Supplementary Materials

The Analytical Capabilities of Electrochemical Sensors Based on Transition Metal Oxide Nanomaterials

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Table S1. Conditions of voltammetric determination of the antioxidants at the metal oxide nanomaterial modified electrodes.

Analyte	Electrode	Method	ΔE_{pulse} (mV)	t_{pulse} (ms)	t_{acc} (s)	υ (mV s^{-1})	Potential range (V)
Quercetin and rutin	CeO_2 NPs–SDS/GCE	DPV	75	25	—	10	0.0–0.9
Gallic acid	SnO_2 NPs–CPB/GCE	DPV	75	25	—	10	0.0–0.6
Hesperidin	SnO_2 NPs–CPB/GCE	AdADPV	75	25	120	10	0.2–0.8
Taxifolin	SnO_2 NPs–CPB/GCE	DPV	100	75	—	10	0.0–0.5
Eugenol	CeO_2 NPs–CPB/GCE	DPV	75	25	—	10	0.2–0.65
Vanillin	SnO_2 NPs–CPB/GCE	DPV	100	25	—	10	0.5–1.2
Propyl gallate	CeO_2 NPs–CPB/GCE	DPV	75	25	—	10	0.0–0.7
α-Lipoic acid	SnO_2 NPs–CTPPB/GCE	DPV	100	50	—	10	0.4–1.2
	CeO_2·Fe_2O_3 NPs/GCE	DPV	100	25	—	20	0.5–1.2
Tartrazine	CeO_2 NPs–CTPPB/GCE	LSV	—	—	—	250	0.4–1.6
Tartrazine and Brilliant blue FCF	MnO_2 NRs–CPB/GCE	DPV	75	25	—	20	0.5–1.2
Sudan I	MnO_2 NRs–CPB/GCE	DPV	100	25	—	20	0.0–0.9

S2.1. Sample Preparation

S2.1.1. Preparation of the medicinal plant extracts for the determination of quercetin and rutin

Commercially available medicinal plant material (St. John's wort herb (*Hyperici herba*), marigold flowers (*Calendulae officinalis flores*), and bearberry leaves (*Arctostaphyli uvae ursi folia*)) were studied. Their infusions and decoctions were obtained ccording to the standard Pharmacopoeia method. An accurately weighed portion of a medicinal plant material (10.000 ± 0.005 g) was placed in an enameled bowl. To prepare the decoctions, 200 mL of distilled water at room temperature was added and boiled in a water bath for 30 min. In the case of infusions, medicinal plant materials were poured with 200 mL of boiling distilled water and infused for 15 min. Then the extracts were cooled at room temperature (10 min for decoctions), filtered, and made up to volume with water.

Ethanolic extracts were obtained by placing an accurately weighed portion of a raw material (1.0000 ± 0.0005 g) in a 50-mL separation funnel and 20 mL (for marigold flowers and bearberry leaves) or 30 mL (for St. John's wort herb) of the ethanol was added. The extraction time providing the highest yield of the analyte was 20 min for marigold flowers, 10 min for bearberry leaves, and 15 min for St. John's wort herb. The extracts were filtered and used for further research.

To obtain hydrolysates, an accurately weighed portion (1.0000 ± 0.0005 g) of raw material was placed in a round-bottomed flask, poured with 20.0 mL (for bearberry leaves and marigold flowers) or 30.0 mL (for St. John's wort herb) of 1.1 M HCl in ethanol, and boiled in a water bath for 10 (for bearberry leaves), 15 (for St. John's wort herb), or 20 min (for marigold flowers) with a reflux. The resulting hydrolysates were filtered and made up to the appropriate volume with alcohol.

S2.1.2. Orange juices treatment for hesperidin quantification

Orange juices (one sample of fresh and two samples of commercially available) were studied. 6 mL of juice were mixed with 6 mL of methanol, sonicated for 15 min, fil-

tered through 0.45 μm pore size nylon membrane filters and used for further measurements.

S2.1.3. Bioadditives and pharmaceutical dosage forms treatment for taxifolin and α-lipoic acid determination

Commercial taxifolin bioadditives in tablets and pharmaceutical dosage forms of α-lipoic acid were studied. The average weight of the tablet was measured before sample treatment. Then, ten or five tablets were ground thoroughly in a porcelain mortar and the exact weight of powder in the range of 0.1–0.2 g was taken and dissolved in 5 (for taxifolin) or 15 (for α-lipoic acid) mL of ethanol. The solution was filtered, diluted if necessary, and used for further measurements. The concentrate of α-lipoic acid for the infusion preparation was 10-fold diluted with ethanol prior to measurements.

S2.1.4. Essenstial oils and spices treatment for eugenol determination

Clove, cinnamon, basil and nutmeg essential oils were obtained from the local pharmacies. Their exact amount (0.0030–0.3600 g depending on the oil nature) was dissolved in 5.0 mL of ethanol and used for further measurements.

Clove spices purchased from local supermarket were used. Preliminary extraction of eugenol with ethanol was applied. A representative portion of the milled cloves (0.1000–0.0003 g) was accurately weighted and quantitatively transferred into separating funnel. Then, 2.0 mL of ethanol were added and shaked for 15 min. The extract was collected and used for further measurements.

S2.1.5. Perfumes and vanilla essential oils treatment for vanillin quantification

Sample preparation consisted in the preliminary twofold dilution of the samples with ethanol.

S2.1.6. Vegetable oil treatment for propyl gallate quantification

Preliminary liquid extraction of propyl gallate form vegetable oils with ethanol was used. 2.0 mL of oil were mixed with 5.0 mL of extractant and sonicated for 15 min, stored till the phase separation (5–10 min) and then the ethanolic layer was collected for further measurements.

S2.1.7. Sample treatment for the colorants quantification

The soft and isotonic sports drinks were preliminary degassed in an ultrasonic bath for 10 min? then filtered through a 0.45 μm pore size nylon membrane filter and used for further investigations.

In the case of sudan I, commercial spices (dried and smoked paprika) and Atlantic salmon were studied. An accurate weighed portion of the ground sample (1.0000 ± 0.0002 g) was spiked with 0.80, 2.0, or 4.0 mg of Sudan I and the mixture was thoroughly mixed. Then, 10 ml of methanol was added to the spiked sample and placed in an ultrasonic bath for 10 min. After phase separation, the supernatant liquid was collected and the volume of methanol was adjusted to 10 ml and used for the colorant quantification.

Table S2. Electrochemical impedance parameters of the bare GCE and modified electrodes (n = 5; P = 0.95).

Electrode	E (V)	Frequency range (Hz)	R_s (Ω)	R_{et} (kΩ)	Q (μΩ^{-1})	n	W (μΩ^{-1})	χ^2
GCE	0.23	10,000–0.04	101 ± 6	72.5 ± 0.9	0.45 ± 0.05	0.860	—	0.016
SnO_2 NPs–CPB (500μM)	0.23		113 ± 4	0.13 ± 0.03	2.1 ± 0.1	0.904	557 ± 6	0.033
SnO_2 NPs–CPB (1000μM)	0.23		112 ± 2	0.11 ± 0.01	2.3 ± 0.1	0.915	560 ± 5	0.026
CeO_2 NPs–CPB (500μM)	0.23		84 ± 5	0.034 ± 0.002	3.5 ± 0.1	0.825	410 ± 115	0.028
GCE	0.24	10,000–0.5	360 ± 50	173 ± 9	3.1 ± 0.1	0.777	—	0.022
CeO_2 NPs–CPB (450μM)	0.24		280 ± 40	2.6 ± 0.03	8.5 ± 0.2	0.724	125 ± 5	0.025
GCE	0.175	100,000–1.0	67 ± 2	114 ± 8	0.94 ± 0.03	0.913	—	0.015
SnO_2 NPs–CPB (500μM)	0.175		66 ± 3	0.140 ± 0.005	99 ± 5	0.429	307 ± 6	0.011
GCE	0.23	10,000–0.04	75 ± 5	181 ± 7	1.4 ± 0.1	0.813	—	0.020
SnO_2 NPs–CTPPB	0.23		89 ± 1	10.8 ± 0.4	3.0 ± 0.1	0.803	250 ± 8	0.017
GCE	0.23	10,000–0.04	245 ± 5	72 ± 3	3.7 ± 0.2	0.789	—	0.028
CeO_2·Fe_2O_3 NPs	0.23		92 ± 1	4.1 ± 0.2	0.448 ± 0.009	0.883	236 ± 12	0.021
MnO_2 NRs–CPB	0.23		98 ± 3	1.0 ± 0.2	108 ± 6	0.507	440 ± 10	0.031

Table S3. Scanning electron microscopy based size and shape of the NPs at the electrode surface after drop casting of dispersion in water or surfactant media (n = 5; P = 0.95).

NPs	Water medium		Surfactant medium	
	NPs size, nm	NPs shape	NPs size, nm	NPs shape
SnO_2 NPs	30–200	Spherical and rhomboid structures and their aggregates	20–40	Spherical particles
SnO_2 NPs	22–35 40–100	Particles Spherical, elliptical and rhomboid aggregates	20–40	Spherical particles
CeO_2 NPs	20–200	Spherical and rhomboid structures and their aggregates	20-60 <100	Spherical particles Rhomboid particles
CeO_2·Fe_2O_3 NPs	25–60	Spherical particles and their aggregates	—	—