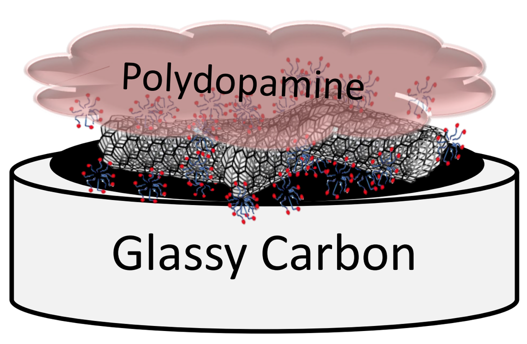


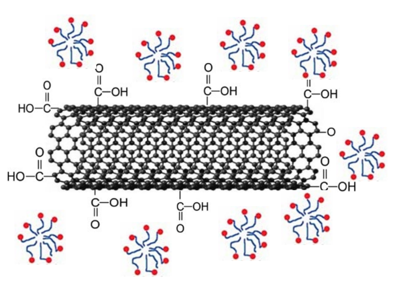
SnO$_2$ nanoparticles (NPs)
D < 100 nm
(Aldrich, Germany)



Cetyl pyridinium bromide (CPB)

c = 1.0 mg mL^{-1} in 0.5 mM surfactant, sonication for 10 min



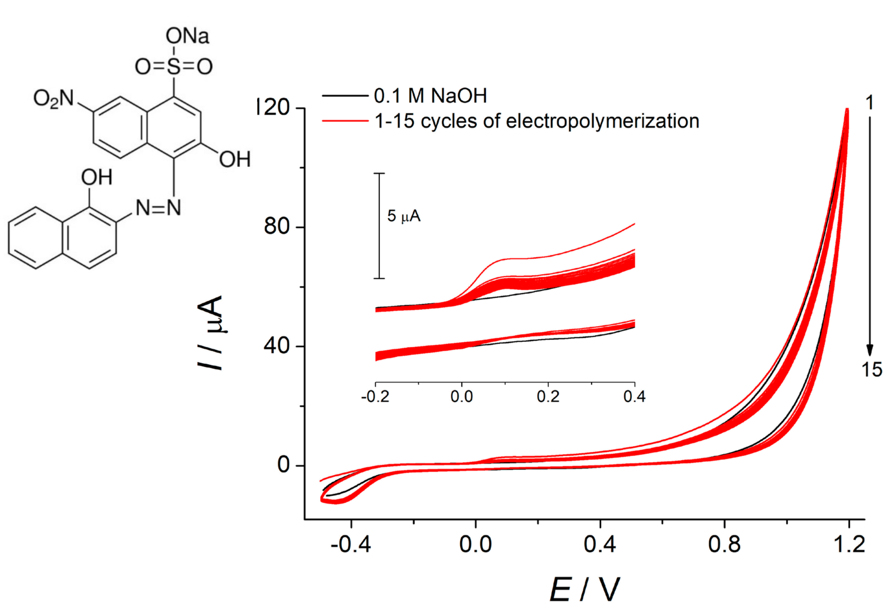


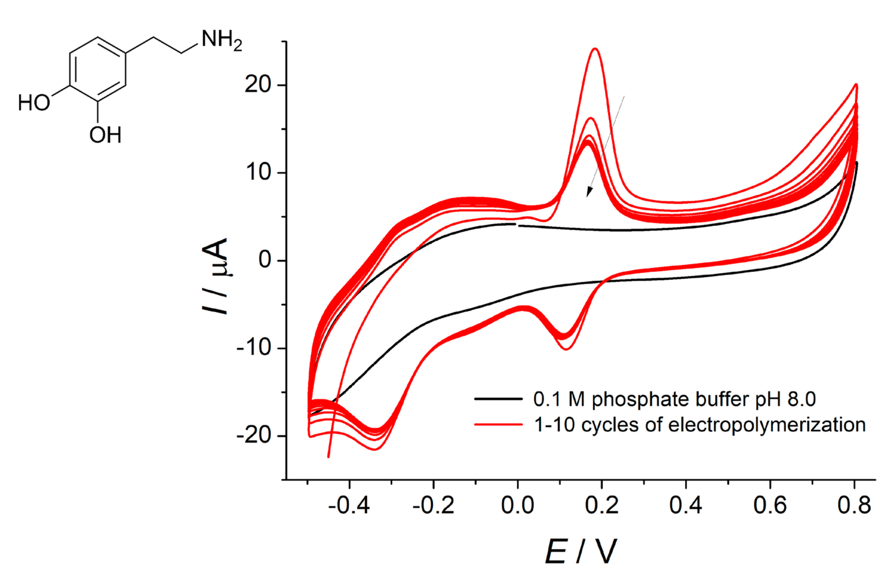
Carboxylated multi-walled carbon nanotubes (MWCNTs–COOH)
(D = 9.5 nm, l = 1.5 µm, carboxylation degree >8%)
(Aldrich, Germany)
c = 0.5 mg mL^{-1} in 0.5% SDS, sonication for 15 min

Modification steps

1. Electrode surface polishing on Al_2O_3
2. Drop casting of 4 µL SnO_2 NPs–SDS dispersion or 2 µL MWCNTs–COOH suspension
3. Electropolymerization of Eriochrome Black T or dopamine

Electropolymerization of monomers





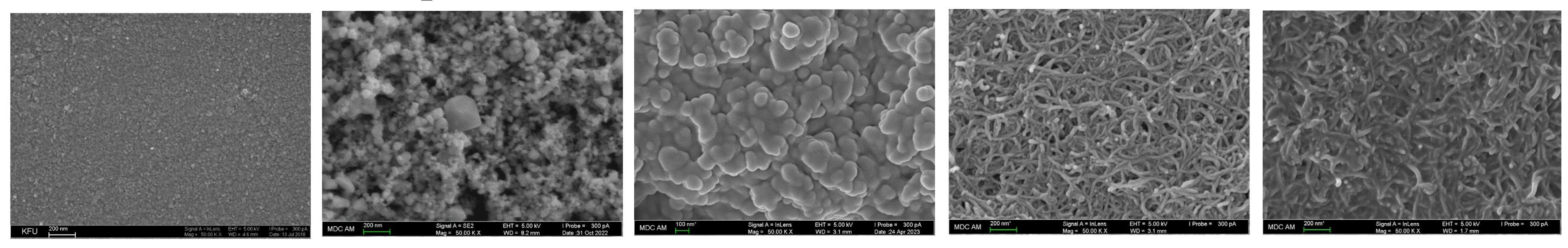
Optimal conditions of electropolymerization on the basis of the target analyte response

Sensing layer (from outer to inner layer)	$c_{monomer}$, µM	Number of cycles	Potential range, V	υ, mV s^{-1}	Supporting electrolyte
Poly(Eriochrome Black T)/ SnO$_2$ NPs–SDS	75	15	-0.5 – 1.2	100	0.1 M NaOH
Polydopamine/ MWCNTs–COOH	100	10	-0.5 – 0.8	125	0.1 M phosphate buffer pH 8.0

RESULTS & DISCUSSION

Electrode characterization

Bare GCE | SnO$_2$ NPs/GCE | Poly(Eriochrome Black T)/ SnO$_2$ NPs/GCE | MWCNTs–COOH/ GCE | Polydopamine/ MWCNTs–COOH/ GCE



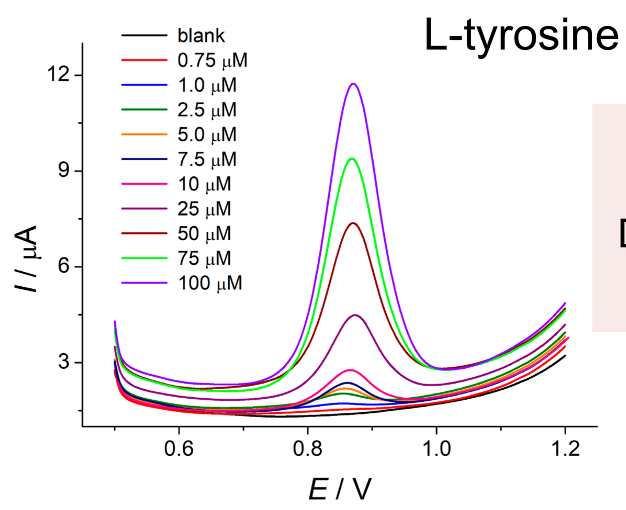
Electrochemical characteristics of the electrodes

Electrode	A, mm^2	R_{ct}, kΩ	k_{et}, cm s^{-1}
Bare GCE	8.9±0.3	72.5±0.9	4.12×10^{-5}
Poly(Eriochrome Black T)/SnO$_2$ NPs–SDS/GCE	85.2±0.2	2.9±0.4	1.08×10^{-4}
Polydopamine/MWCNTs–COOH/GCE	125±1	1.3±0.1	1.34×10^{-4}

L-Tyrosine and diosmin electrooxidation parameters

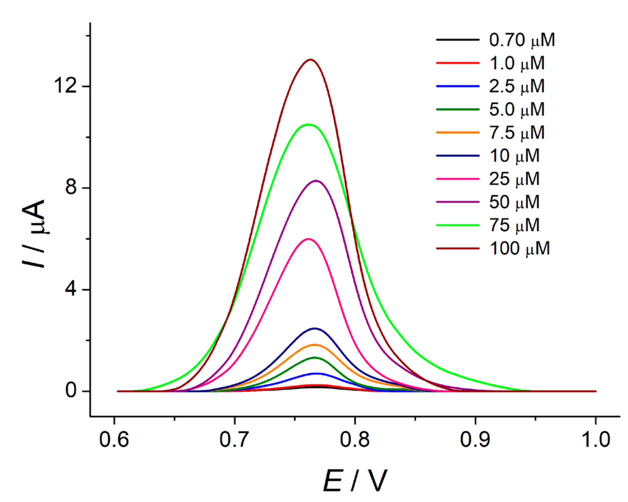
Analyte	Electrode	Electrolyte	Limiting step nature	Electrooxidation parameters
L-Tyrosine	Poly(Eriochrome Black T)/SnO$_2$ NPs–SDS/GCE	Britton-Robinson buffer pH 2.0	Diffusion	H$^+$ transfer involved α_a = 0.43, n = 2 D = (2.1±0.3)×10^{-5} k^0 = 1.69×10^{-3}
Diosmin	Polydopamine/MWCNTs–COOH/GCE		Mixed	H$^+$ transfer involved

Voltammetric sensors for L-tyrosine and diosmin



Linear range 0.75–100 µM
Detection limit 0.66 µM

ΔE_{pulse} = 100 mV, t_{pulse} = 50 ms, υ = 10 mV s^{-1}



Linear range 0.75–25 µM and 25–100 µM
Detection limit 0.25 µM

ΔE_{pulse} = 100 mV, t_{pulse} = 25 ms, υ = 10 mV s^{-1}

Bioadditives analysis (P = 0.95)

Analyte	Sample	Labeled amount, mg	Voltammetry, mg	RSD	HPLC, mg	RSD	t-test*	F-test**
L-Tyrosine	1	500	500±8	0.01	497±27	0.02	0.488	2.64
	2	250	259±9	0.01	263±4	0.006	2.40	2.50
	3	225	223±4	0.01	220±5	0.09	0.41	2.49
Diosmin	1	600	599±5	0.006	595±12	0.008	1.33	1.59
	2	600	600±15	0.02	604±21	0.01	0.528	1.71
	3	300	300±3	0.007	298±9	0.01	0.836	2.47

* $t_{critical}$ = 2.45 at P = 0.95 and f = 6 ** $F_{critical}$ = 19.25 at P = 0.95 and f_1 = 4, f_2=2

CONCLUSION

Voltammetric sensors based on layer-by-layer combination of various nanomaterials and electropolymerized coverages have been developed for the L-tyrosine and diosmin quantification. The sensors are simple in fabrication, highly reproducible, and provide a sensitive, selective, and reliable response to target analytes. Future development could be focused on the design of screen-printed electrodes as a platform for sensing layer immobilization.