

Supporting Information: An Amperometric Sensor with Anti-fouling Properties for Indicating Xylazine Adulterant in Beverages

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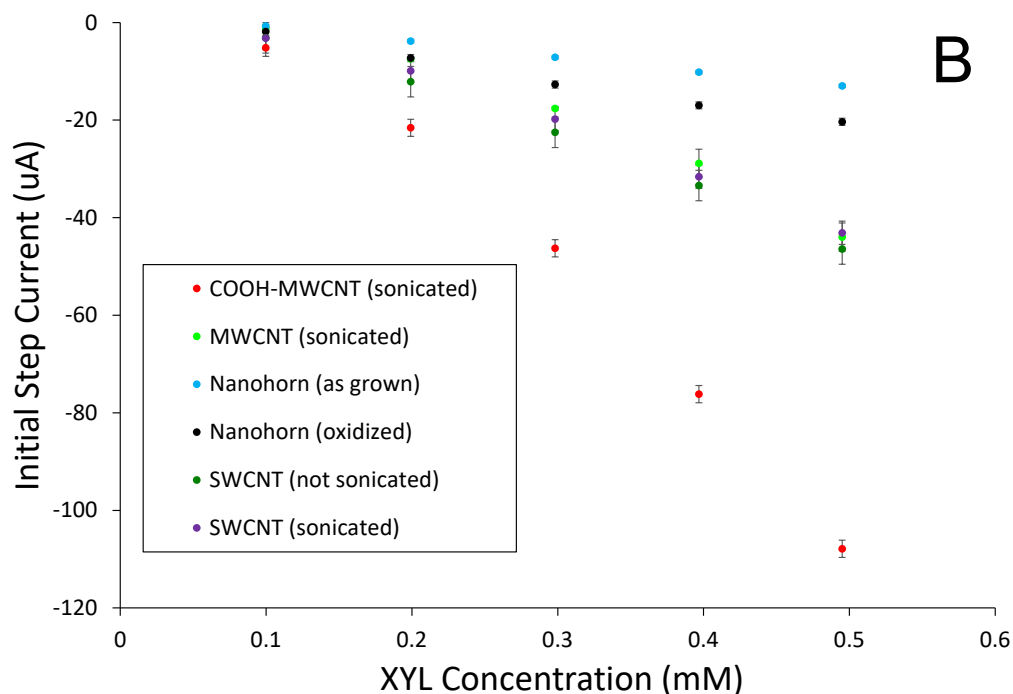
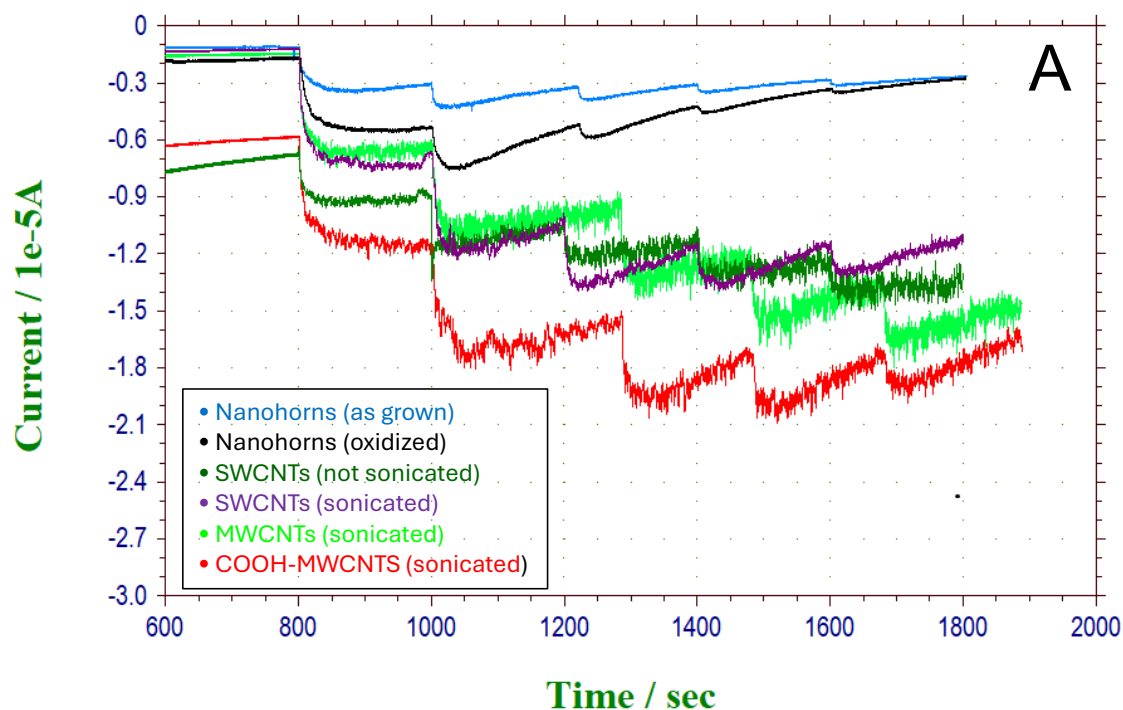


Figure S1. (A) Representative amperometric I-t curves during five successive injections of 0.1 mM XYL at GCE electrodes modified with various nanomaterials (sonicated with β -CD and deposited (7 μ L) and capped with a Nafion layer (7 μ L); (B) initial step current tracking with various incorporated NMs (n=3).

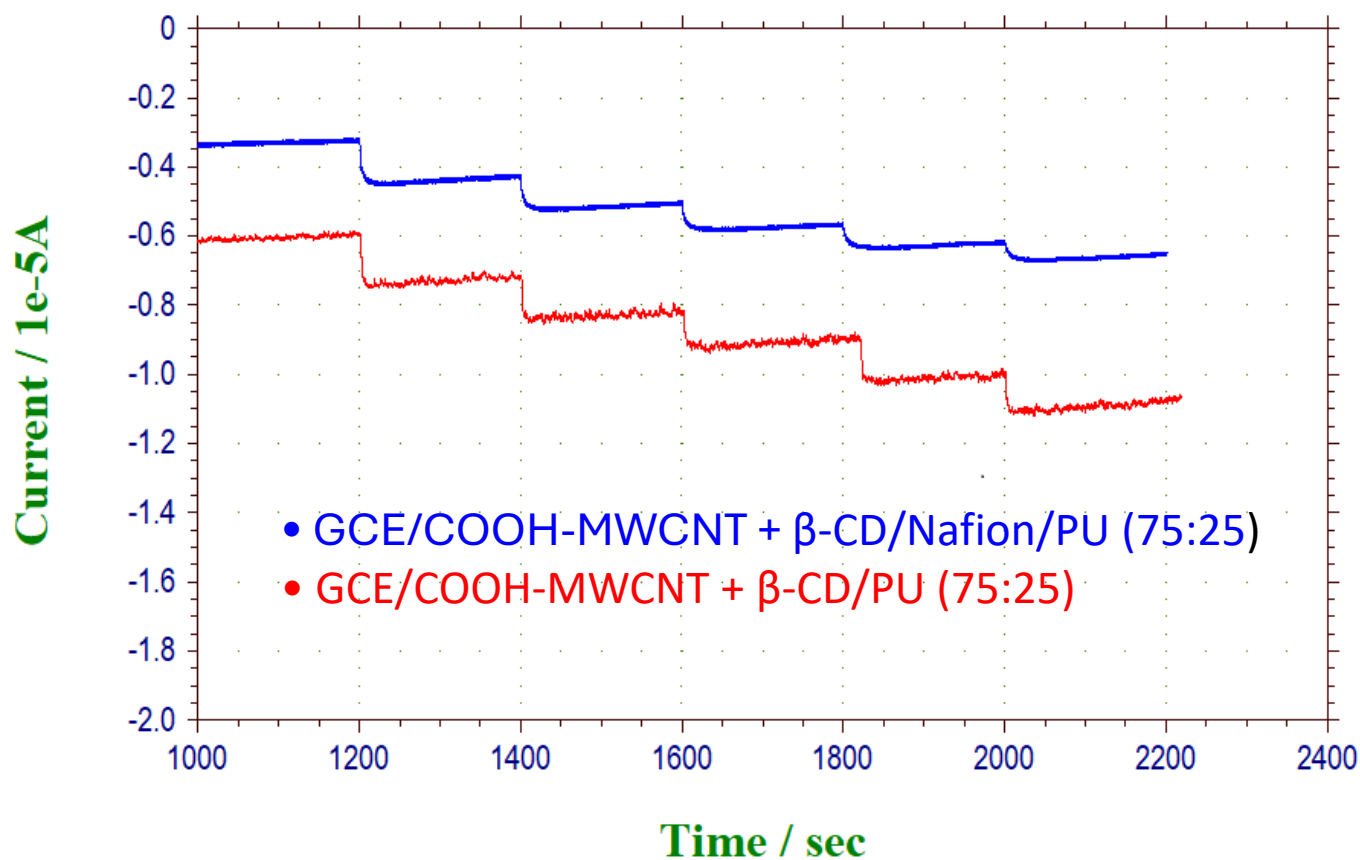


Figure S2. Representative amperometric I-t curves during five successive injections of 0.1 mM XYL at GCE electrodes modified COOH-MWCNTs with β -CD and capped with either Nafion and an outer PU blended layer or only a PU-blended layer. More defined and regular stepping was consistently observed on systems without the Nafion layer and sonication technique/application did not affect this trend.

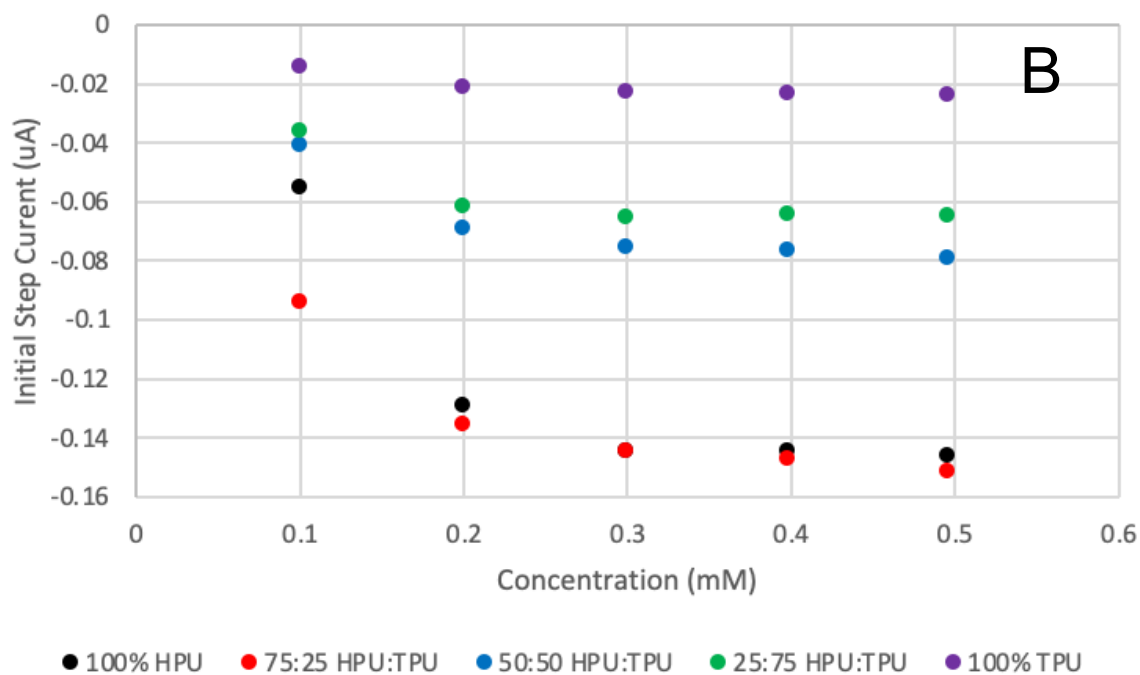
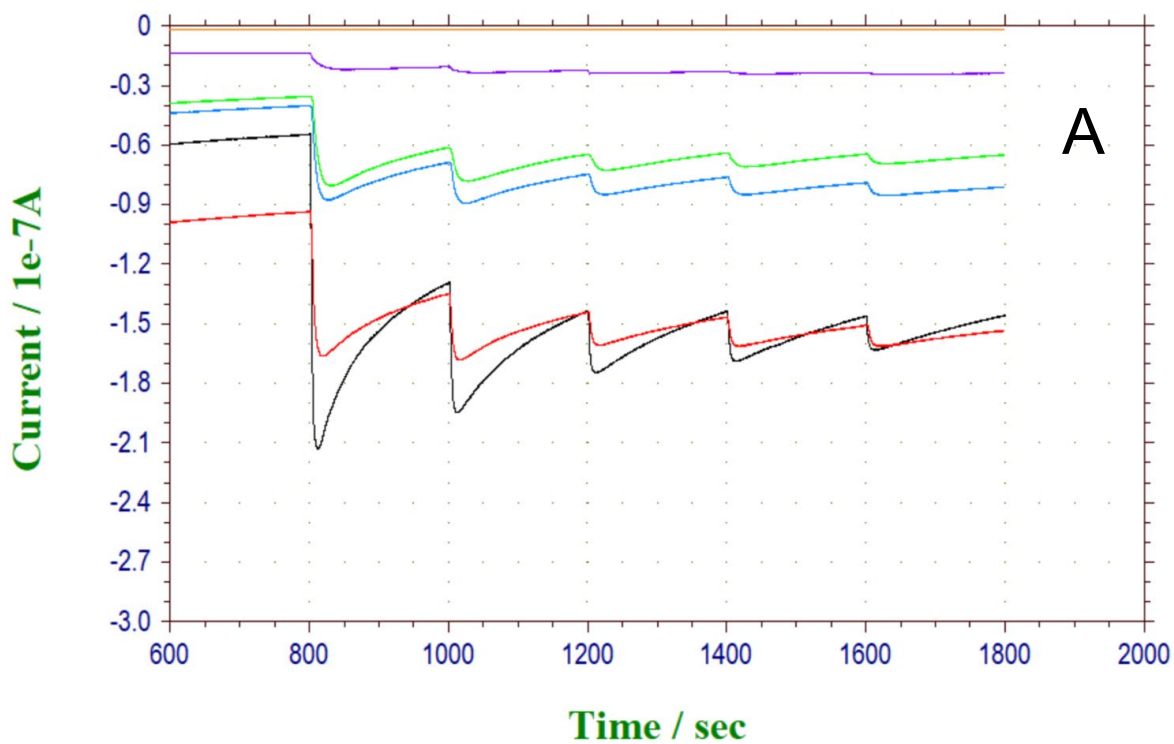


Figure S3. (A) Representative amperometric I-t curves and (B) corresponding current tracking example during five successive injections of 0.1 mM XYL at unmodified (bare) GCEs modified with only different blends of PU (i.e., different ratios of HPU to TPU).

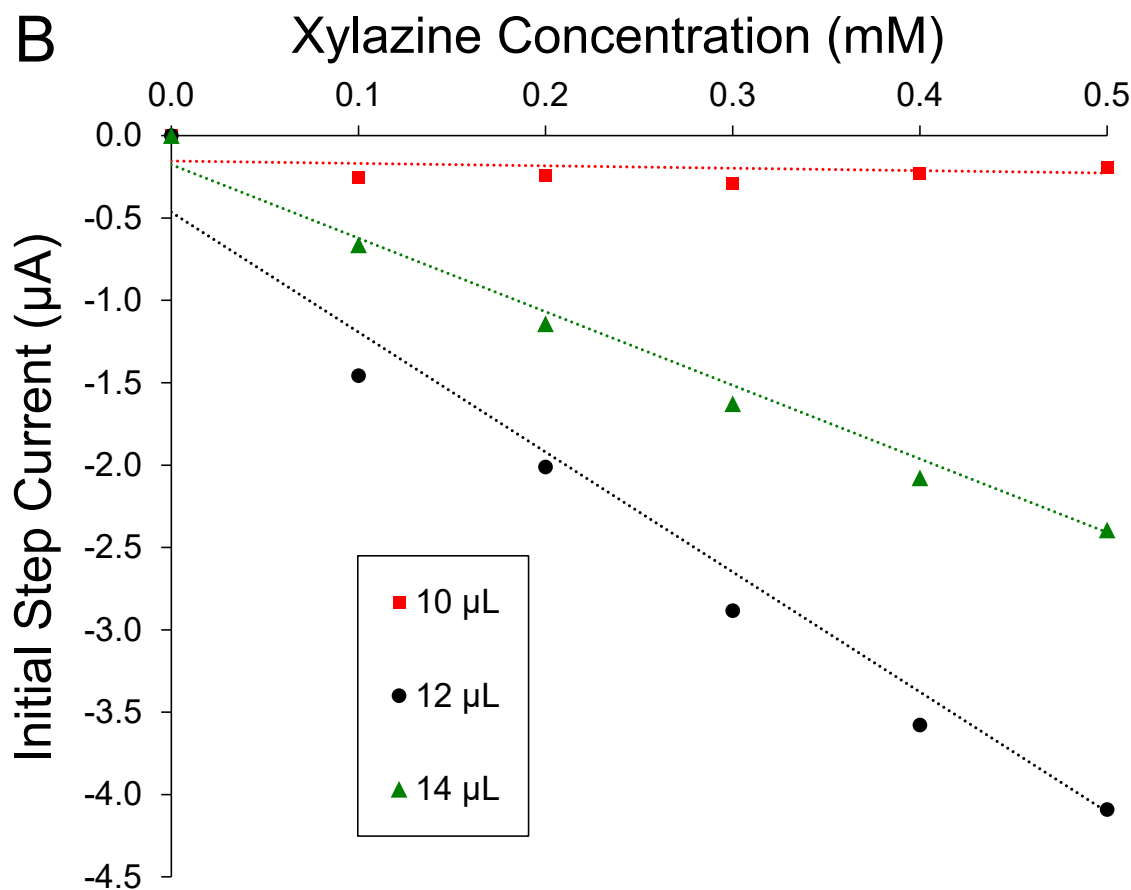
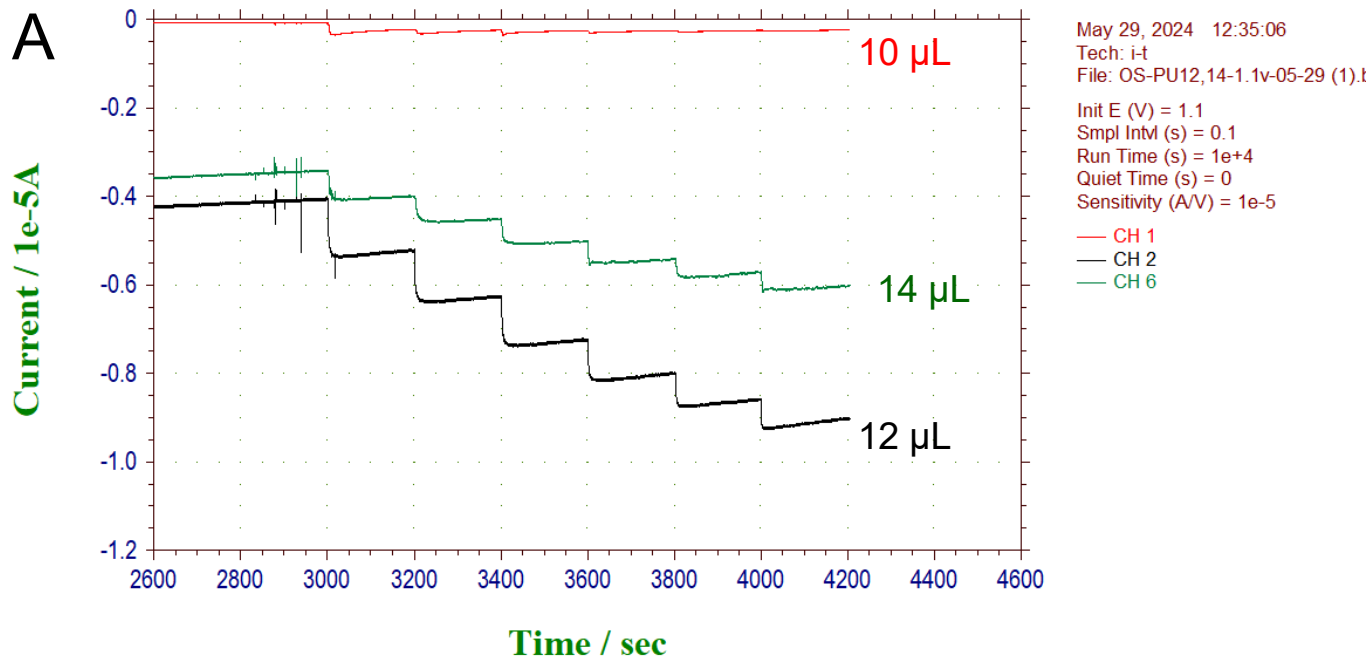


Figure S4. (A) Representative amperometric I-t curves and (B) corresponding current tracking example during five successive injections of 0.1 mM XYL at fully modified electrodes (GCE/COOH-MWCNT/ β -CD/PU (75:25) where PU deposition volume (thickness of PU layer) is varied.

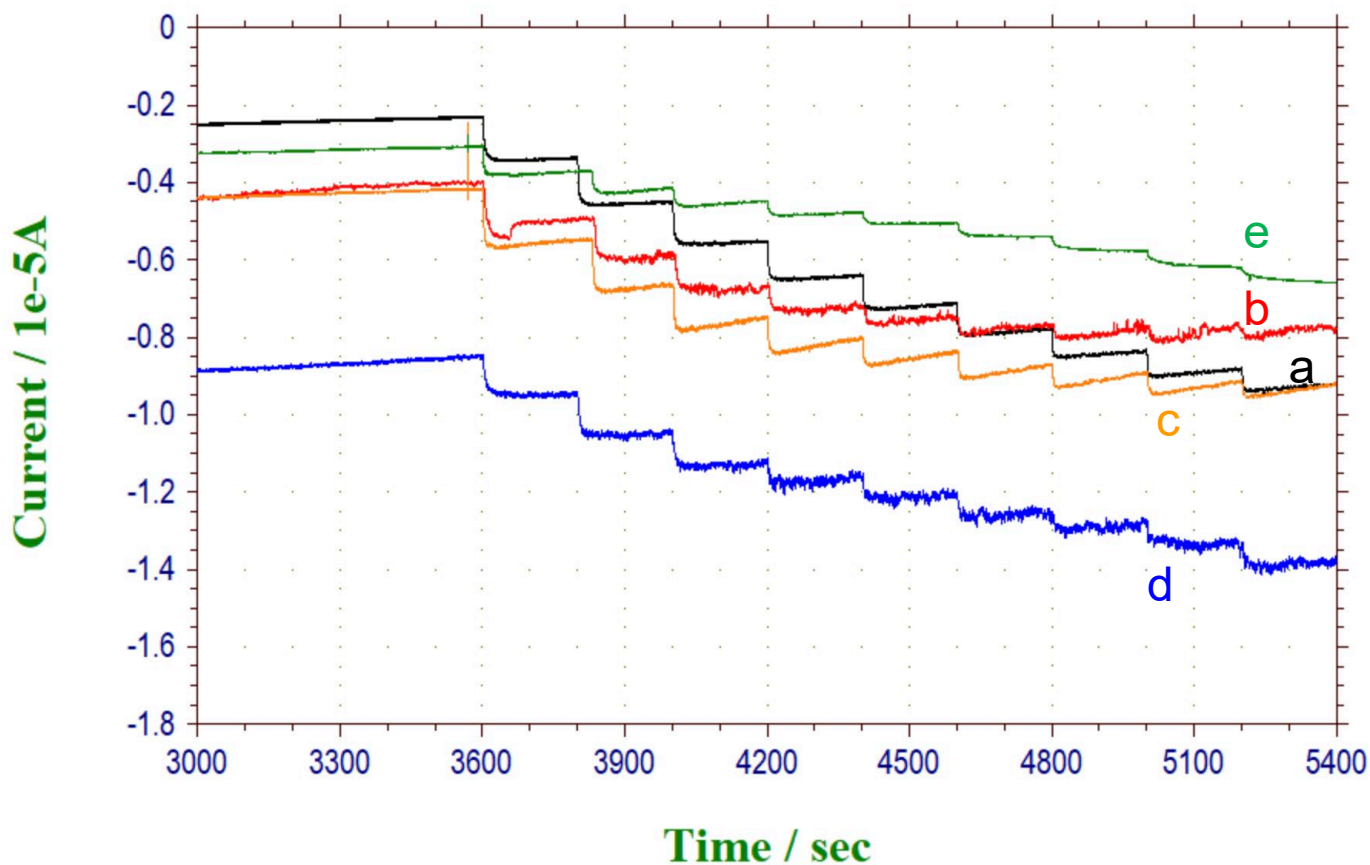


Figure S5. Representative amperometric I-t curves during successive injections of 0.1 mM XYL at fully modified GCE (GCE/COOH-MWCNT/PU) featuring different composition ratios (i.e., blends) of HPU to TPU: (a) 100:0; (b) 75:25; (c) 50:50; (d) 25:75; (e) 0:100.

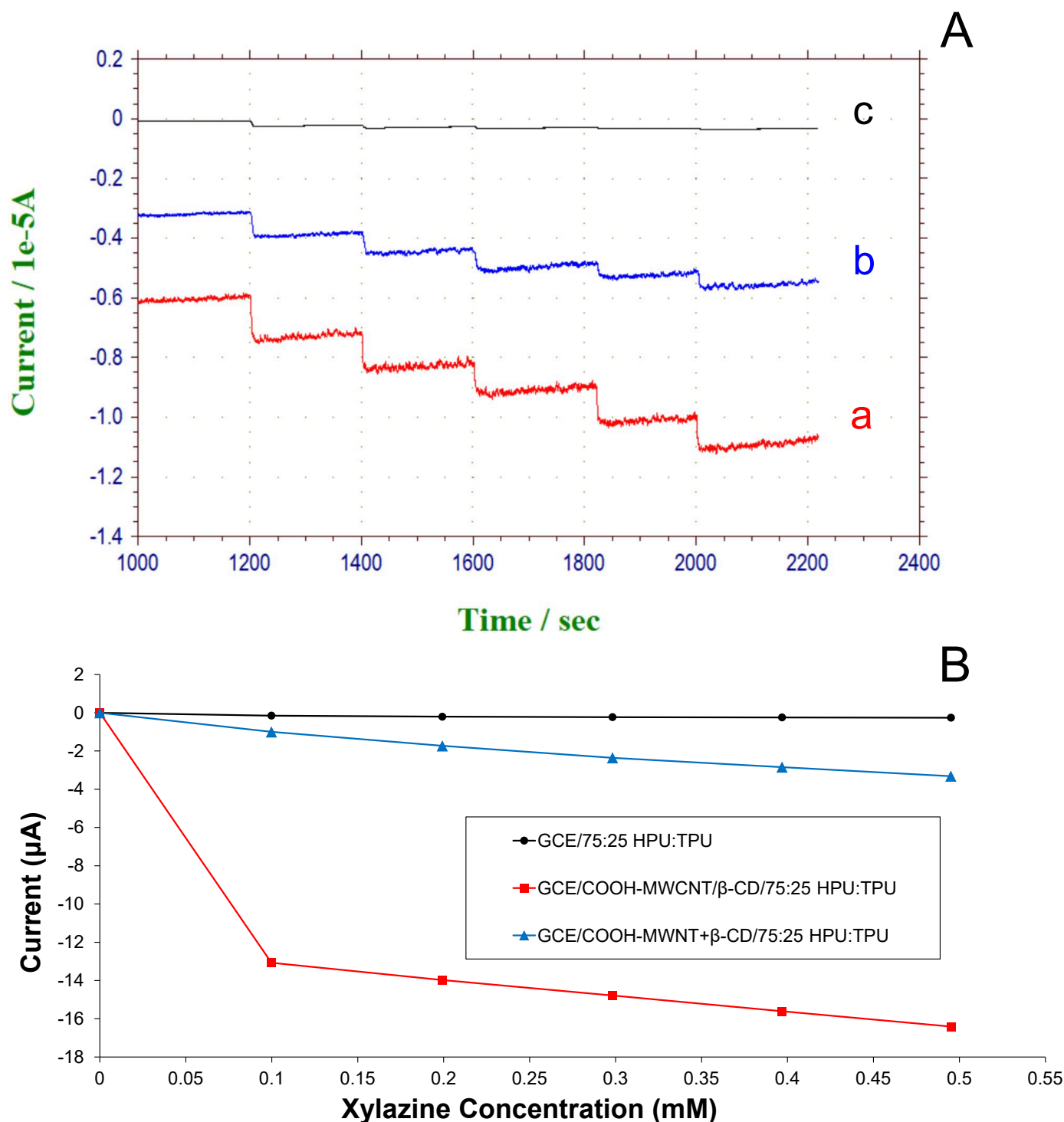


Figure S6. (A) Representative amperometric I-t curves and (B) corresponding tracking of current as a function of XYL concentration during five successive injections of 0.1 mM XYL at GCE electrodes modified with COOH-MWCNTs and β -CD and capped with PU (75:25) where the MWCNT and β -CD were (a) layered separately after sonication, (b) sonicated as a mixture and layered together, or (c) not incorporated into the film (i.e., GCE modified with only PU (75:25)).

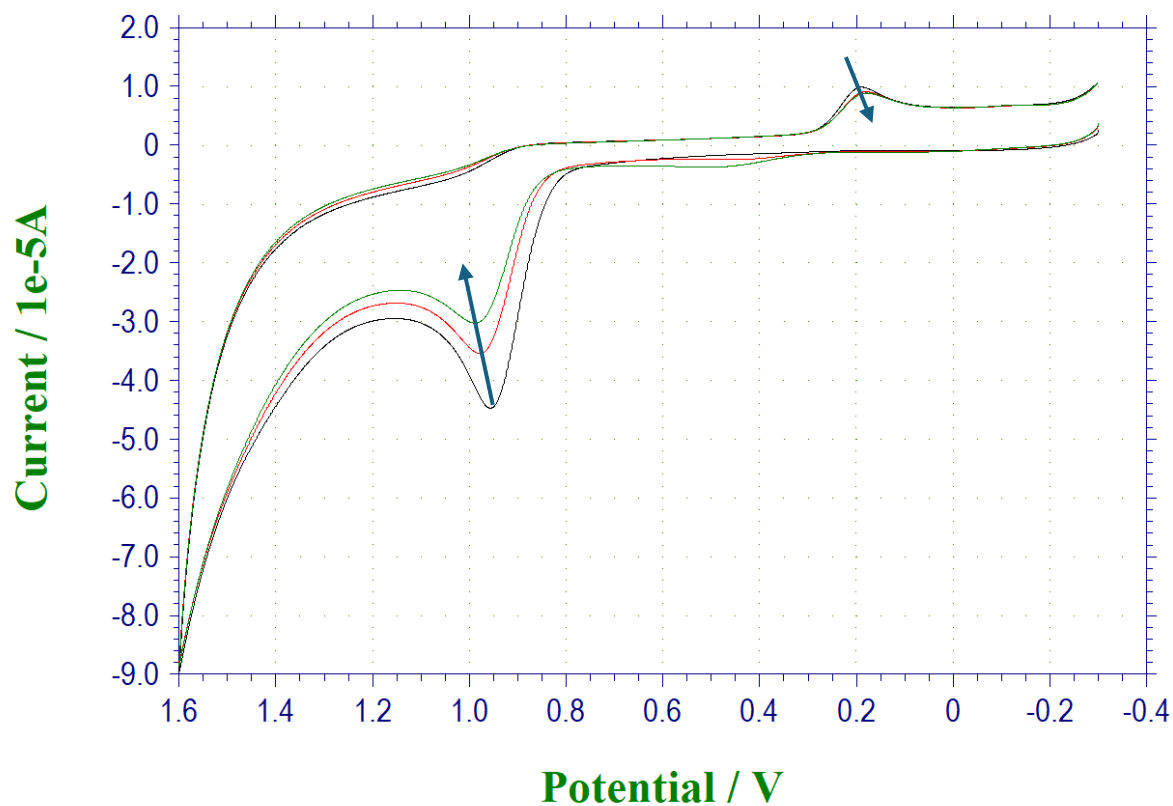


Figure S7. Typical CV of 1 mM XYL in 150 mM PBS (pH = 7) showing three full scans of XYL at a bare/unmodified GCE with peaks showing XYL oxidation at ~ 0.95 V and the reduction of that oxidation product at ~ 0.2 V (vs. Ag/AgCl, satrd. KCl) including evidence of electrode fouling as oxidation peaks diminish and shift more positive with each scan.

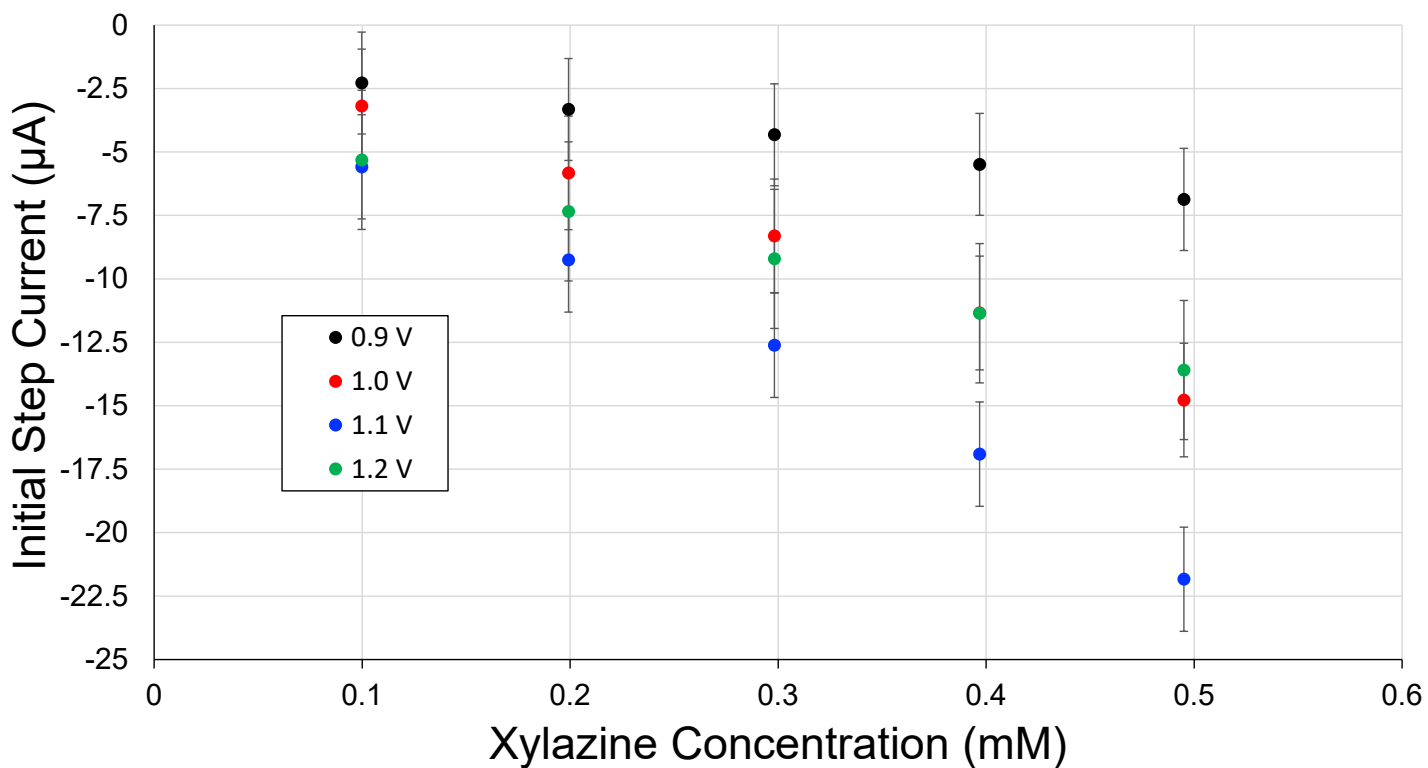


Figure S8. Example of corresponding current tracking from **Fig. 2C** for fully-modified electrode (GCE/COOH-MWCNT/ β -CD/PU(75:25)) during injections of 0.1 mM XYL at different applied holding potentials: +0.9, +1.0, +1.1, and +1.2 V.

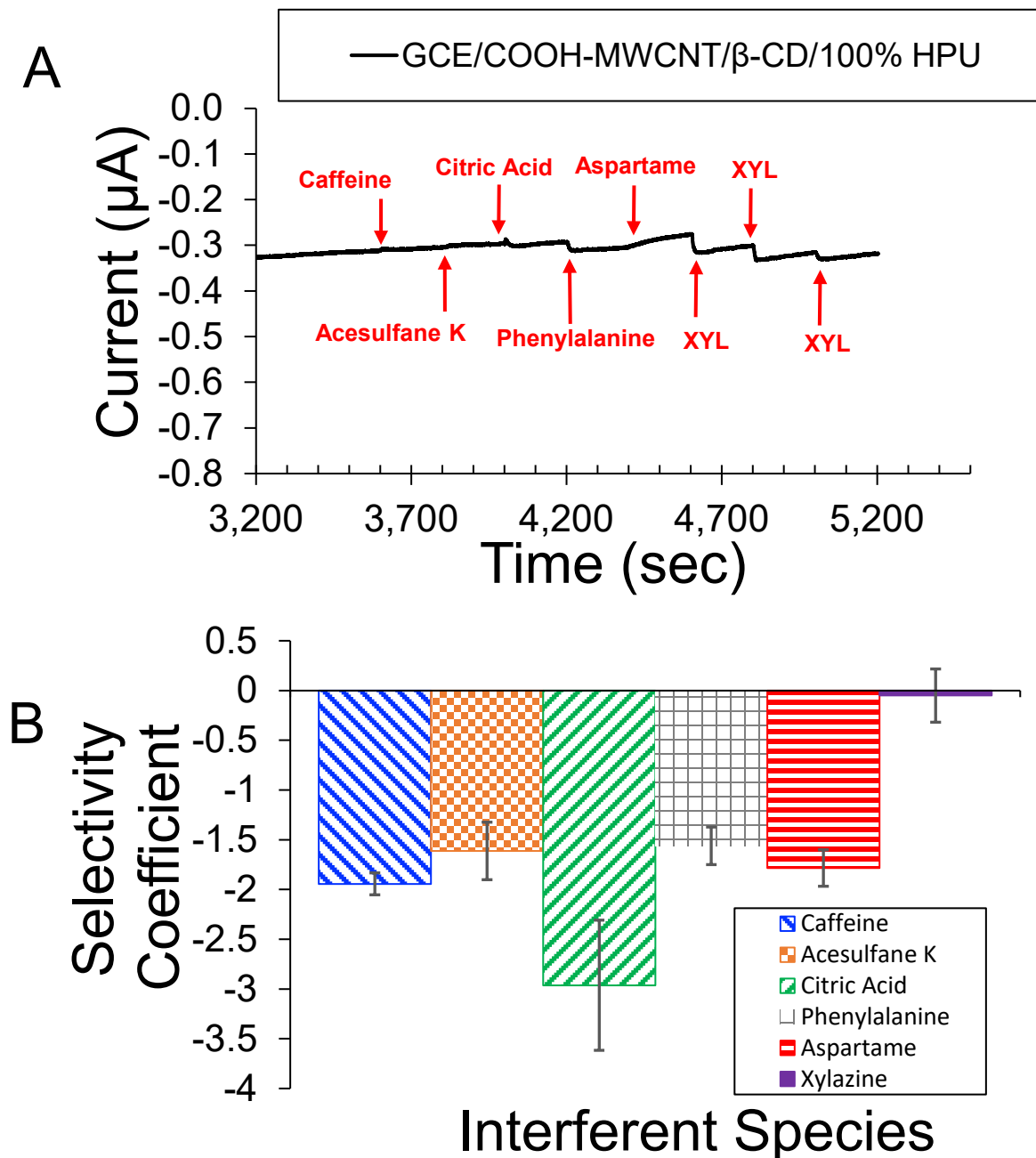
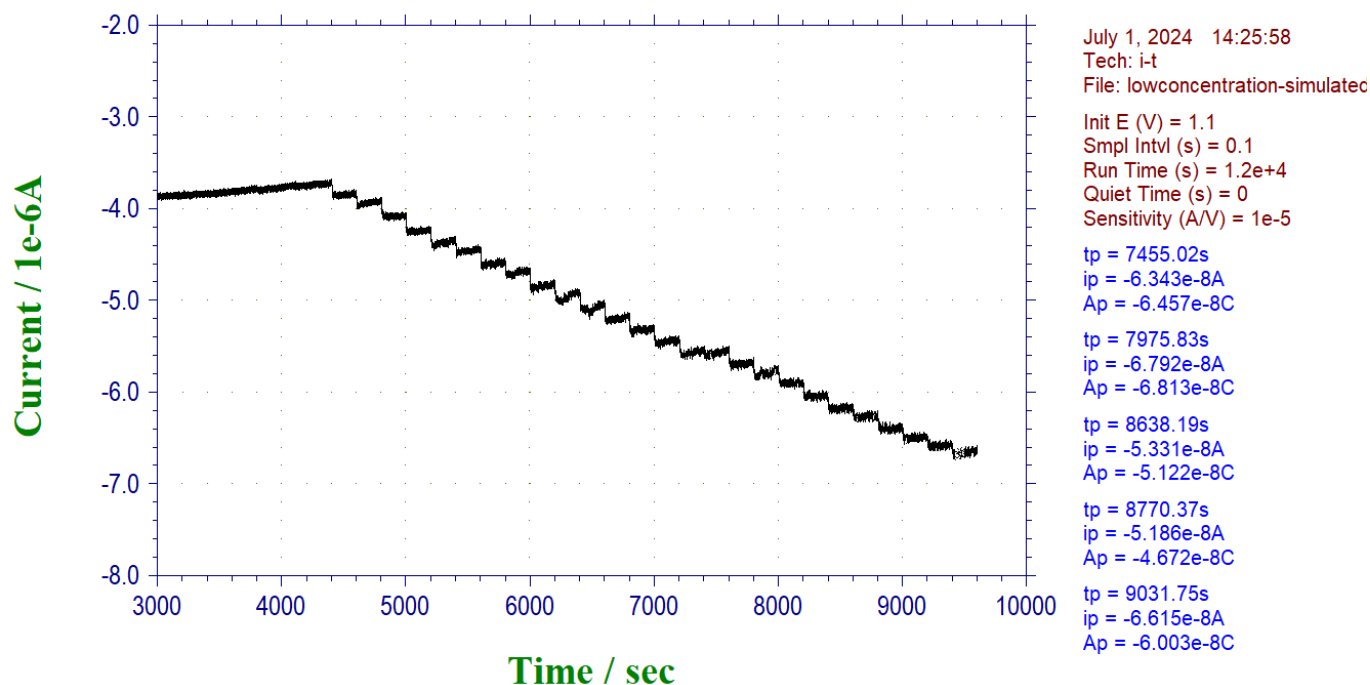


Figure S9. (A) Amperometric I-t curves during XYL injections (50 μL of 50 mM XYL standard) and potential interferent species in **diet soda** including (0.49 mM caffeine, 0.21 mM Acesulfane K, 8.95 mM citric acid, 0.95 mM phenylalanine, 2.21 mM aspartame at a modified electrode; (B) corresponding graph of calculated selectivity coefficients for the potential interferent species.

A



B

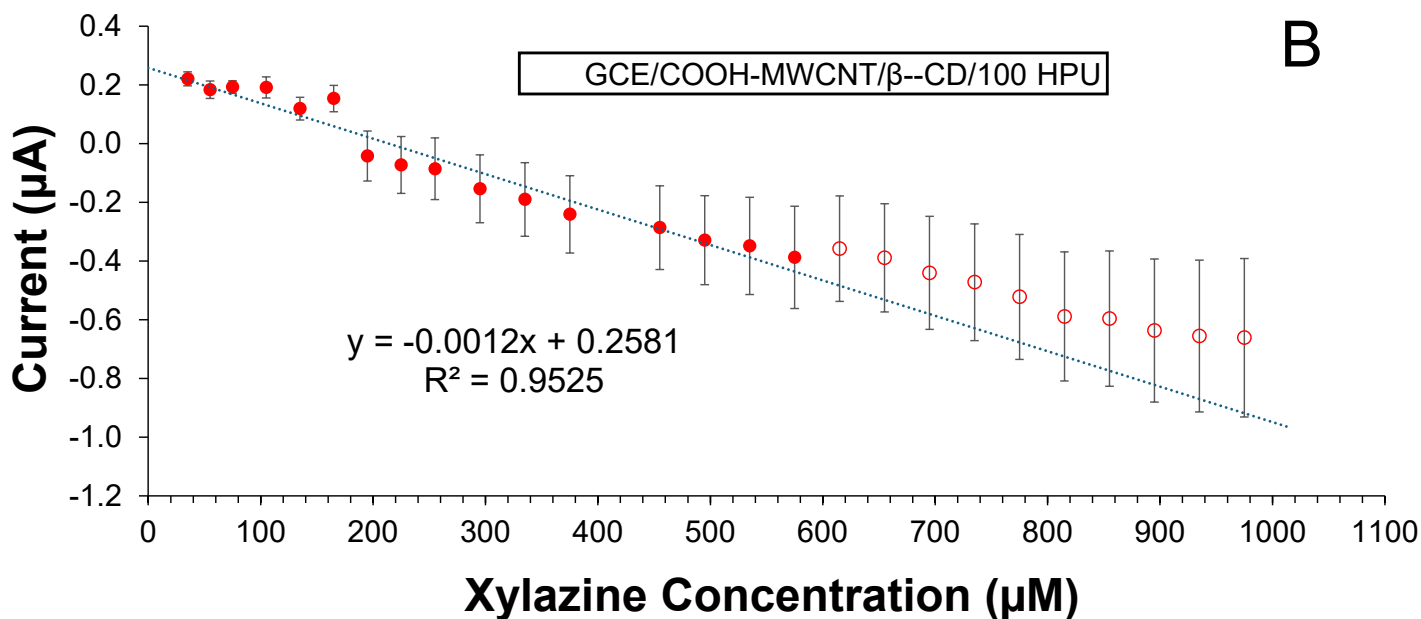
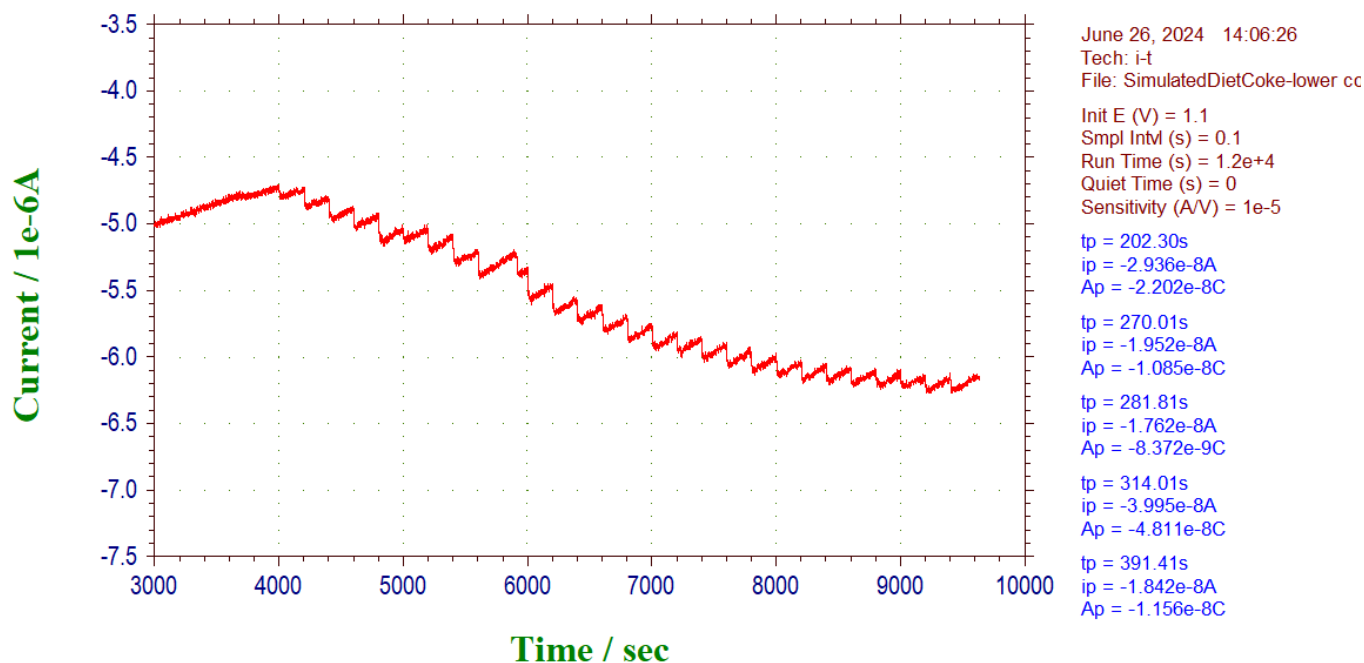


Figure S10. (A) Representative amperometric I-t curve example and (B) corresponding calibration curve (n=3) for successive injections of 0.1 mM XYL at modified electrodes (GCE/COOH-MWCNT/β-CD / PU (100:0) immersed in a **simulated non-diet soda** solution including the linear range (closed symbols) and dynamic range (open symbols). Note: In some cases, standard error bars are smaller than markers denoting the average.

A



B

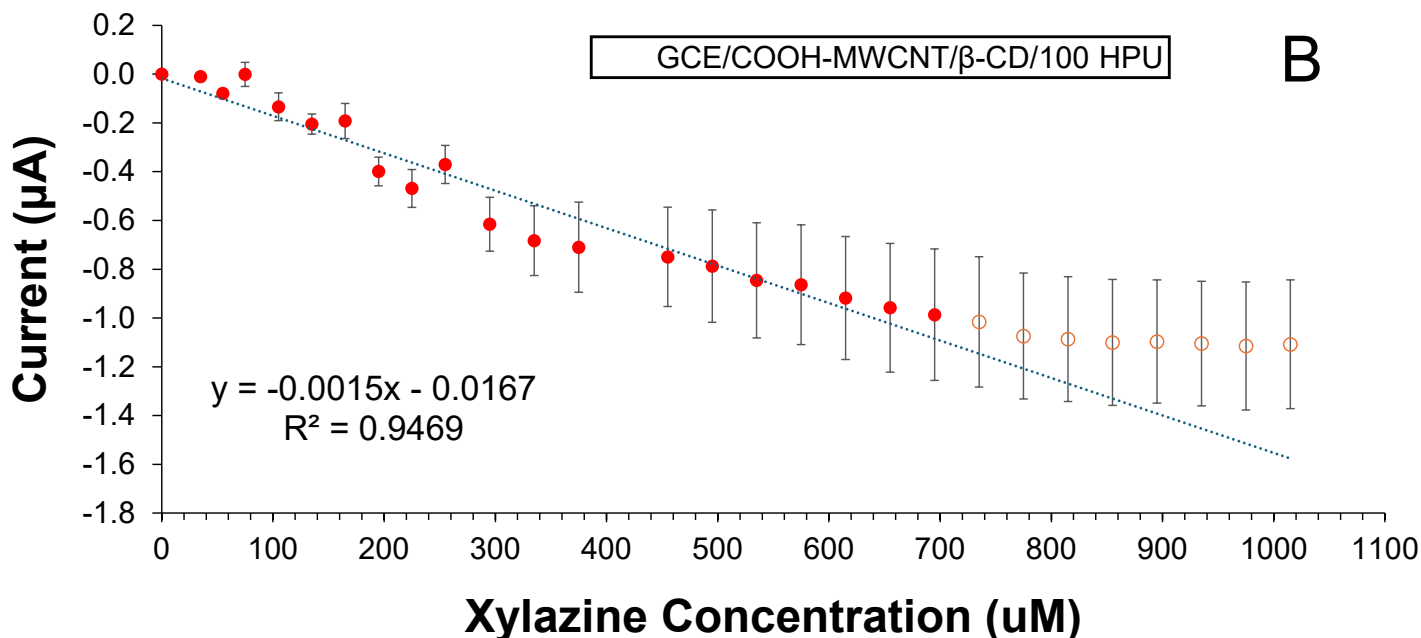


Figure S11. (A) Representative amperometric I-t curve example and (B) corresponding calibration curve (n=5) for successive injections of 0.1 mM XYL at modified electrodes (GCE/COOH-MWCNT/β-CD / PU (100:0) immersed in a **simulated diet soda** solution including the linear range (closed symbols) and dynamic range (open symbols). Note: In some cases, standard error bars are smaller than markers denoting the average.

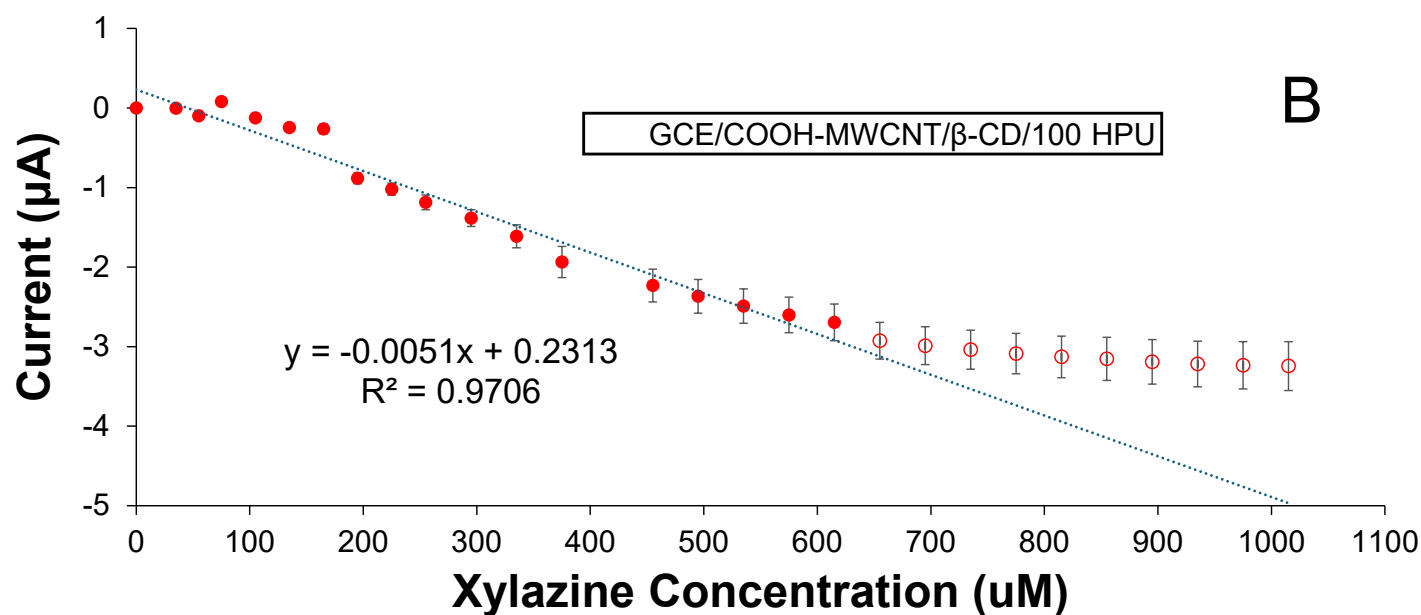
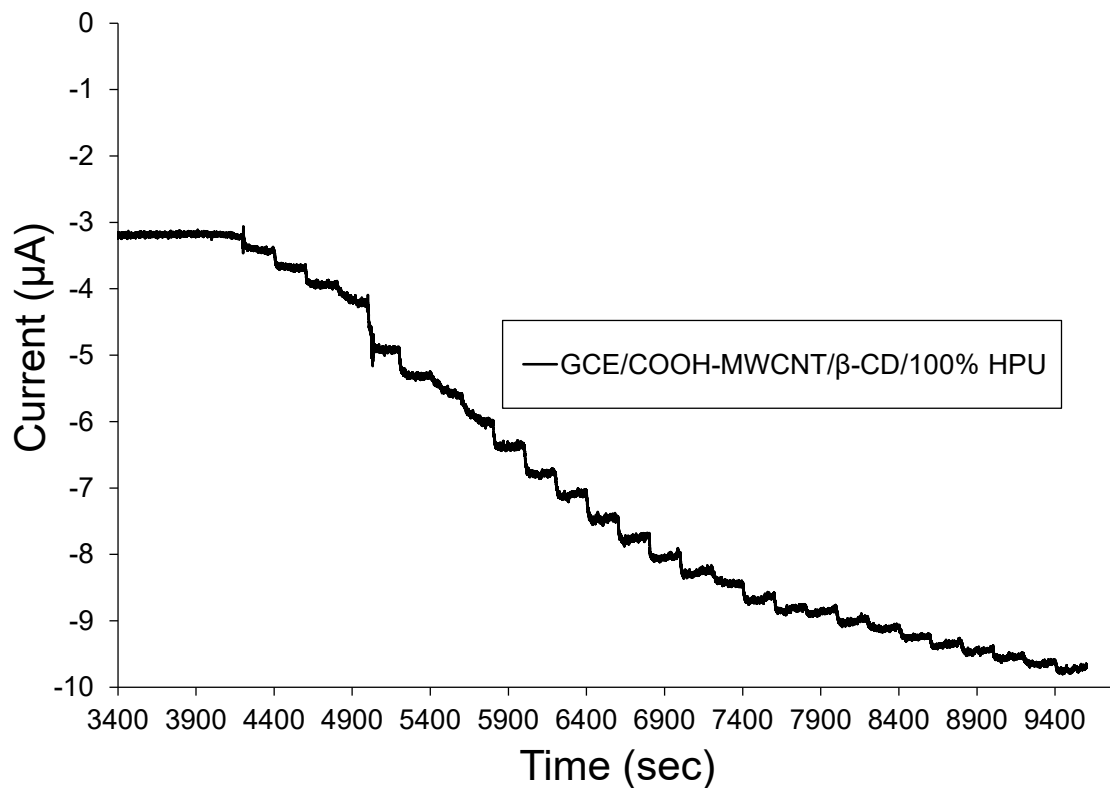
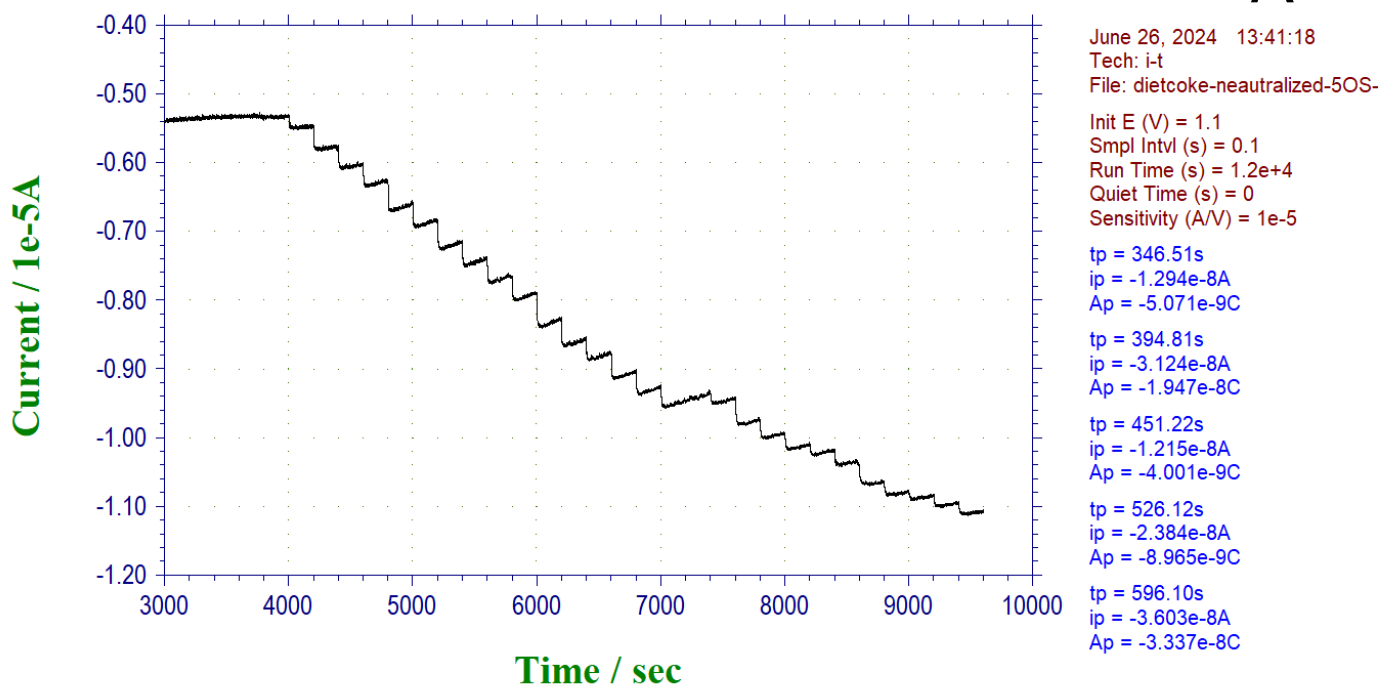


Figure S12. (A) Representative amperometric I-t curve example and (B) corresponding calibration curve ($n=5$) for successive injections of 0.1 mM XYL at modified electrodes (GCE/COOH-MWCNT/ β -CD / PU (100:0) immersed in a **soda (i.e., Coke)** solution including the linear range (closed symbols) and dynamic range (open symbols). Note: In some cases, standard error bars are smaller than markers denoting the average.

A



B

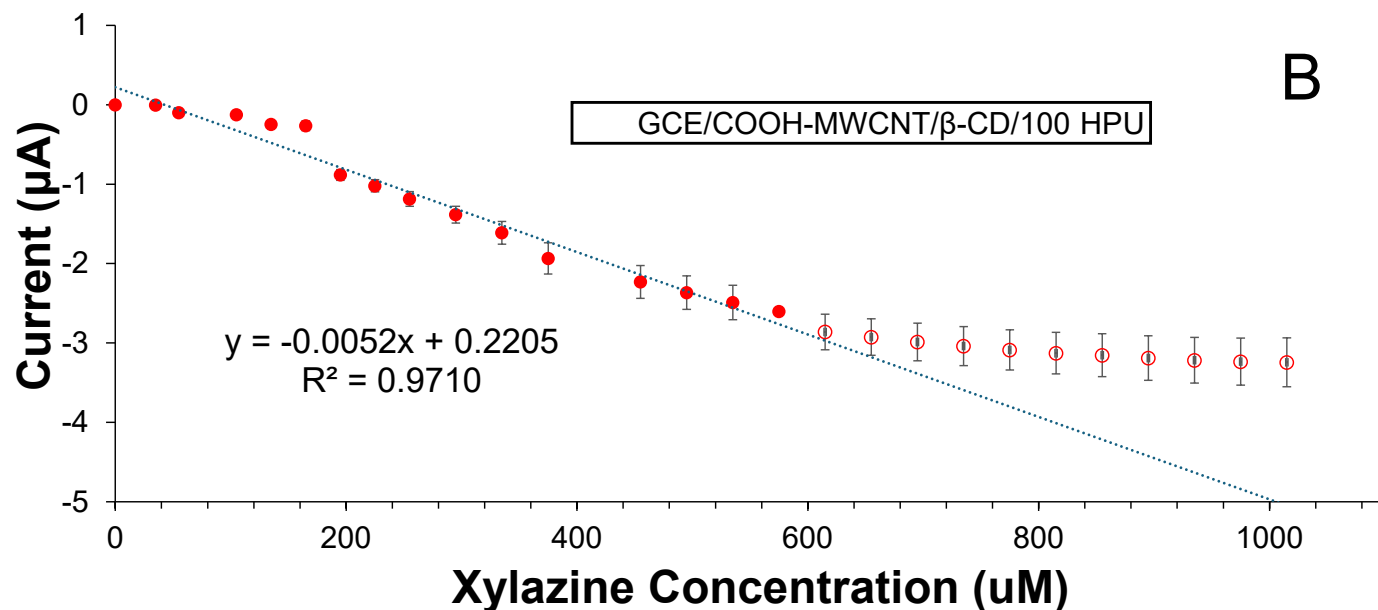


Figure S13. (A) Representative amperometric I-t curve example and (B) corresponding calibration curve (n=5) for successive injections of 0.1 mM XYL at modified electrodes (GCE/COOH-MWCNT/ β -CD / PU (100:0) immersed in a **diet soda** (i.e., **Diet Coke**) solution including the linear range (closed symbols) and dynamic range (open symbols). Note: In some cases, standard error bars are smaller than markers denoting the average.

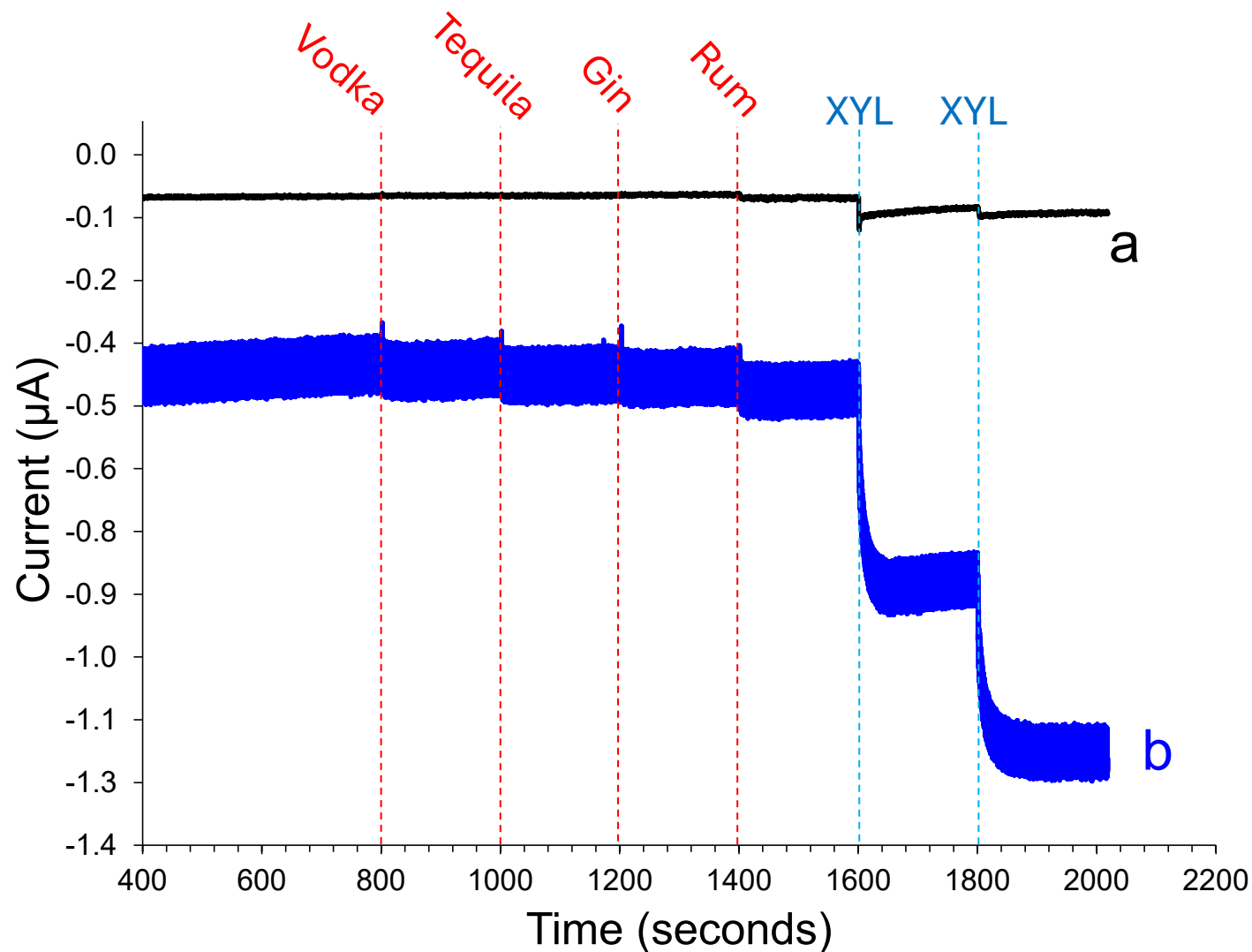


Figure S14. Representative amperometric I-t curves for (a) bare/unmodified GCE versus (b) fully modified GCE (GCE/COOH-MWCNT/β-CD/PU) during successive 500 μL injections of potential interferents (**alcoholic beverages**) including vodka (800 sec), tequila (1000 sec), gin (1200 sec), and rum (1400 sec) as well as **XYL standards** (50 μL of 50 mM XYL at 1600 and 1800 sec) into 25 mL of 150 mM PBS.

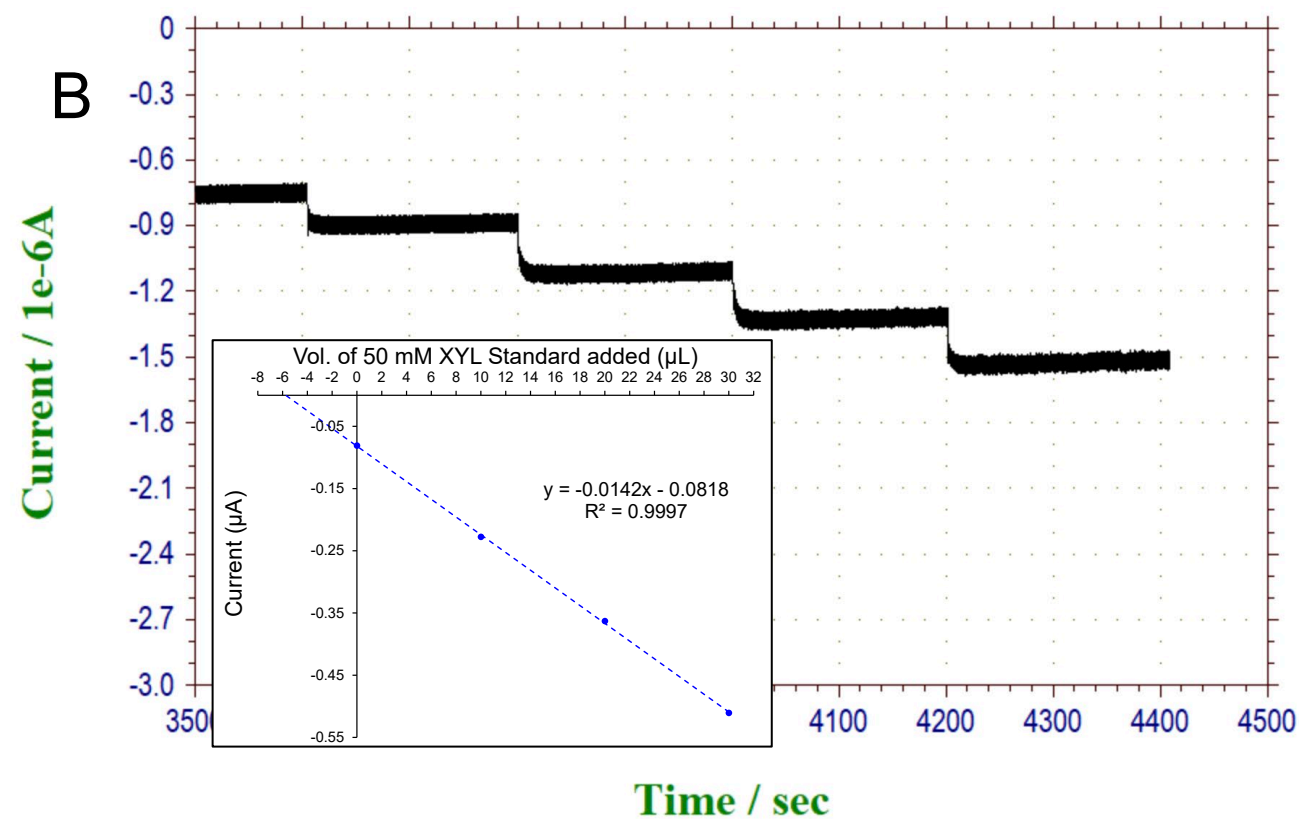
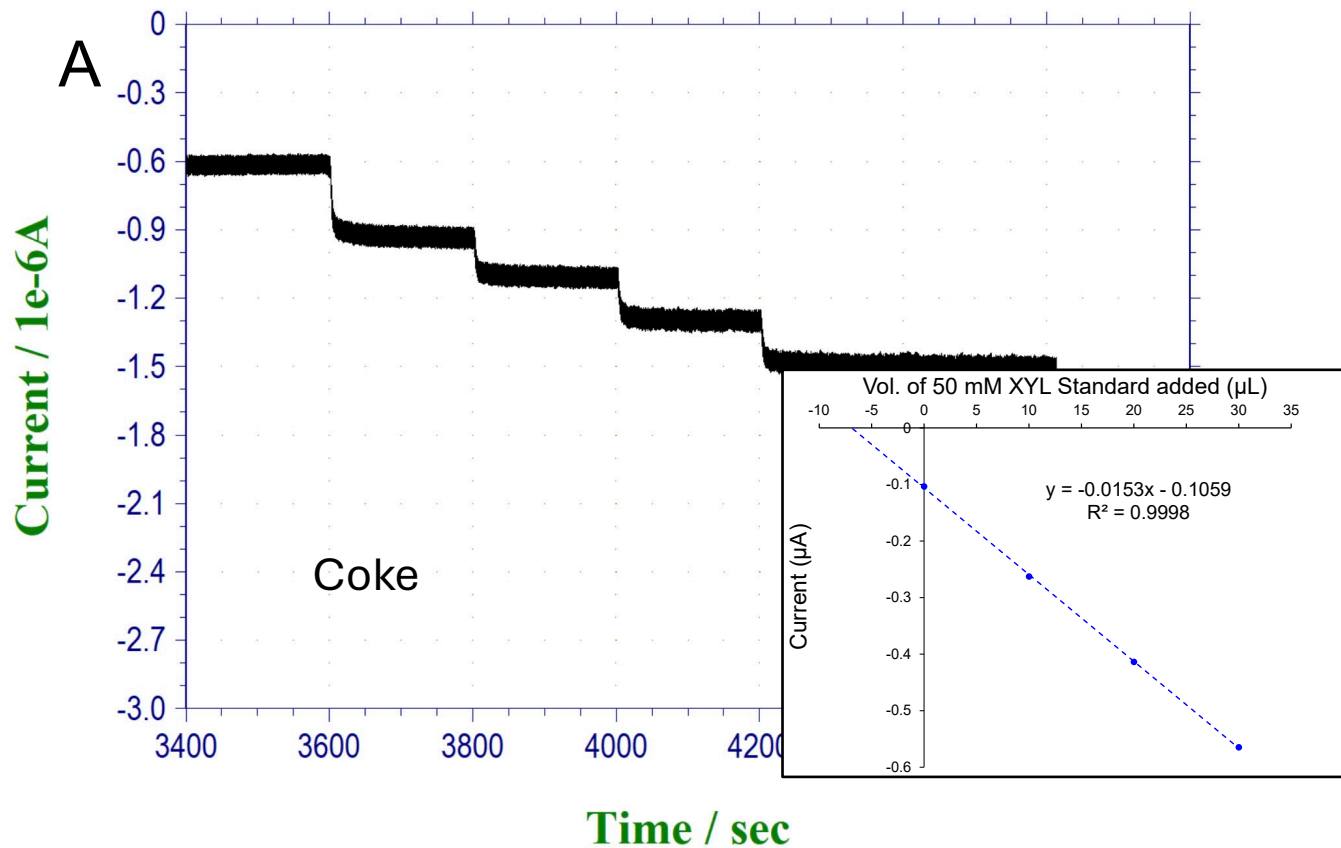


Figure S15. Representative amperometric I-t curve and typical standard addition plot (**inset**) for XYL analysis in (A) gin and (B) rum.

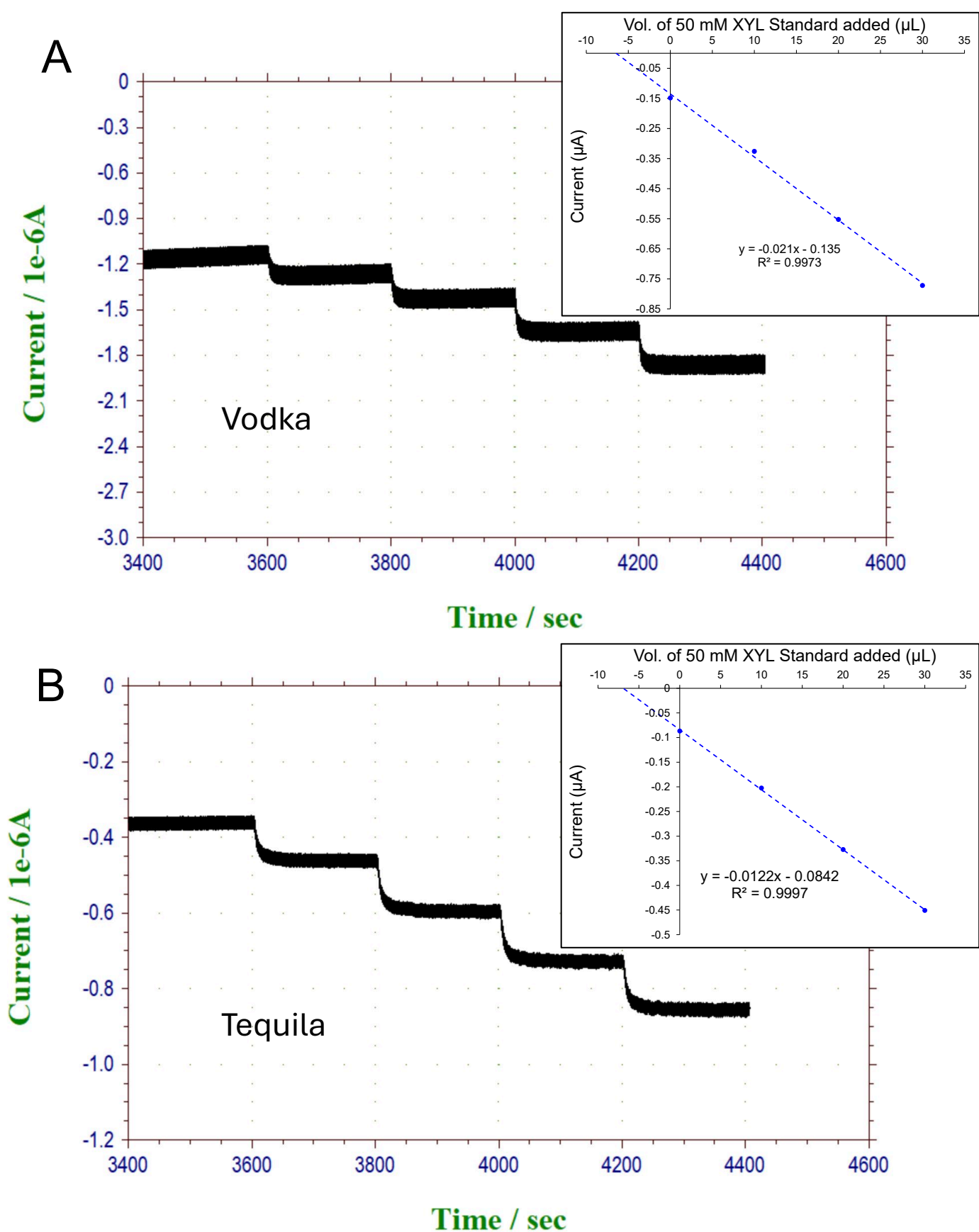


Figure S16. Representative amperometric I-t curve and typical standard addition plot (inset) for XYL analysis in (A) vodka and (B) tequila.

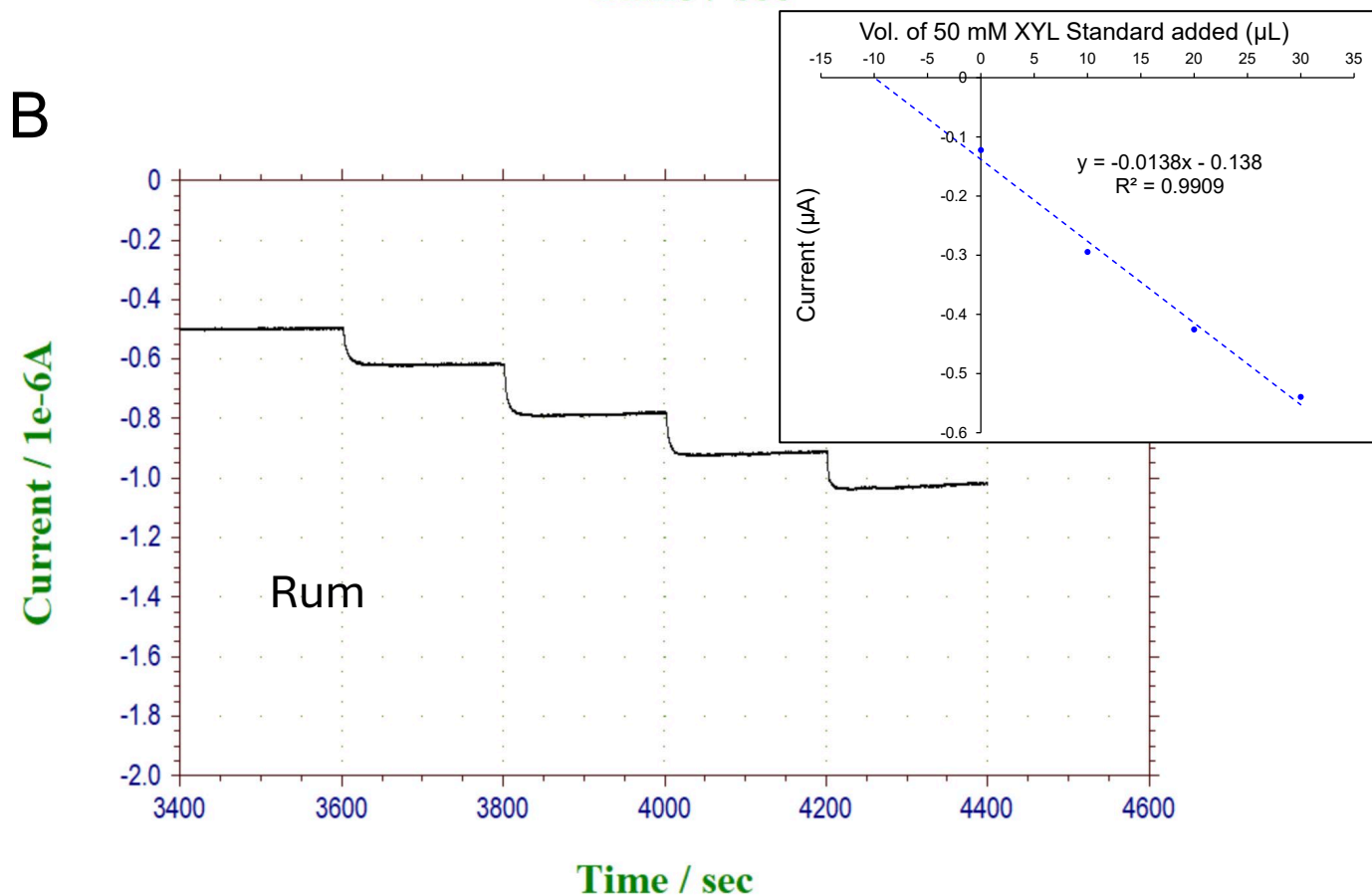
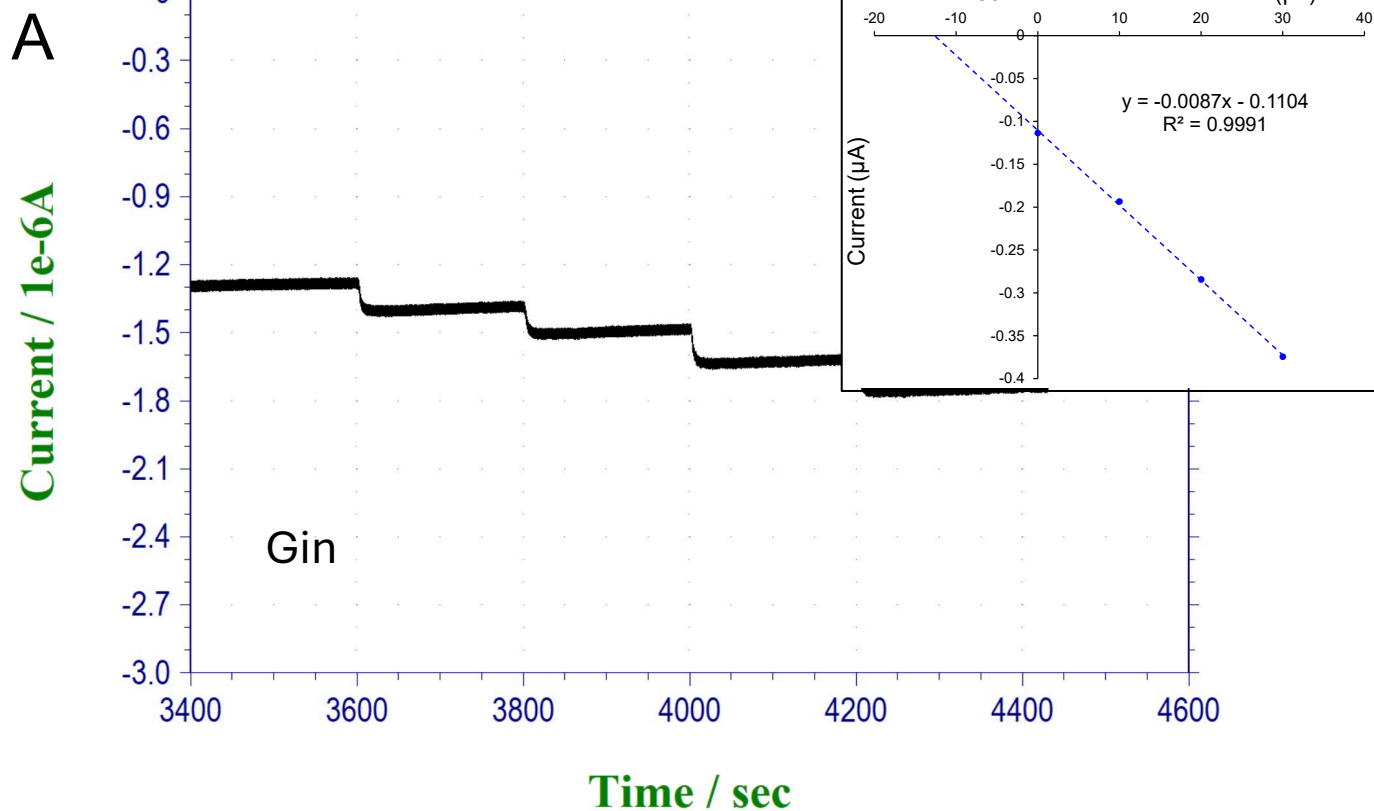


Figure S17. Representative amperometric I-t curve and typical standard addition plot (**inset**) for XYL analysis in (A) gin and (B) rum.

Table S-1. Comparison of XYL Detection Techniques in Literature

Technique	Method	Material or Electrode	As Reported Sensitivity (units vary)	Approx. Reported LOD (units vary)	Application	Ref
Echem	DPV	GCE	0.4 $\mu\text{A}/(\mu\text{g}/\text{mL} \cdot \text{cm}^2)$	120 nM (0.03 ppm)	Sexual assault (urine)	1
Echem	DPV	MWCNT (carbon paste)	2.6 ^a $\mu\text{A}/(\text{ng}/\text{mL})$	4.8 nM (0.001 ppm)	Blood Serum	2
Echem	Volt	Graphene (nanoplates)	12.5 $\mu\text{A}/(\mu\text{g}/\text{mL} \cdot \text{cm}^2)$	0.1 mg/L (0.1 ppm)	Sexual assault (beverages)	3
Echem	DPV	Graphene (nanocoral)	10.4 $\mu\text{A}/(\mu\text{g}/\text{mL} \cdot \text{cm}^2)$	0.03 mg/L (0.03 ppm)	Sexual assault (beverages)	4
Optical	UV-Vis	Polymers/ Dyes	0.09 a.u./mM	1.36 mM (300 ppm)	Sexual assault (beverages)	16
Echem	SWV	Graphene (laser-scribed)	0.07 ^a $\mu\text{A}/\mu\text{M}$	140 nM (0.03 ppm)	Sexual assault (beverages)	22
Echem	Amp	GCE (modified)	0.06 $\mu\text{A}/(\mu\text{M} \cdot \text{cm}^2)$	1-10 ppm	Sexual assault (beverages)	This work

Notes: Echem = electrochemistry; DPV = differential pulse voltammetry; Volt = stripping voltammetry; SWV = square wave voltammetry; Optical = spectroscopy; UV-Vis = ultraviolet-visible spectroscopy; Amp = amperometry; LOD = limit of detection; ^a Sensitivity not normalized to surface area (geometric or real).

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