Supporting Materials

Electropolymerized Layers as Selective Membranes in First Generation Uric Acid Biosensors

Kaiwen Chen,[a, †] Grace E. Conway,[a, †] Gregory A. Hamilton,[b] Matthew L. Trawick,[b] and Michael C. Leopold [a,*]

[a]*Department of Chemistry, Gottwald Center for the Sciences, University of Richmond, Richmond, VA 23173*

[b]*Department of Physics, Gottwald Center for the Sciences, University of Richmond, Richmond, VA 23173*

Contents:

† These authors contributed equally to this work**.**

* To whom correspondence should be addressed. Email: mleopold@richmond.edu.
Phone: (804) 287-6329. Fax: (804) 287-1897.

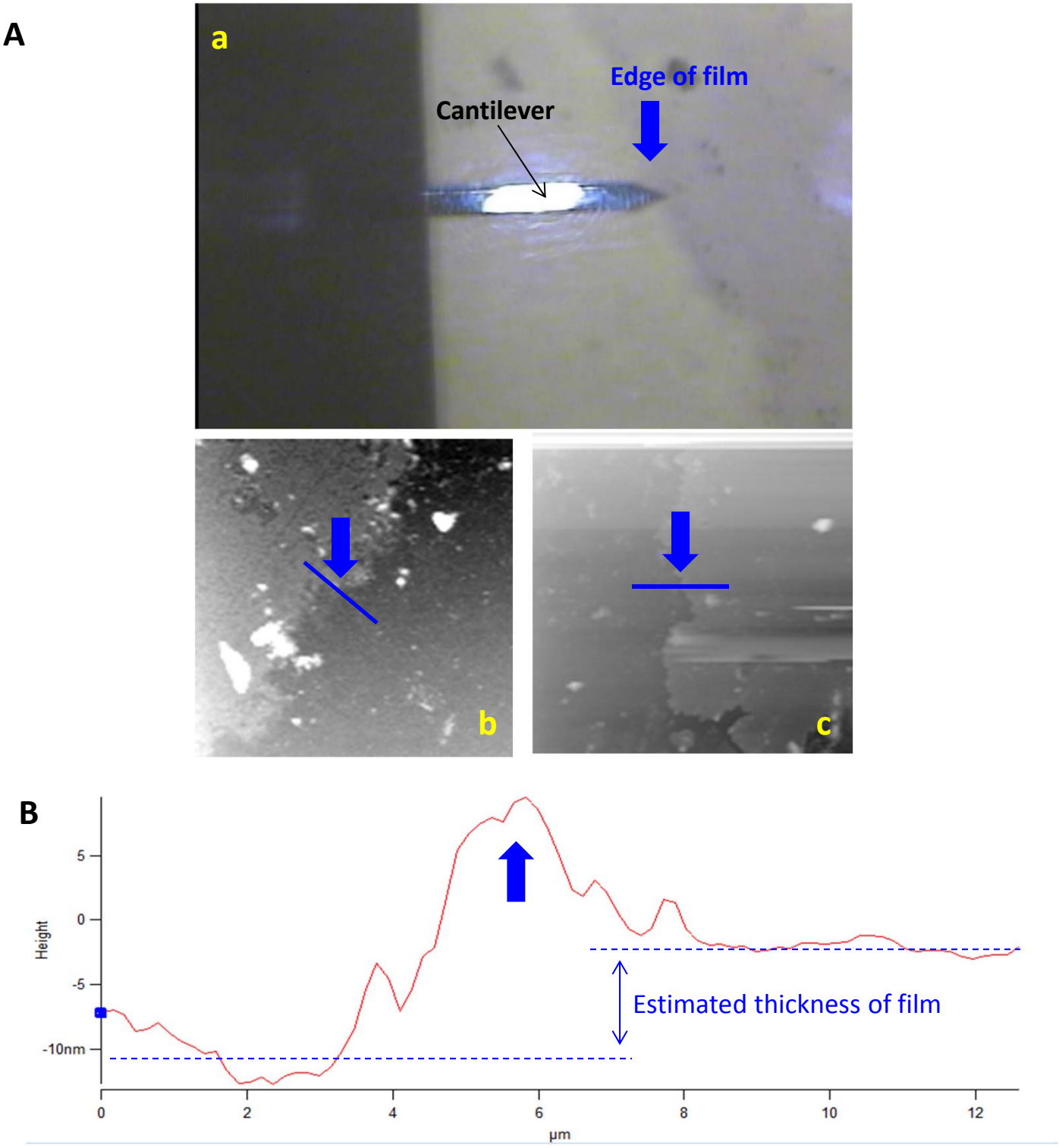

Figure SM-1. Representative images **(A)** for profilometric AFM measurement of the polymerized film thickness: **(a)** optical image of polyphenol film electropolymerized at a evaporated gold substrate and 20 x 20 µm images of the edge of polymerized films of phenol **(b)** and tyramine **(c)**; **(B)** cross-sectional analysis of the polyphenol film across the edge of the polymer film.

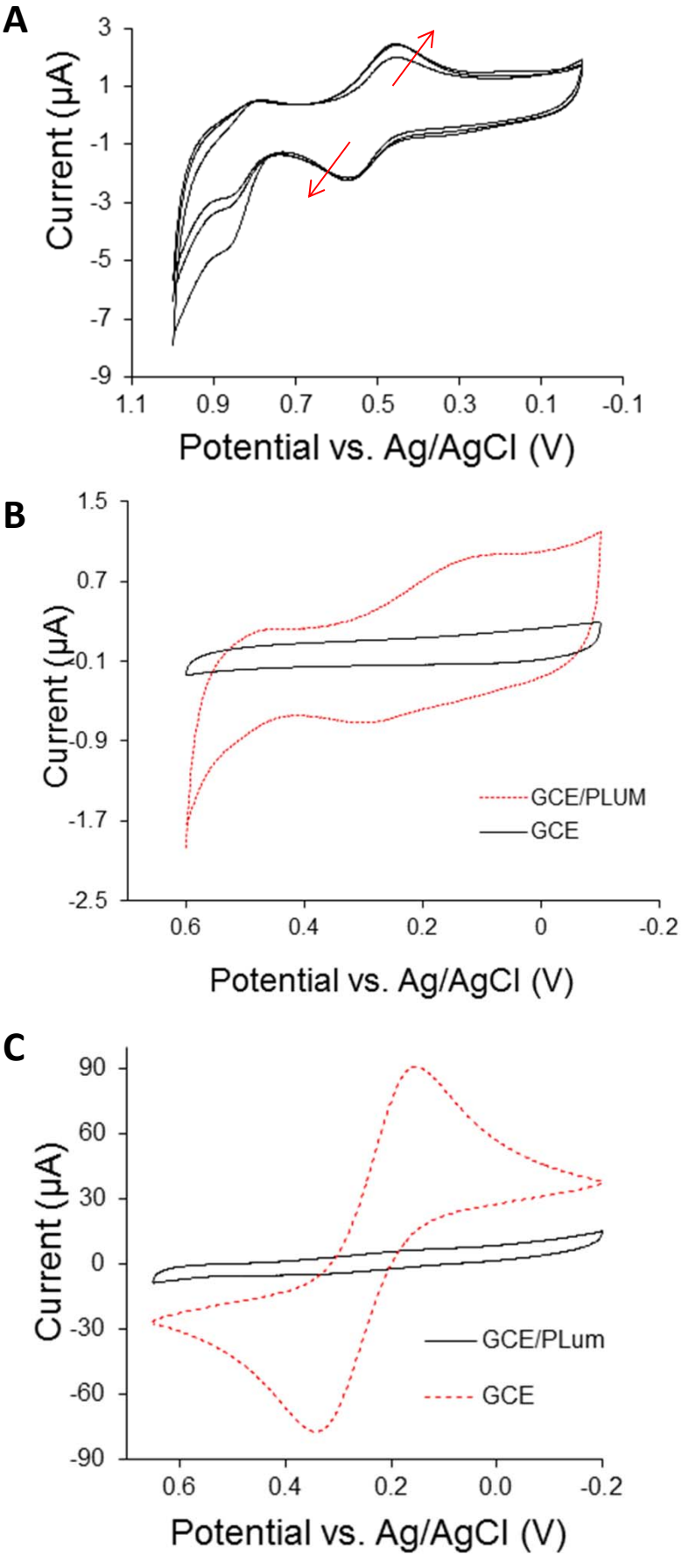

Figure SM-2. Cyclic voltammetry for **(A)** 0.5 mM luminol (degassed 0.1 M H_2SO_4) during electropolymerization at a GCE (50 mV·sec^{-1}); **(B)** polyluminol (PLUM) modified and bare GCEs in 65.55 mM PBS (no monomer) solution (40 mV·sec^{-1}); and; (C) 5 mM ferricyanide (0.5 M KCl) at bare and PLUM-modified GCE to confirm the presence of the electropolymer film (250 mV· sec^{-1}).

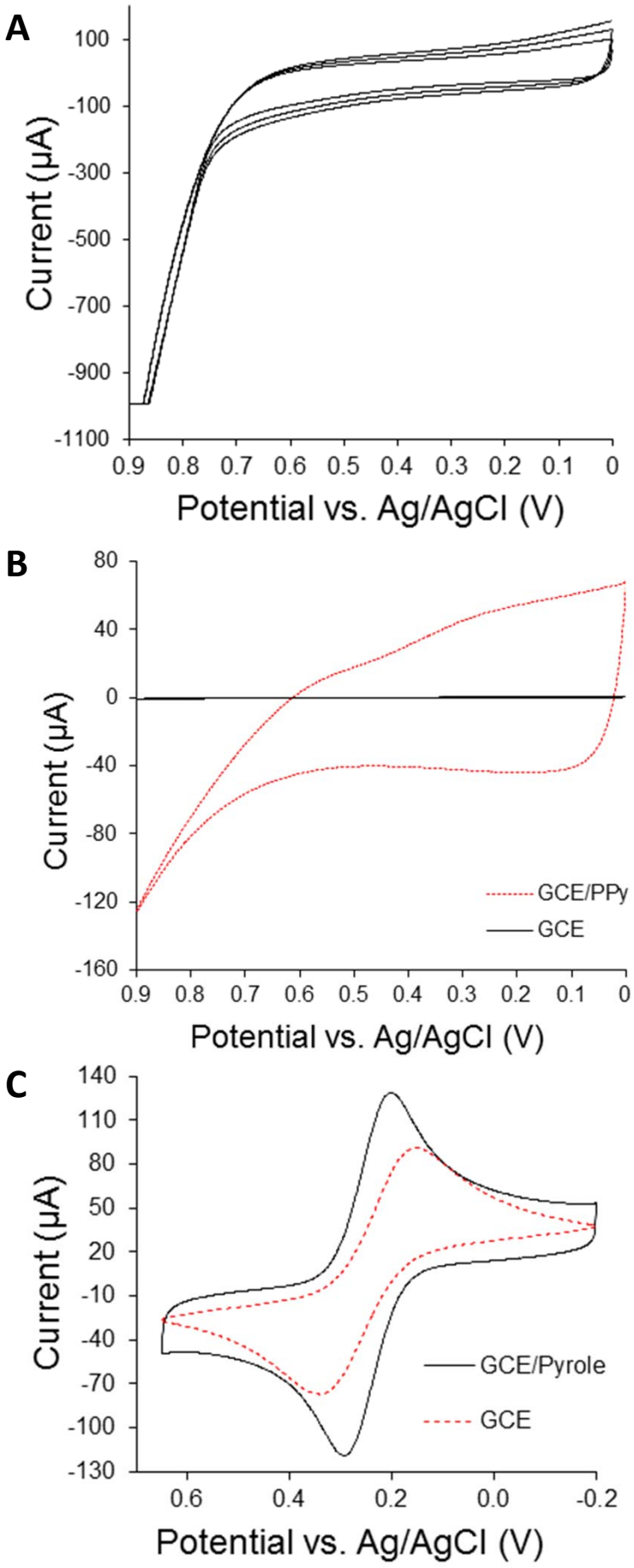

Figure SM-3. Cyclic voltammetry for **(A)** 0.1 M pyrrole (0.1 M H_2SO_4, degassed) during electropolymerization at a GCE (50 mV·sec^{-1}); **(B)** polypyrrole modified and bare GCEs in 65.55 mM PBS (no monomer) solution (50 mV·sec^{-1}); and; (C) 5 mM ferricyanide (0.5 M KCl) at bare and polypyrrole-modified GCE to confirm the presence of the electropolymer film (250 mV·sec^{-1}).

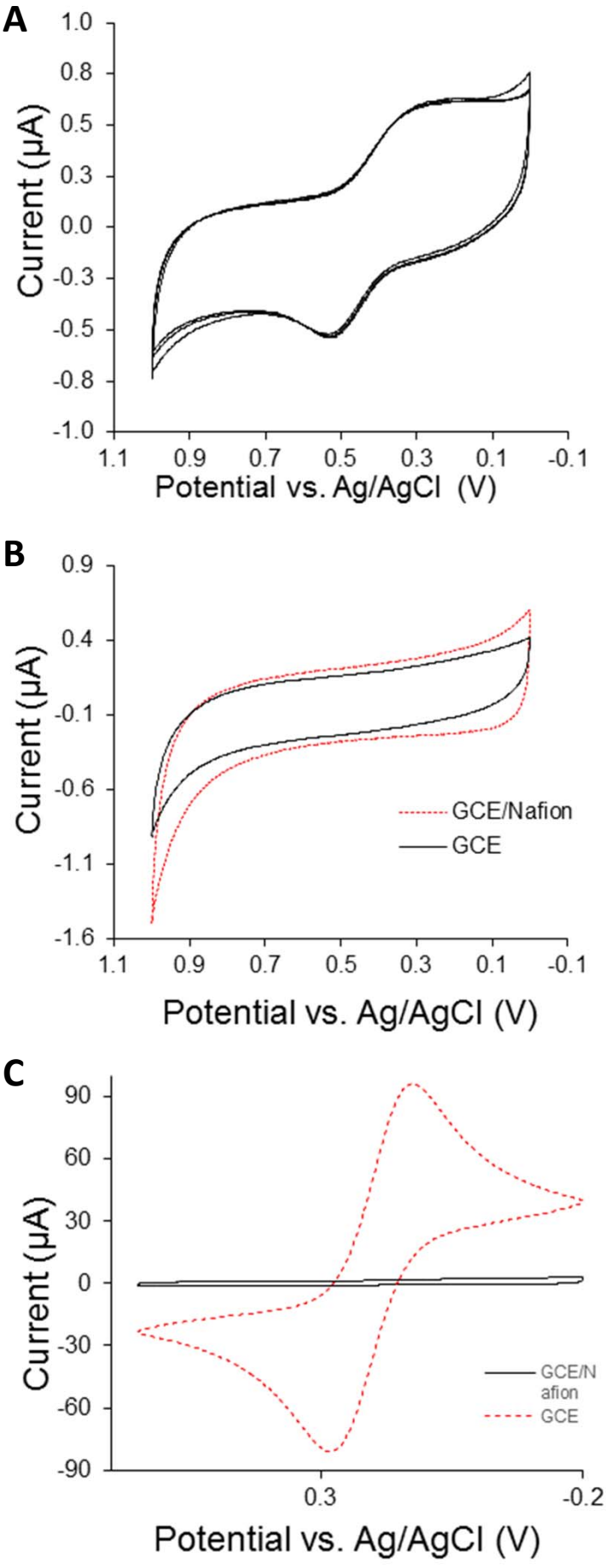

Figure SM-4. Cyclic voltammetry for **(A)** 5% Nafion during electropolymerization at a GCE (50 mV· sec^{-1}); **(B)** Nafion-modified and bare GCEs in 65.55 mM PBS (no monomer) solution (50 mV· sec^{-1}) and; (C) 5 mM ferricyanide (0.5 M KCl) at bare and Nafion-modified GCE to confirm the presence of the electropolymer film (250 mV· sec^{-1}).

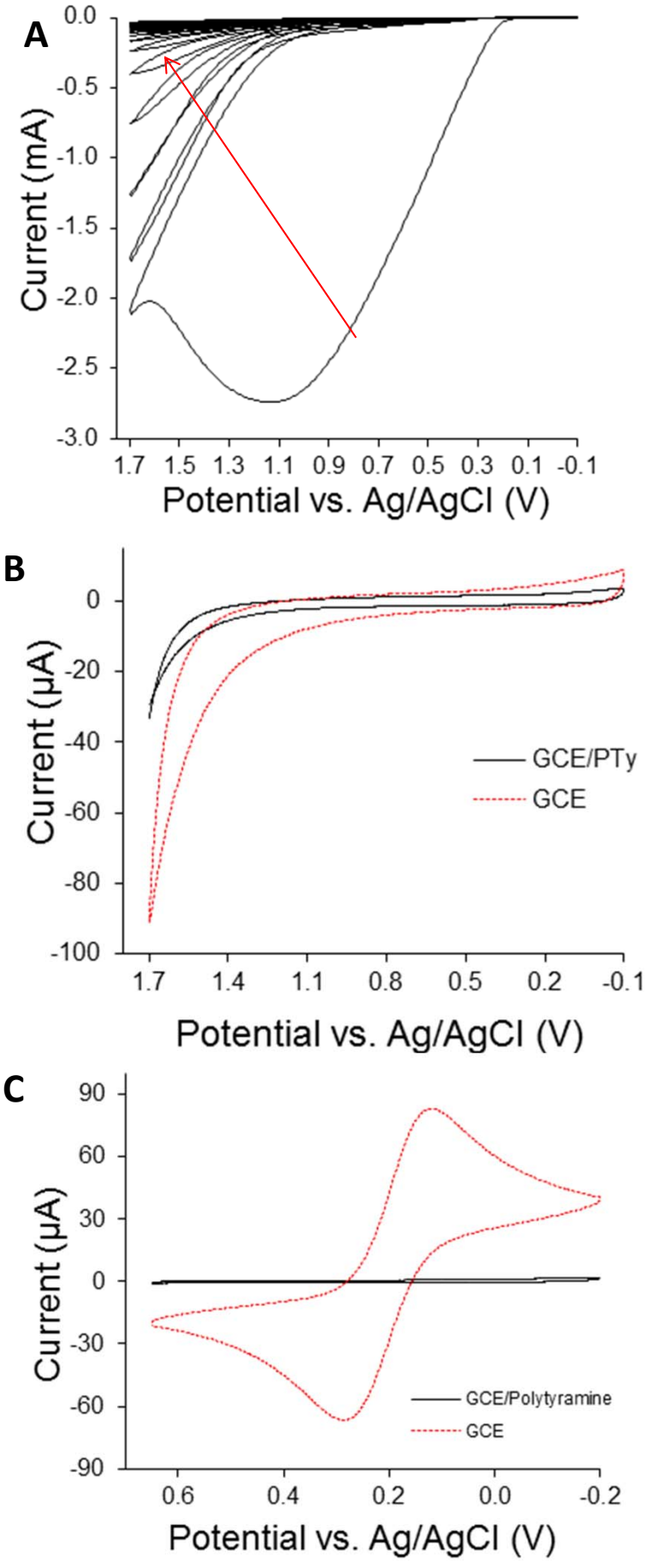

Figure SM-5. Cyclic voltammetry for **(A)** 0.1 M tyramine (0.3 M NaOH, MeOH) during electropolymerization at a GCE (500 mV· sec^{-1}); **(B)** polytyramine-modified GCE in 65.55 mM PBS (no monomer) solution (500 mV· sec^{-1}) and; (C) 5 mM ferricyanide (0.5 M KCl) at bare and polytyramine-modified GCE to confirm the presence of the electropolymer film (250 mV· sec^{-1}).

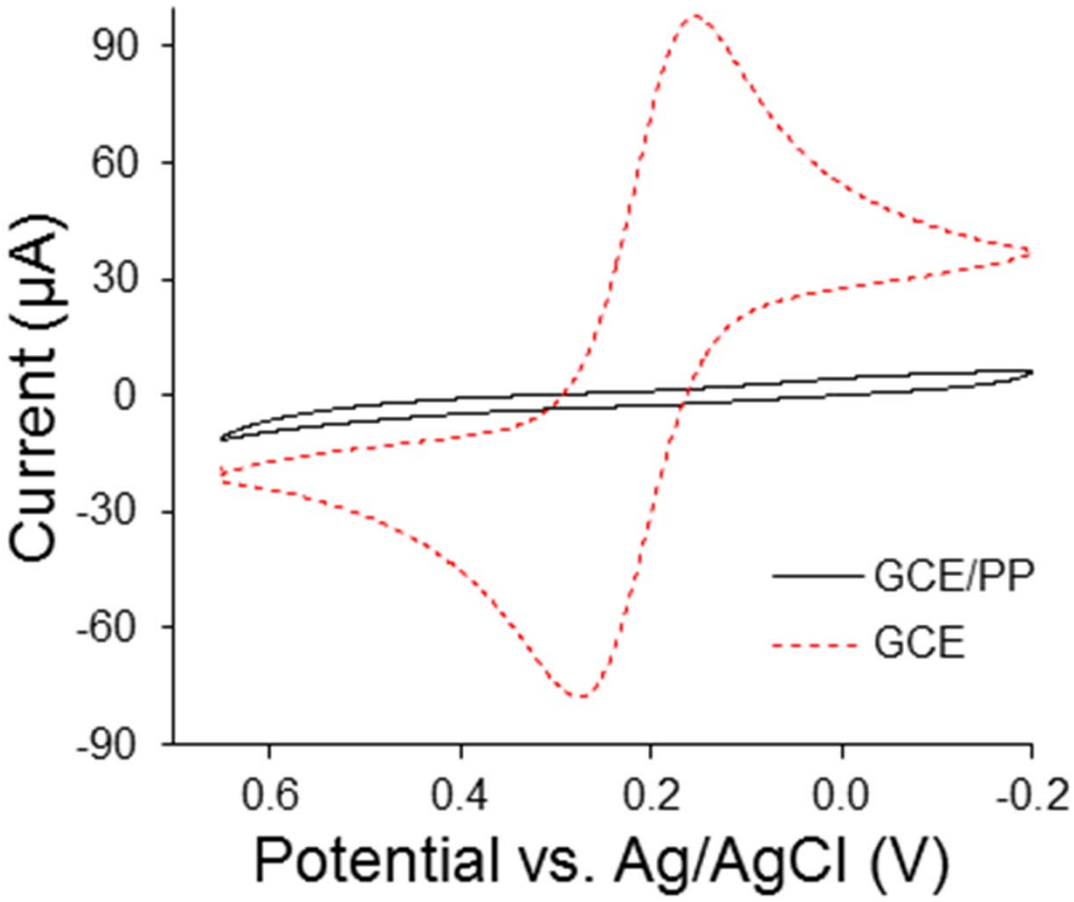

Figure SM-6. Cyclic voltammetry for 5 mM ferricyanide (0.5 M KCl) at bare and phenol-modified GCE to confirm the presence of the electropolymer film (250 $mV \cdot sec^{-1}$).

Additional mixed polymer film formation procedures:

Pyrrole-Luminol 1:10 Mixture[26,27]

For the application of the polypyrrole to luminol, 1:10 mixture, selective membrane, the glassy carbon electrodes were immersed in a solution 17.3μL of pyrrole, 0.01 M, combined with 0.443g of luminol, 0.1M (25 mL). The solution was degassed with nitrogen to remove the oxygen. The electropoloymerization was achieved using cyclic voltammetry, cycling between 0.0 V and 1.0 V (vs. Ag/AgCl, saturated KCl) for 5 cycles. The pyrrole-luminol coated electrodes were then rinsed with nanopure water and allowed to dry (15 min).

Pyrrole-Luminol 10:1 Mixture[26,27]

For the application of the polypyrrole to luminol, 10:1 mixture, selective membrane, the glassy carbon electrodes were immersed in a solution 173.5 μL of pyrrole, 0.1 M, combined with 0.0443 g of luminol, 0.01 M (25 mL). The solution was degassed with nitrogen to remove the oxygen. The electropoloymerization was achieved using cyclic voltammetry, cycling between 0.0 V and 1.0 V (vs. Ag/AgCl, saturated KCl) for 5 cycles. The pyrrole-luminol coated electrodes were then rinsed with nanopure water and allowed to dry (15 min).

Table SM-1. Permeability Indices (PI)[†] for Interferents and Uric Acid at Electropolymerized Films on Glassy Carbon Electrodes (%)

Monomer System	Ref.	Molar Ratio[‡] or Condition[#]	Acetaminophen (40 µM)	Ascorbic Acid (40 µM)	Uric Acid (100 µM)	Ratio: UA to Aceto	Ratio: UA to AA	UA Sensor
Phenol	12,20	-	0.0 (±0.05); n=3	0.15 (±0.05); n=3	0.00_3 ($\pm0.00_3$); n=3	0.0	0.0	
Phenol	12,20	Stirred	41.9 (±21.8); n=4	3.9 (±4.4); n=4	14.0 (±9.0); n=4	0.3341	3.5897	✓
Aniline	25	-	0.4 (±0.2); n=4	0.2 (±0.1); n=4	0.0 n=4	0.0	0.0	
Aniline	25	Stirred	5.5 (±6.8); n=3	0.0 n=3	0.0 n=3	0.0	0.0	
Aniline-Luminol	25,26	$10:1_{mix}$	0.0 n=3	0.0 n=3	0.0 n=3	0.0	0.0	
Aniline-Luminol	25,26	$50:50_{mix}$	0.0 n=5	0.0 n=5	0.0 n=5	0.0	0.0	
Aniline-Luminol	25,26	seq	22.8 (±2.2); n=2	2.2 (±0.3); n=2	1.8 (±0.1); n=2	1.4419	0.8182	
Luminol-Aniline	26,25	seq	65.8 (±88.0); n=2	12.9 (±17.9); n=2	7.0 (±9.7); n=2	0.1064	0.5426	
Pyrrole	27	-	25.7 (±2.5); n=4	20.5 (±3.9); n=4	1.3 (±0.8); n=4	0.0505	0.0634	
Pyrrole	27	Stirred	0.0 n=3	0.0 n=3	0.0 n=3	0.0	0.0	
Aniline-Pyrrole	27	$10:1_{seq}$	0.0 n=4	25.1 (±8.3); n=4	0.0 n=4	0.0	0.0	
Aniline-Pyrrole	27	$50:50_{seq}$	0.0 n=4	0.0 n=4	0.0 n=4	0.0	0.0	
Pyrrole-Luminol	27,26	$10:1_{mix}$	0.0 n=4	0.0 n=4	0.0 n=4	0.0	0.0	
Pyrrole-Luminol	27,26	$1:10_{mix}$	0.5 (±0.4); n=4	0.4 (±0.3); n=4	0.2 (±0.2); n=4	0.4	0.5	
Luminol-Pyrrole	26,27	$10:1_{seq}$	20.1 (±12.2); n=4	7.1 (±7.2); n=4	4.8 (±2.0); n=4	0.2388	0.6761	
Pyrrole-Luminol	27,26	$10:1_{seq}$	3.1 (±3.3); n=4	5.4 (±3.8); n=4	1.7 (±3.7); n=4	0.5484	0.3148	✓
Luminol	26	-	172.9 (±46.3); n=6	119.0 (±26.9); n=6	162.3 (±31.5); n=6	0.9387	1.3639	
Luminol	26	Stirred	33.4 (±5.0); n=4	41.5 (±8.3); n=4	46.3 (±6.5); n=4	1.3862	1.1157	✓
Luminol-Aniline	31	1:10	67.0 (±5.0); n=6	26.2 (±13.4); n=6	30.3 (±15.7); n=6	0.4522	1.1565	✓
Luminol-Aniline	31	$1:10_{N\&G}$	104.4 (±22.7); n=2	23.6 (±3.5); n=2	22.5 (±23.0); n=2	0.2155	0.9534	

Luminol-Aniline	31	10:1	94.0 (±18.9); n=3	52.0 (±6.7); n=3	59.5 (±10.4); n=3	0.6330	1.1442	✓
Luminol-Aniline	31	$10:1_{N\&G}$	58.3 (±6.6); n=5	28.9 (±9.1); n=5	35.7 (±6.4); n=5	0.6123	1.2353	
Luminol-Pyrrole	26	$1:10_{mix}$	7.3 (±1.6); n=4	0.0 n=4	0.5 (±0.7); n=4	0.0685	NA	
Luminol-Pyrrole	26,27	$1:200_{seq}$	81.5 (±20.3); n=3	16.4 (±2.7); n=3	16.7 (±4.1); n=3	0.2049	1.0183	
Pyrrole-Luminol	26,27	$200:1_{seq}$	21.9 (±6.2); n=3	17.6 (±4.1); n=3	5.7 (±2.8); n=3	0.2603	0.3239	
Luminol-Phenol	26	1:10	101.9 (±19.3); n=5	0.0 n=5	32.6 (±13.6); n=5	0.3199	NA	
Phenol-Luminol	26,12, 20	$800:1_{seq}$	1.3 (±0.5); n=3	0.2 ($\pm0.0_5$); n=3	0.4 (±0.1); n=3	0.3077	2.0	
Luminol-Phenol	26,12, 20	$1:800_{seq}$	1.0 (±0.3); n=3	0.1 ($\pm0.0_2$); n=3	0.1 ($\pm0.0_1$); n=3	0.1	1.0	
Nafion™	28	-	2.3 (±1.4); n=3	0.0 n=3	0.1 (±0.1); n=3	0.0435	NA	
Nafion	28	Stirred	9.0 (±1.2); n=3	1.2 (±0.2); n=3	0.5 (±0.1); n=3	0.0556	0.4167	
Nafion	28	CV	109.6 (±44.1); n=4	67.9 (±46.2); n=4	126.6 (±83.0); n=4	1.1551	1.8645	✓
Nafion-Luminol	28	10:1	45.8 (±28.8); n=3	25.3 (±21.1); n=3	14.5 (±14.3); n=3	0.3166	0.5731	
Nafion-Luminol	26	$10:1^{CV}$	36.8 (±26.9); n=4	0.0 n=4	7.5 (±11.4); n=4	0.2038	NA	
Nafion-Luminol	26	$10:1_{(CV\text{-}N_2)}$	59.7 (±27.0); n=3	28.5 (±29.4); n=3	26.1 (±25.6); n=3	0.4372	0.9158	✓
Tyramine	29	-	70.8 (±3.8); n=2	15.8 (±3.2); n=2	2.3 (±1.6); n=2	0.0325	0.1456	
Tyramine	30	Stirred	56.8 (±4.9); n=2	14.5 (±0.7); n=2	3.8 (±1.0); n=2	0.0669	0.2621	
Tyramine	29	-	0.06 (±0.07); n=3	0.03 (±0.03); n=3	0.01 (±0.01); n=3	0.1667	0.3333	
Tyramine	30	Stirred	0.1 (±0.1); n=3	0.02_9 (±0.02); n=3	0.01 (±0.01); n=3	0.1	0.5	
Tyramine-Luminol	29,26	Seq	62.1 (±2.7); n=3	3.7 (±0.4); n=3	5.2 (±0.4); n=3	0.0837	1.4054	
Luminol-Tyramine	26,29	Seq	88.7 (±21.7); n=3	16.6 (±9.3); n=3	24.7 (±31.7); n=3	0.2785	1.4880	✓

Notes: † PI determined from ratio of current response of a species at a polymerized film modified GCE to the current response of the same species at a bare GCE. ‡Applies for polymeric mixtures (mix) only; # Other conditions include sequential (seq) layering or nucleation (N) and growth (G) procedures for electro-Polymerization[31] or the use of cyclic voltammetry (CV). No significant permeability was measured for oxalic acid, glucose, and sodium nitrite.

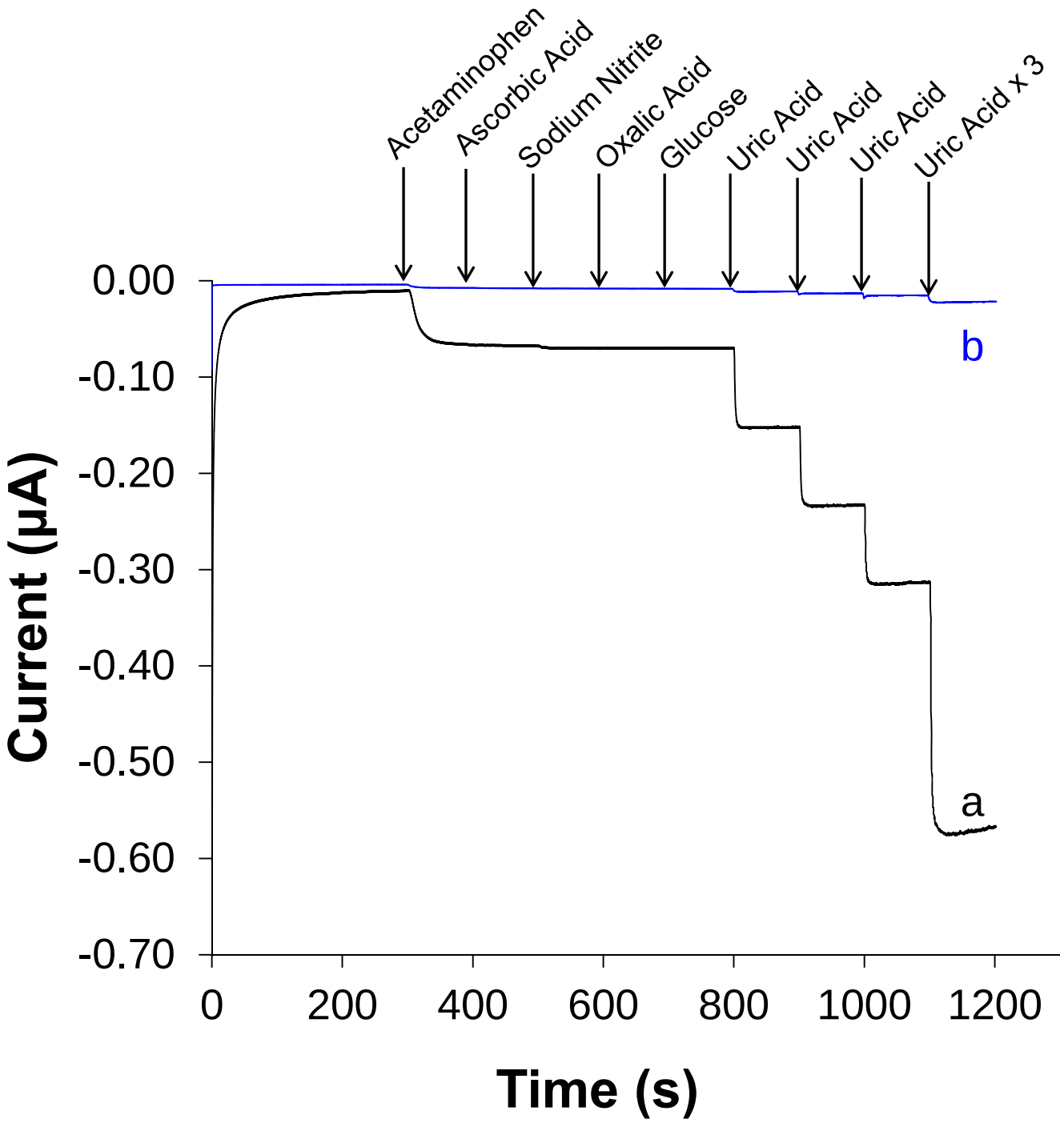

Figure SM-7. Amperometric I-*t* curve for successive injections of common interferent species (40 μM) and uric acid (100 μM and/or 300 μM) at a platinum electrode modified with L-B-L construction of UOx-doped OTMS xerogel and undoped OTMS xerogel with a **(a)** polyluminol-polyaniline (1:10) mixture or **(b)** aniline and 100% hydrothane polyurethane capping layers. The composite film with the aniline electropolymer layer is unable to distinguish and respond to uric acid while the PLUM:PANI film prevents interferent signal and promotes uric acid signal, with the exception of acetaminophen. Note: Glucose was tested at 100 μM.

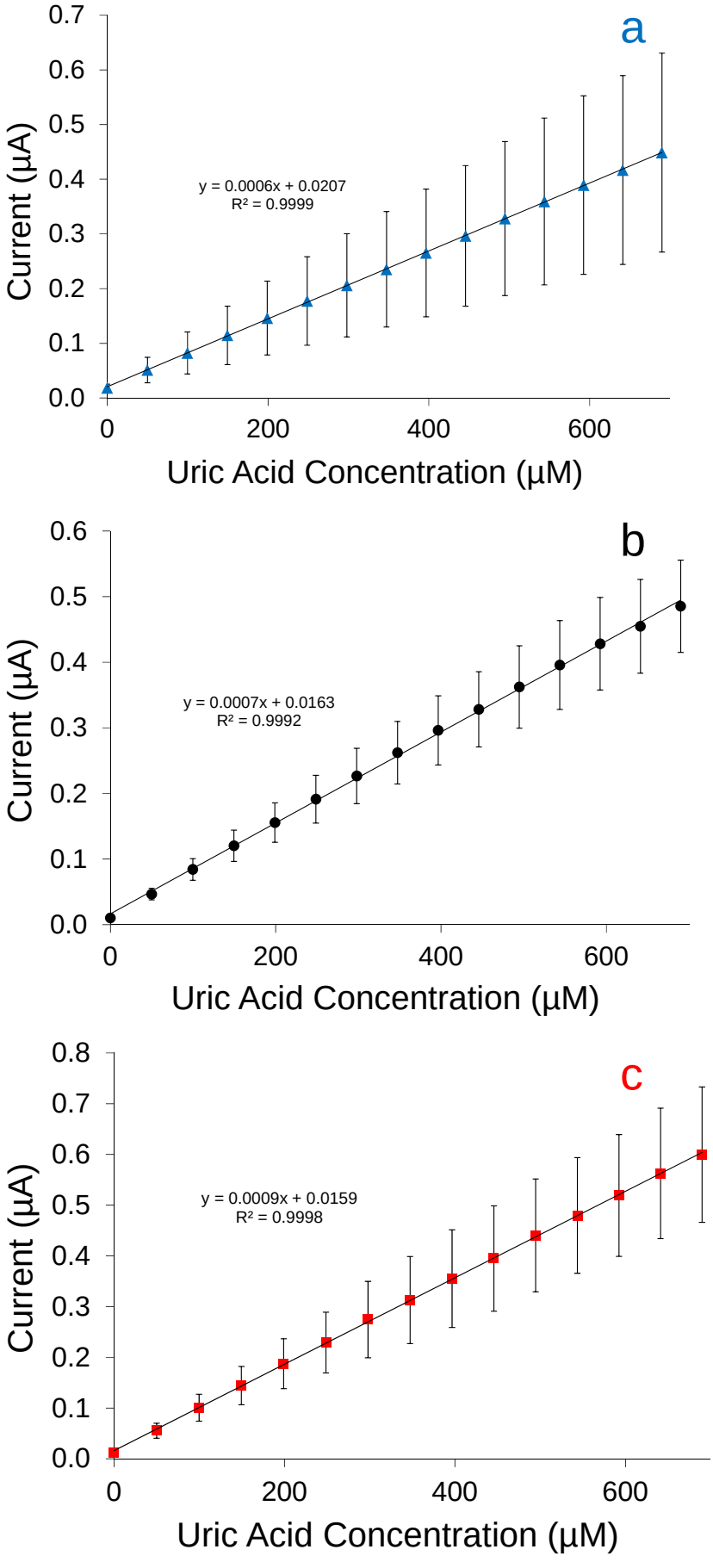

Figure SM-8. Calibration curves for successive 50µM injections of uric acid at a platinum modified electrode with UOx-doped OTMS xerogel, undoped OTMS xerogel, **(a)** Nafion-Luminol, **(b)** luminol-aniline (1:10), **(c)** luminol-aniline (10:1) formed with no nucleation and growth and all capped with hydrothane polyurethane (n=3; standard deviation shown).