Electrochemically grown Cu,Ni-BTC film for electrochemical detection of caffeic acid in fruits

(SI)

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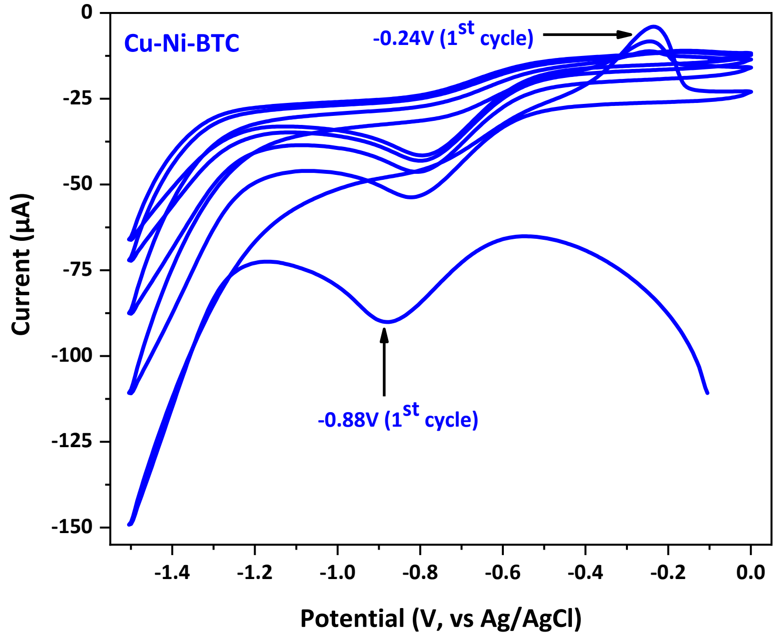


Fig 1S. CV curves recorded during the electrochemical growth of Cu, Ni-BTC film. The cyclic voltammograms were recored on glassy carbon electrode in DMF solution containing 10 mM Et_3N, 15 mM H_3BTC, 9 mM $CuCl_2.2H_2O$ and 1mM $NiCl_2.6H_2O$

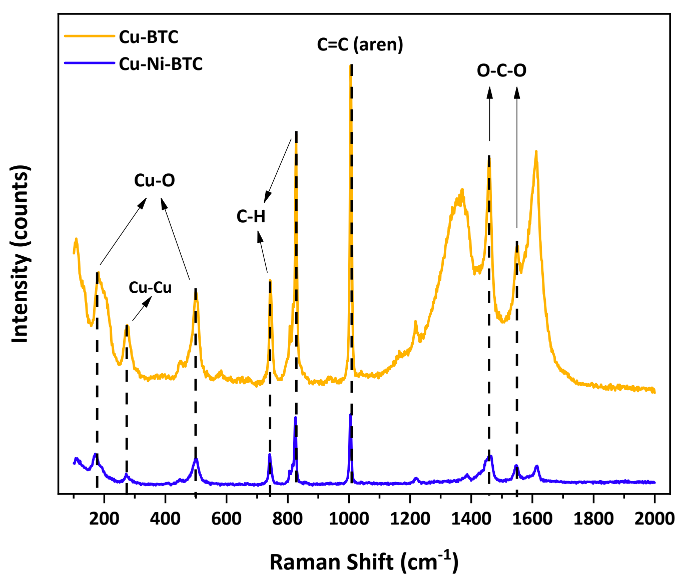


Fig 2S. Raman spectra of Cu-BTC and Cu, Ni-BTC electrodeposited films.

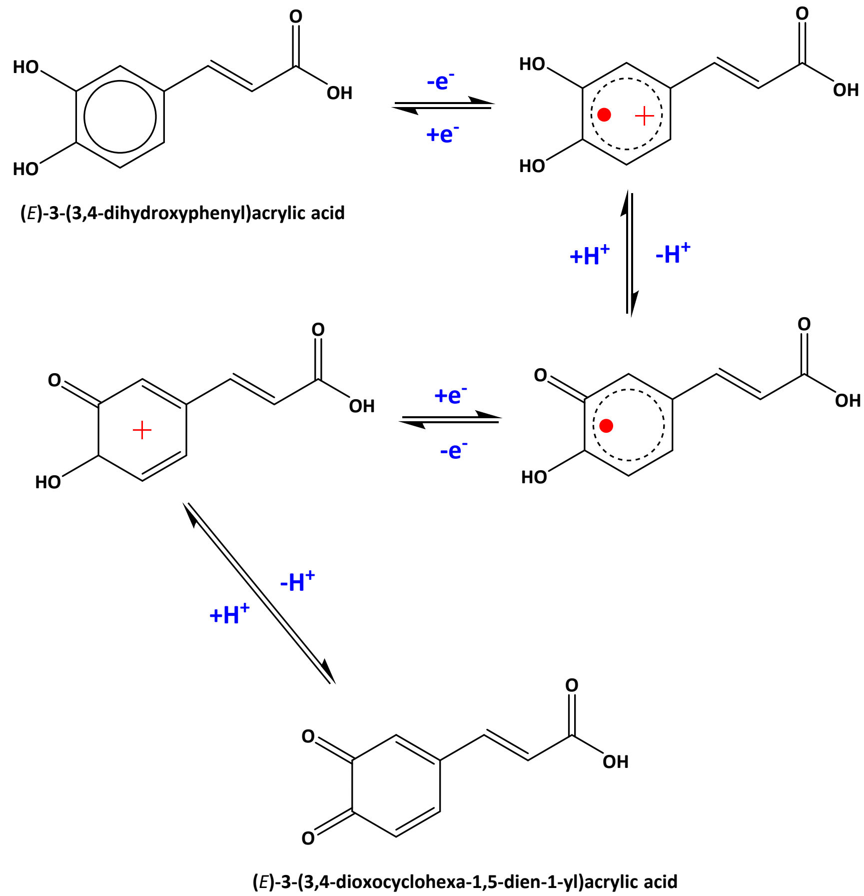


Fig 3S. Redox mechanism of CA on GCE [62]

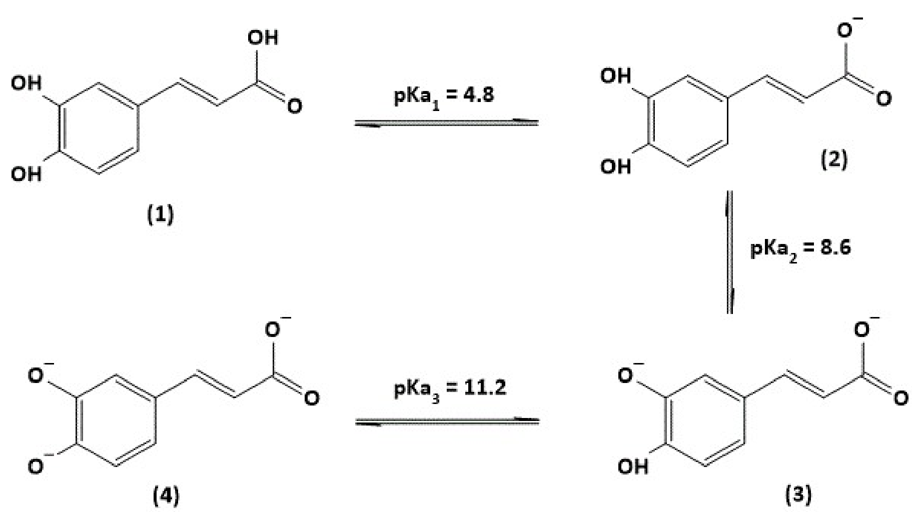


Fig 4S. Different forms of caffeic acid.

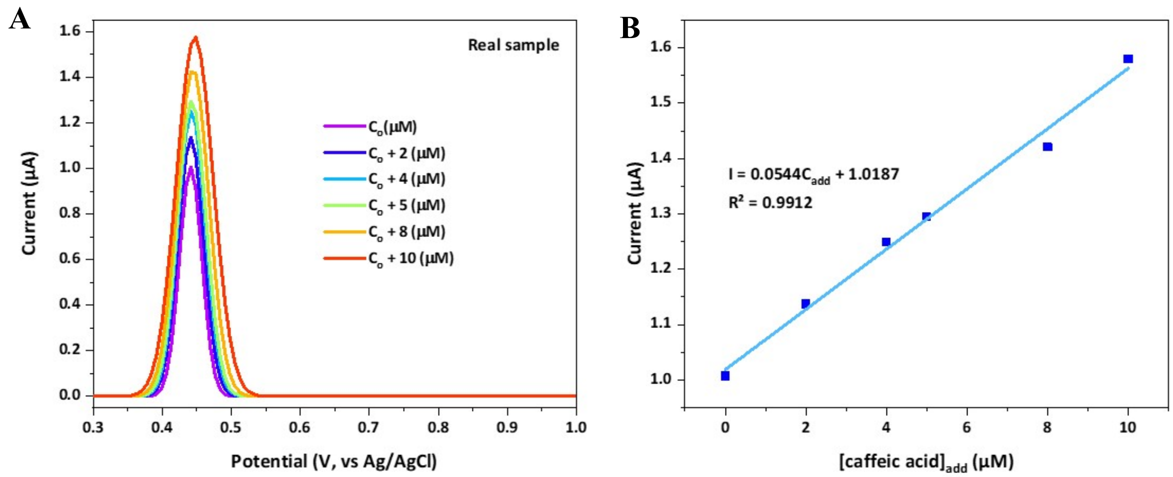


Fig 5S. Real sample tests. (A) DPV curves recorded on Cu,Ni-BTC electrodeposited GCE electrodes in apple juice adding different concentrations of caffeic acid (2 – 10 μM); (B) Calibration curves

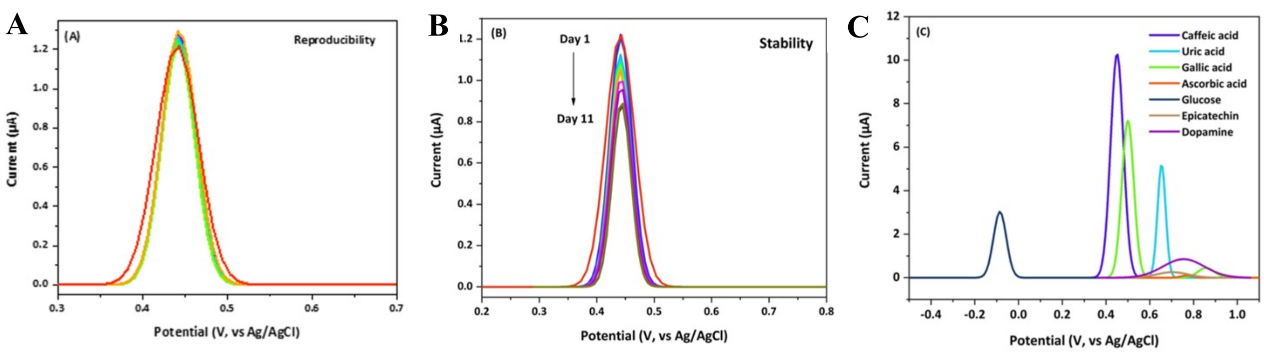
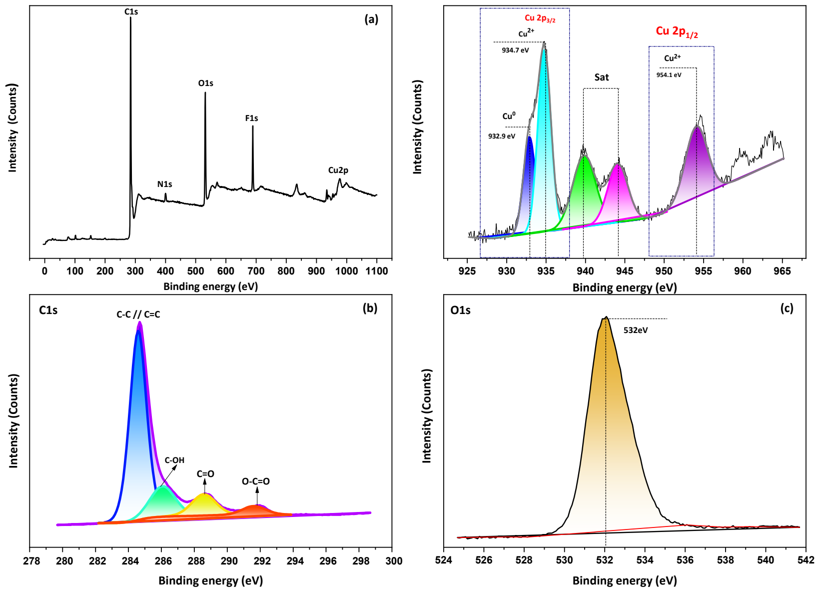
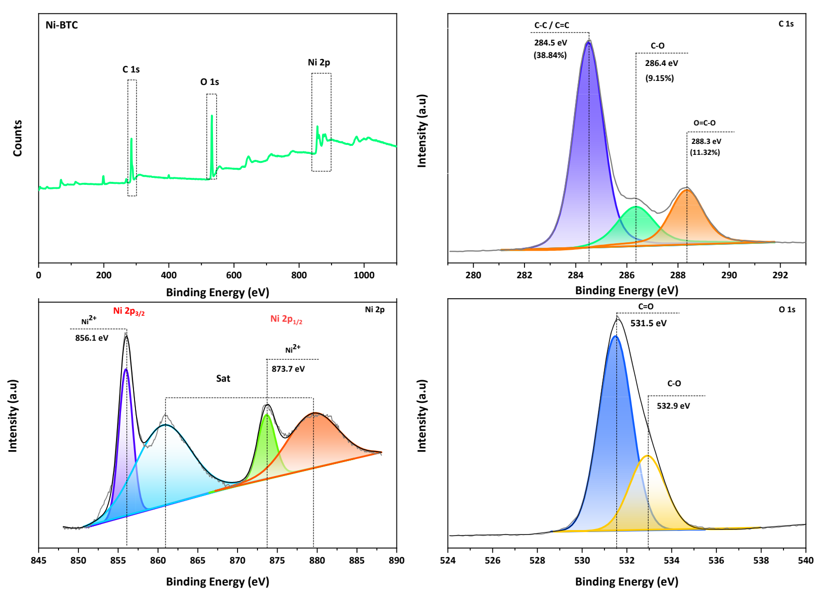


Fig 6S: DPV test (A) Reproducibility, (B) stability and (C) interference tests.



(A) XPS survey spectrum and C 1s, O 1s, Cu 2p high-resolution spectra of Cu-BTC film



(B) XPS survey spectrum and C 1s, O 1s, Ni 2p high-resolution spectra of Ni-BTC film

Fig 7S: XPS survey and high-resolution XPS spectra of (A) Cu-BTC and (B) Ni-BTC eletrochemically grown on glassy carbon electrode.

Table 1S. EDX and XPS Analysis on elemental composition in Cu, Ni – BTC film electrodeposited onto GCE.

Element	EDX analysis		XPS analysis	
	% wt.	**% at.**	**% wt.**	**% at.**
C	53.8	74.01	49.22	65.13
O	17.8	18.38	29.71	29.71
Cu	22.3	5.80	16.56	4.14
Ni	5.6	1.58	4.51	1.22
Cl	0.5	0.23	N/A	N/A
Total	100	100	100	100

Table 2S. Calculation of the charges accumulated during the electrochemical of Cu, Ni – BTC film at different applied potentials (-0.8 V to -1.1 V).

Note that: $q = \int idt$

Applied potential (V)	q (mC)
-0.8	**-12.8**
-0.9	**-11.8**
-1.0	**-11.2**
-1.1	**-16.2**

Table 3S. Analysis on electrochemical behaviors of Cu, Ni – BTC electrodeposited on GCE electrodes.

Parameters / Electrode	R_{CT} (Ω) (*)	ΔE (mV) (**)	ΔI (mV) (**)	V_{Cu} (mV) (***)	V_{Ni} (mV) (***)
Cu,Ni-BTC/GCE	**58.7 ± 3.2**	75.5	193.2	V_{Cu1} = -130mV V_{Cu2} = 156 mV	393
Cu-BTC/GCE	**86.0 ± 8.6**	90.6	154.7	V_{Cu1} = -210mV V_{Cu2} = 81 mV	N/A
Ni-BTC/GCE	**270.4 ± 3.1**	85.6	117.4	N/A	611
GCE	**1286 ± 11.4**	100.7	98.7	N/A	N/A

* derivated from EIS spectra recorded in 100 mM KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$

** derivated from CV curves recorded in 100 mM KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$

*** derivated from CV curves recorded in 100 mM KCl solution.

V_{Cu1}: from Cu(0) to Cu(I)

V_{Cu2}: from Cu(I) to Cu(II)

Table 4S. Reproducibility test.

Electrode	Current (µA)
1st	1.2563
2nd	1.2327
3rd	1.1635
4th	1.1861
5th	1.1017
6th	1.1950
7th	1.2150
RSD = 2.61%	

Table 5S. Stability test.

Day	Current (µA)
1st	1.2563
2nd	1.1850
3rd	1.1550
4th	1.0817
5th	1.0570
6th	1.0600
7th	1.0150
	RSD = 6.4 %
8th	0.9931
9th	0.9558
10th	0.8890
11th	0.8773
RSD = 11.37 %	

Table 6S. Interference test.

Interference	Current (µA)	Error
Caffeic acid (20 µM)	1.26	0.063
Caffeic acid (20 µM) + Uric acid (2 µM)	1.3	0.065
Caffeic acid (20 µM) + Gallic acid (2 µM)	1.08	0.054
Caffeic acid (20 µM) + Ascorbic acid (2 µM)	1.2	0.06
Caffeic acid (20 µM) + Glucose (2 µM)	1.24	0.062
Caffeic acid (20 µM) + Epicatechin (2 µM)	1.19	0.059
Caffeic acid (20 µM) + Dopamine (2 µM)	1.22	0.061

Table 7S. Real sample test.

Added $C_{caffeic\ acid}$ (μM)	Found $C_{caffeic\ acid}$ (μM)	Recovery (%)
0	18.7 ± 0.4	-
2	20.7 ± 0.3	92.2
4	22.7 ± 0.2	96.1
5	23.7 ± 0.4	96.9
8	26.7 ± 0.5	98.1
10	28.7 ± 0.2	98.4