

# Functionalization of Screen-Printed Sensors with A High Reactivity Carbonaceous Material for Ascorbic Acid Detection in Fresh-Cut Fruit with Low Vitamin C Content

Ylenia Spissu <sup>1</sup>, Antonio Barberis <sup>1,\*</sup>, Gianfranco Bazzu <sup>1</sup>, Guy D'hallewin <sup>1</sup>, Gaia Rocchitta <sup>2</sup>, Pier Andrea Serra <sup>2</sup>, Salvatore Marceddu <sup>1</sup>, Claudia Vineis <sup>3</sup>, Sebastiano Garroni <sup>4</sup> and Nicola Culeddu <sup>5</sup>

<sup>1</sup> Institute of Sciences of Food Production, National Research Council, 07100 Sassari, Italy; yspissu82@gmail.com (Y.S.); gbazzu@uniss.it (G.B.); guy.dhallewin@cnr.it (G.D.); salvatore.marceddu@cnr.it (S.M.)

<sup>2</sup> Department of Medical, Surgical and Experimental Medicine, Medical School, University of Sassari, 07100 Sassari, Italy; grocchitta@uniss.it (G.R.); paserra@uniss.it (P.A.S.)

<sup>3</sup> Institute of Intelligent Industrial Technologies and Systems for Advanced Manufacturing (CNR-STIIMA), National Research Council of Italy, 13900 Biella, Italy; claudia.vineis@stiima.cnr.it

<sup>4</sup> Department of Chemistry and Pharmacy, University of Sassari, 07100 Sassari, Italy; sgarroni@uniss.it

<sup>5</sup> Institute of Biological Chemistry, National Research Council, 07100 Sassari, Italy; nicola.culeddu@icb.cnr.it

\* Correspondence: antonio.barberis@cnr.it

## Supplementary Materials

- Effect of functionalization on the AA oxidative capacity of the C-SPEs

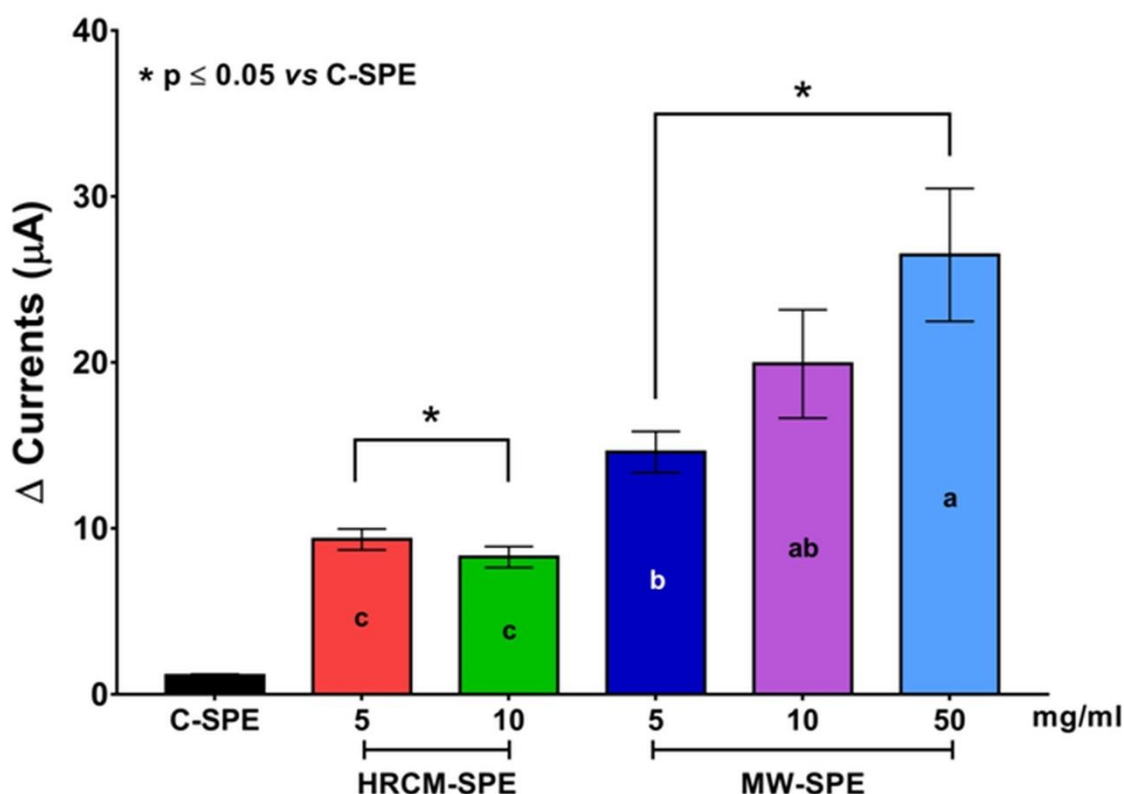


Figure S1. In the histogram,  $\Delta$ current is the difference between AA oxidation current and baseline current, at +120 mV (dashed vertical line in the voltammograms of Figure 3). The  $\Delta$ current was calculated for each sensor. The statistical difference between  $\Delta$ current values (HRCM-SPEs vs C-SPEs and MW-SPEs vs C-SPEs), was evaluated by Student's *t*-test ( $p \leq 0.05$ ). The statistical differences among  $\Delta$ current values were compared by ANOVA: mean values indicated with unlike letters differ significantly by Fisher's least significant difference (LSD) test,  $p \leq 0.05$ .

### - Matrix effect on AA currents

The effect of sample matrix on AA current was studied. Samples of watermelon juice were spiked with 5, 10, 20, 50 and 100  $\mu\text{M}$  of AA, while the samples of apple juice were spiked with 5, 10, 20 and 50  $\mu\text{M}$  of AA (standard addition method): these concentration values have been chosen taking into consideration the AA contribution of the juice (about 30  $\mu\text{M}$  for watermelon juice at a dilution of 1: 5, and about 3  $\mu\text{M}$  for apple juice at a dilution of 1: 100), and the need for stay within the 1-100  $\mu\text{M}$  concentration range. 70  $\mu\text{l}$  of spiked samples were deposited on the WE surface of each SPE, and a linear regression analysis was performed on baseline subtracted data. This analysis was performed in triplicate, for all the investigated SPEs.

The outcome of the calibration with the standard addition method is shown in Figure S2. The deposition of spiked samples on the WE surface of C-SPEs, HRCM-SPEs functionalized with 5 mg/ml and MW-SPEs functionalized with 10 mg/ml, determined a linear increase in the baseline-subtracted current values. The results, when statistically compared with those of AA standard, demonstrate that the exposition to watermelon and apple juice did not affect the SPEs performance.

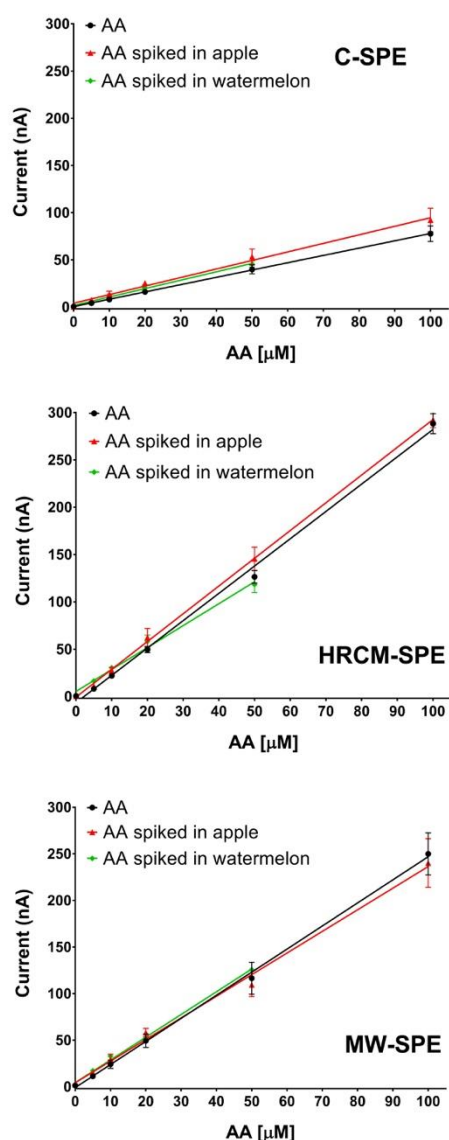


Figure S2. AA calibration with the standard addition method. The deposition of watermelon (green line) and apple (red line) spiked juice on the WE surface of C-SPEs, HRCM-SPEs functionalized with 5 mg/ml and MW-SPEs functionalized with 10 mg/ml, determined a linear increase in the baseline-subtracted current values. The slopes of the calibration curves are not statistically different from those (black lines) obtained by *L*-ascorbic acid (standard from Merck).

Table S1. Sensitivity, linear range and detection limit of screen-printed sensors for AA detection. A literature selection.

Type of SPE	Sensitivity	Linear Range ( $\mu\text{M}$ )	LOD	Reference (DOI)
Cadmium oxide (CdO) nanoparticles modified disposable screen-printed carbon electrode (SPCE)	0.42 A/M/cm <sup>2</sup>	5–150	53.5 nM	10.1016/j.nanoso.2018.05.004
Modified SPCE CV( <i>Callistemon Vicinali</i> ) Fe <sub>3</sub> O <sub>4</sub> NP		10 - 100	15.7 $\mu\text{M}$	10.1007/s10876-021-02030-7
RuO <sub>2</sub> NWSeCeO <sub>2</sub> -AuNFs/f-MWCNTs/GO/SPCE		0.5 - 100	160 nM	10.1016/j.jallcom.2018.12.253
Cu(OH) <sub>2</sub> NRs modified SPE	268 $\mu\text{A}/\text{mM}/\text{cm}^2$ .	12.5 - 10000		10.1007/s00604-017-2391-0
Screen-printed graphene electrode (SPGNE)		4.0 - 4500	950 nM	10.1016/j.bios.2012.01.016
Graphene quantum dots (GQDs) and ionic liquid (IL) modified screen-printed carbon electrode (GQDs/IL-SPCE)		25 - 400	6.64 $\mu\text{M}$	10.1016/j.snb.2020.128059
Screen-printed carbon electrodes (SPEs) modified with an o-aminophenol (o-AP) film	0.32 $\mu\text{A}/\mu\text{M}/\text{cm}^2$	2 - 20	860 nM	10.1021/jf802536k
Screen-printed carbon electrode (SPCE) modified with chemically reduced graphene oxide (rGO) (rGO-SPCE)		5 - 20000	50 $\mu\text{M}$	10.3390/chemosensors4040025
Graphite screen printed electrode modified with NiFe <sub>2</sub> O <sub>4</sub> nanoparticles (NiFe <sub>2</sub> O <sub>4</sub> /SPE)		0.5 - 100	100 nM	Jahani S 2018. Anal. Bioanal. Electrochem., Vol. 10, No. 6, 739-750
Screen- printed electrodes modified by electroactive melanin-like nanoparticles	0.38 nA/ppb	5 - 500 ppb	0.07 ppb	10.1039/c9ra07948c
Graphite screen printed electrode modified with La <sup>3+</sup> /Co <sub>3</sub> O <sub>4</sub> nanocubes transducer	3.47 $\mu\text{A}/\text{mM}$	1 - 900 $\mu\text{M}$	0.3 $\mu\text{M}$	10.5599/jese.643