Electronic Supplementary Information (ESI)

Paper-based Electrochemical Sensor for Direct Detection of Caffeine in Commercial Beverage Samples

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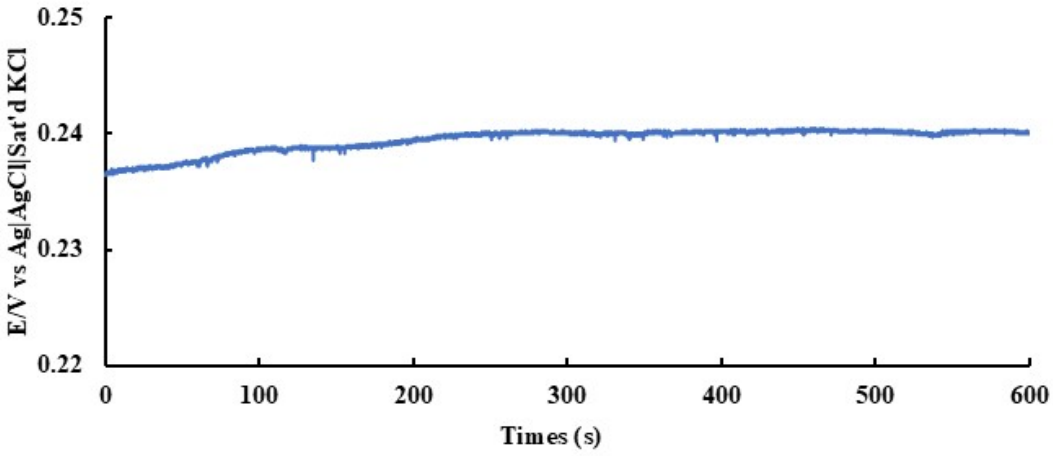


Fig. S1. Stability test of the Ag paste reference electrode in 0.1 M phosphate solution.

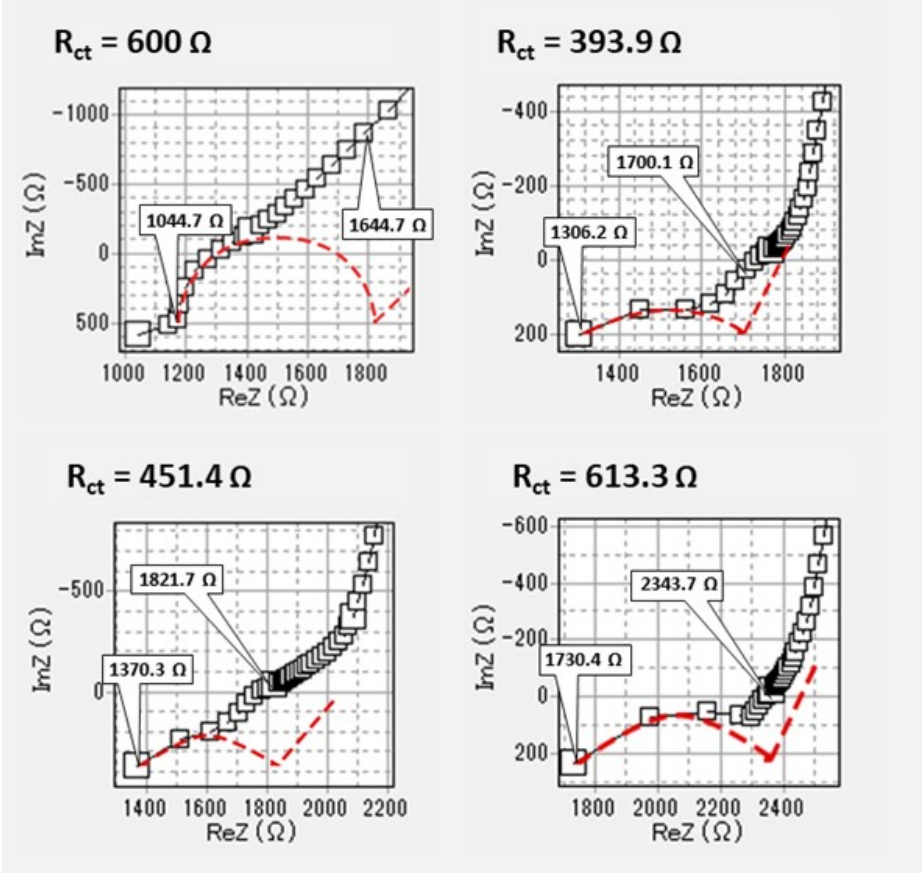


Fig. S2. Nyquist plot for the calculation of charge transfer resistance (R_{ct}) of four different paper-based sensors.

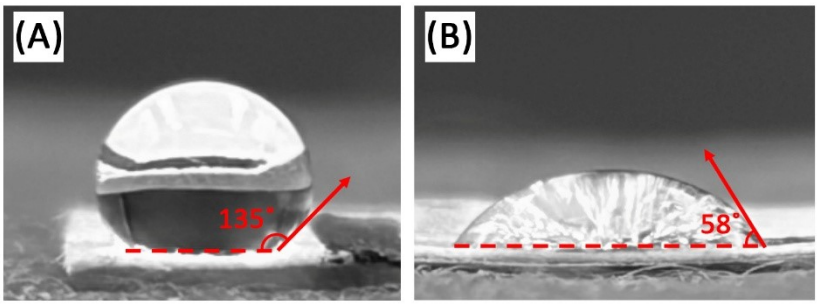


Fig. S3. Contact angle measurement obtained from water drop test image of wax-modified paper (A) showing hydrophobic surface (90˚ < contact angle < 150˚) and CNF film on wax-modified paper (B) showing reduced contact angle (58˚). The decreased contact angle confirmed wettability.

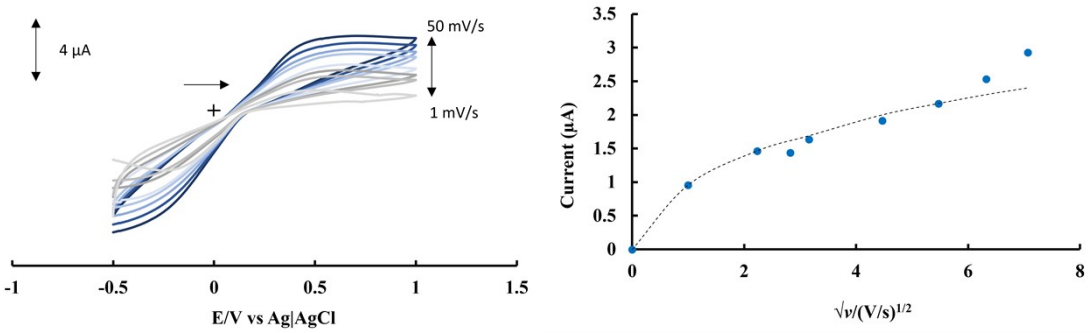


Fig. S4. CV result of 1 mM $K_3[Fe(CN)_6]$ in 0.1 M sodium phosphate solution (pH = 7) at paper-based sensor.

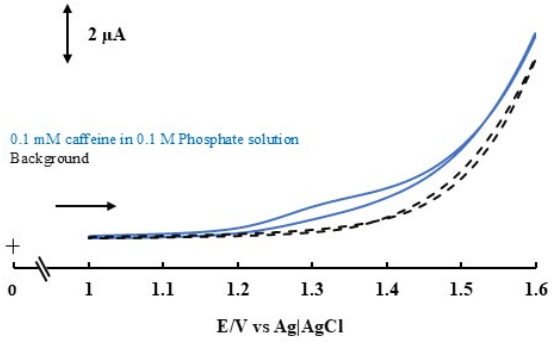


Fig. S5. CV result of 1 mM caffeine in 0.1 M phosphate solution at paper-based sensor.

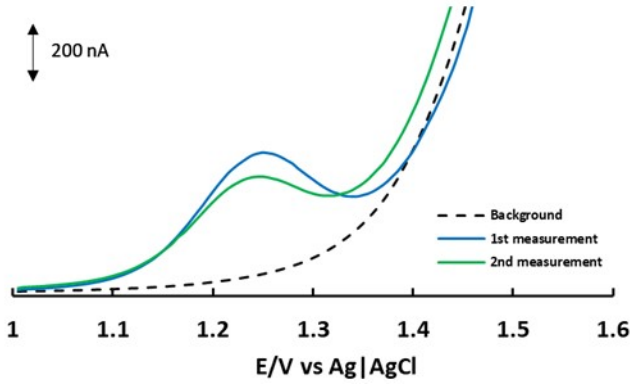
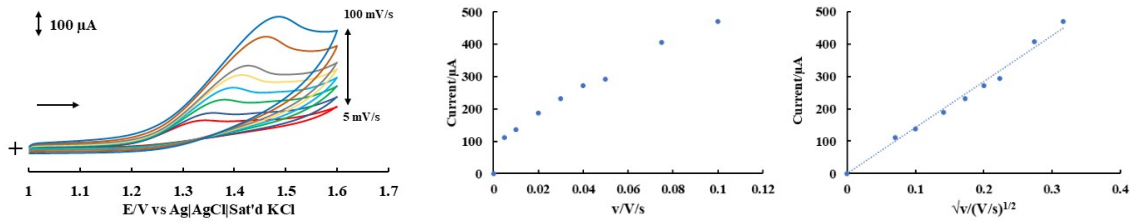


Fig. S6. SWV response of background (broken line) and caffeine detection for 1st measurement (solid blue line) and 2nd measurement (solid green line).

CV plot in 10 mM Caffeine



CV plot in 100 µM Caffeine

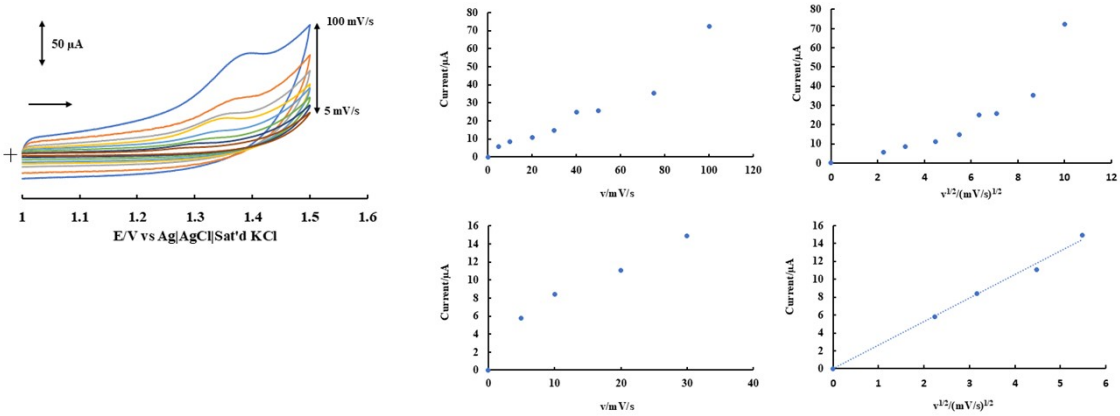


Fig. S7. Current vs square root scan rate ($v^{1/2}$) plot of caffeine in 0.1 M phosphate solution (pH 1) at MWCNTs-modified GCE.

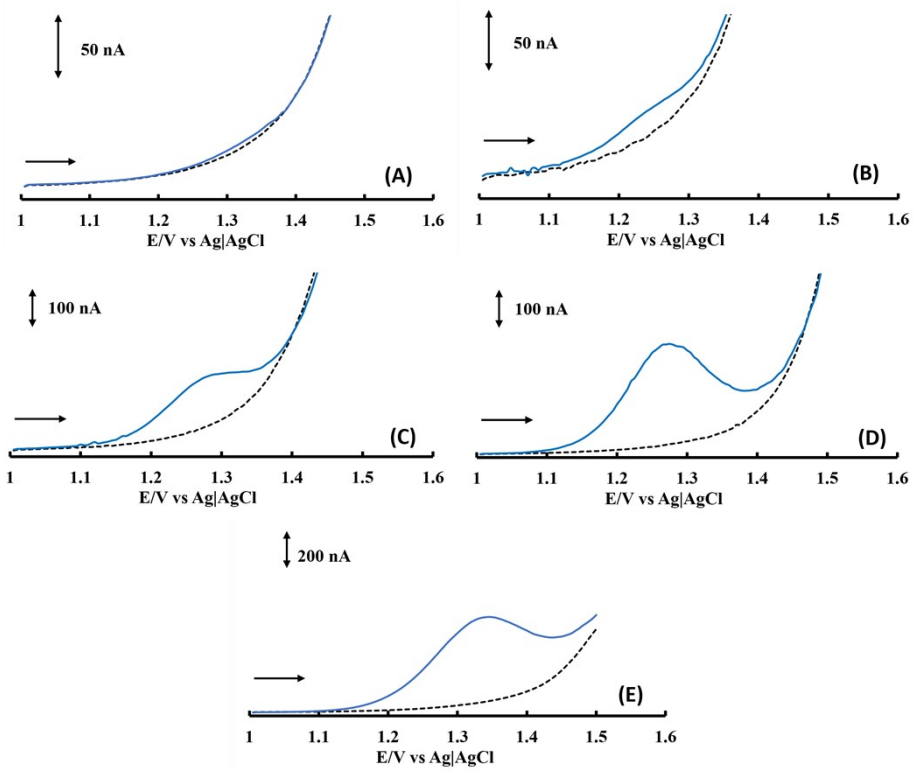


Fig. S8. SWV result of background (broken line) and 5 µM (A), 10 µM (B), 50 µM (C), 100 µM (D) and 200 µM (E) of caffeine (solid line).

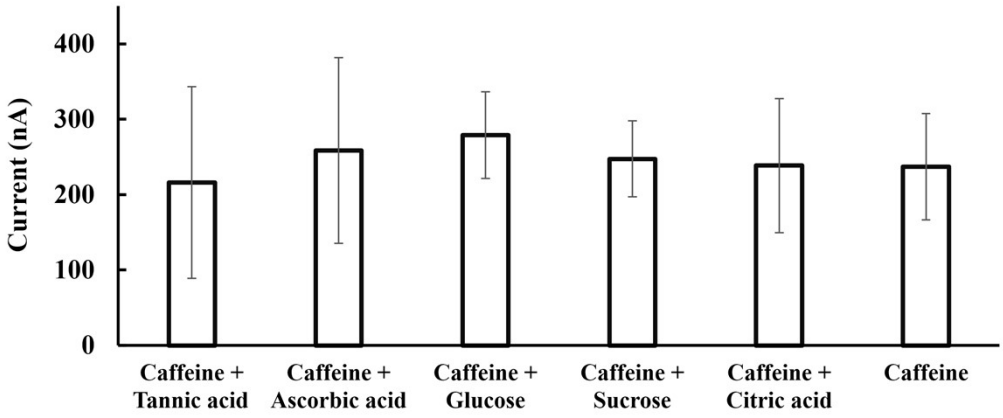


Fig. S9. Interference effect towards the oxidation of 0.1 mM caffeine in 0.1 M phosphate solution (interference: caffeine (10:1)). The reported error bars represented standard deviation from three independent measurements.

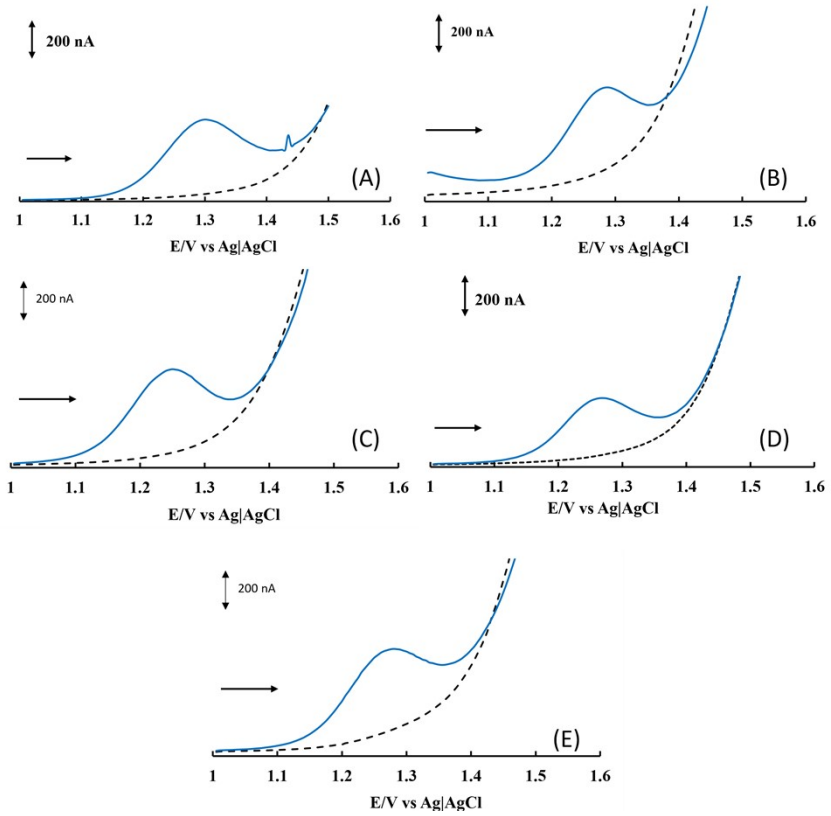


Fig. S10. SWV result of background (broken line) and interference molecule (solid line): tannic acid (A) ascorbic acid (B), glucose (C), sucrose(D) citric acid (E).

ANOVA result of interference study at 1:1 interferent to caffeine ratio

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Sucrose	3	675	225	1294
Glucose	3	721	241	1155
Ascorbic acid	3	716	239	409
Citric acid	3	668	223	6485
Tannic acid	3	753	251	1213
Caffeine	3	711	237	4616

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1625	5	325	0.13	0.98	3.11
Within Groups	30345	12	2529			
Total	31970	17				

ANOVA result of interference study at 10:1 interferent to caffeine ratio

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Tannic acid	3	648	216	24242
Ascorbic acid	3	776	259	28089
Glucose	3	837	279	1222
Sucrose	3	742	247	3812
Citric acid	3	716	239	11881
Caffeine	3	711	237	4616

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6869	5	1374	0.11	0.99	3.11
Within Groups	147723	12	12310			
Total	154592	17				

Table S1. pH values of the solution before and after the addition of the Coca-Cola and Coffee, demonstrating negligible change in the electrolyte acidity

pH of Electrolyte solution		1	1	1
pH after addition of the samples	Coca-Cola	1	1	1
	Coffee	1	1	1

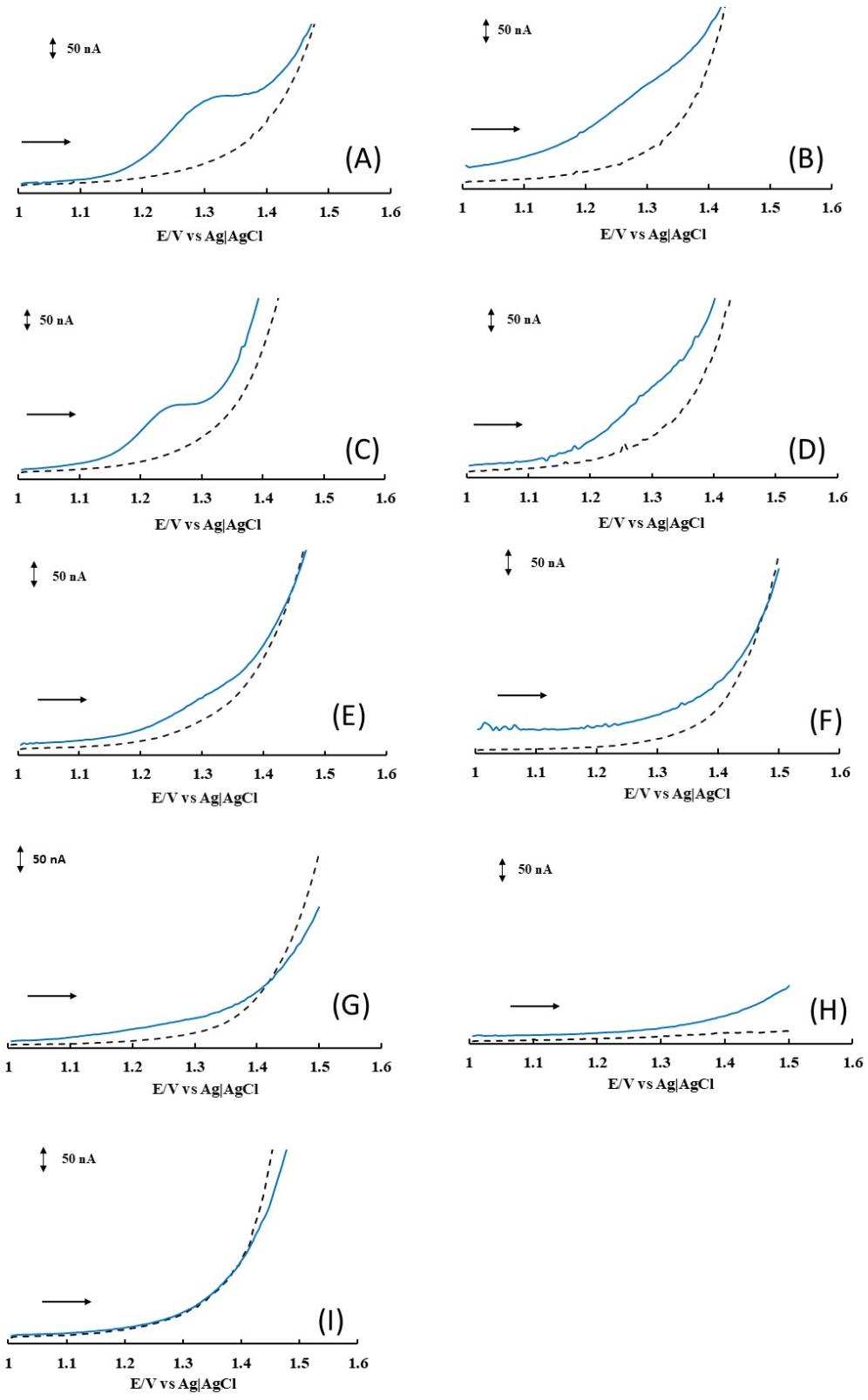


Fig. S11. SWV result of background (broken line) and caffeine drinks (solid line): monster energy (A), Black coffee – Georgia (B), coca – cola (C), oi ocha-green tea(D), CGC - oolong tea (E), oronamin C (F), UCC - decaffeinated coffee (G), kokoa – kikoma (H), Salted lychee (I).

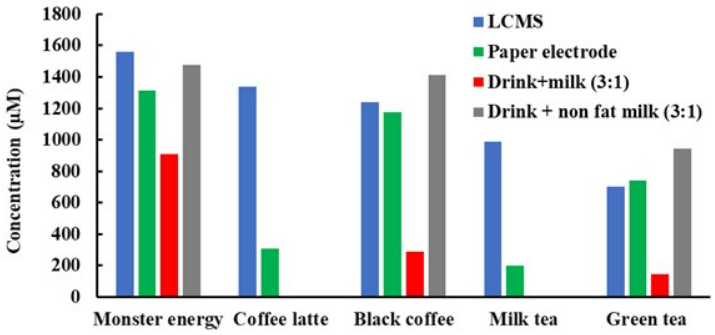


Fig. S12. Comparison of caffeine concentration measured with paper-based electrode and LC-MS in the presence of milk effect.

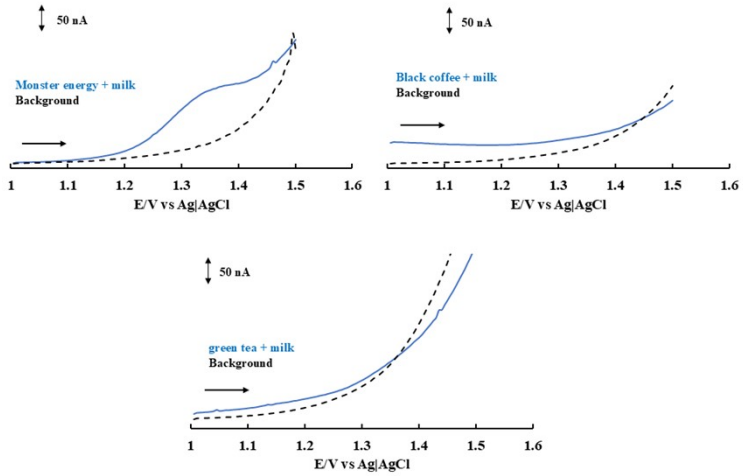


Fig. S13. SWV measurement result of background (broken line) and milk mixture drinks (solid line) for caffeine detection.

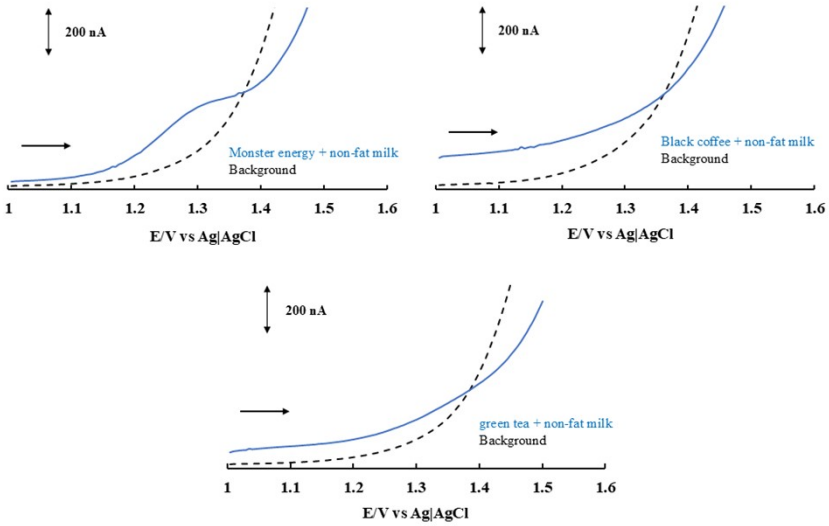


Fig. S14. SWV measurement result of background (broken line) and non-fat milk mixture drinks (solid line) for caffeine detection.

Calculation of diffusion coefficient (D) by Randles-Shevcik equation.

$$i_p = \pm (2.69 \times 10^5) n^{\frac{3}{2}} A D^{\frac{1}{2}} C v^{\frac{1}{2}}$$

Were,

$\frac{i_p}{v^{\frac{1}{2}}}$ = slope of current vs square root scan rate = $1.41 \times 10^{-3}\ A\ V^{-1/2}\ s^{1/2}$

n = electron involved = 4

A = Surface area = $28.3\ mm^2$ = $0.0283\ cm^2$

C = Concentration = $0.00001\ mol\ cm^{-3}$

Therefore,

D = diffusion coefficient = 5.36×10^{-6} cm^2 s^{-1}

Calculation of diffusion coefficient (D) by Stoke-Einstein equation

$$D = \frac{RT}{6\pi r \eta N}$$

Where,

R = gas constant = 8.314×10^7 erg mol^{-1} K^{-1}

T = Temperature = 273 + 25 = 298 K

r = radius

Rx = 0.78 nm

Ry = 0.61 nm

Rz = 0.21 nm

N = Avogrado number = 6.02×10^{23}

η = viscocity of solvent (η_{25} pure water) = 0.00895 poise

Therefore,

Dx = $3.1 \times 10^{-6}\ cm^2 s^{-1}$

Dy = $4 \times 10^{-6}\ cm^2 s^{-1}$

Dz = $1.2 \times 10^{-5}\ cm^2 s^{-1}$