Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Microporous carbon in the selective electro-oxidation of molecular biomarkers: uric acid, ascorbic acid, and dopamine

Tidapa Rattanaumpa,[1] Santi Maensiri,[2] and Kamonwad Ngamchuea*[1]

[1] School of Chemistry, Institute of Science, Suranaree University of Technology, 111 University Avenue, Suranaree, Muang, Nakhon Ratchasima, 30000, Thailand

[2] School of Physics, Institute of Science, Suranaree University of Technology, 111 University Avenue, Suranaree, Muang, Nakhon Ratchasima, 30000, Thailand

*Corresponding author: Kamonwad Ngamchuea, School of Chemistry, Institute of Science, Suranaree University of Technology, 111 University Avenue, Suranaree, Muang, Nakhon Ratchasima, 30000, Thailand. Email: kamonwad@g.sut.ac.th; Tel: +66 (0) 44 224 637

S1 Cyclic voltammetry of AA, DA, and UA at Nafion/MC/GCE electrodes at different pH

Figure S1 shows the cyclic voltammograms of 500 µM AA, 100 µM DA, and 100 µM UA at Nafion/MC/GCE electrodes at different pH. In the main text, we discussed that at pH 7.0 the electrostatic repulsion between the sulfonic groups of Nafion and the negatively charged AA and UA lowered the voltammetric responses of the two species. At pH 1.0, AA, DA, and UA are in their protonated forms, and the clear peaks of all the three species were observed at Nafion/MC/GCE electrodes (Figure S1). The Nafion/MC/GCE electrodes can thus also be used in the simultaneous detection of AA, DA, and UA under acidic conditions (pH < pK_a). However, the responses at Nafion/MC/GCE and MC/GCE (without Nafion) were not significantly different. Nafion was thus not employed in this work.

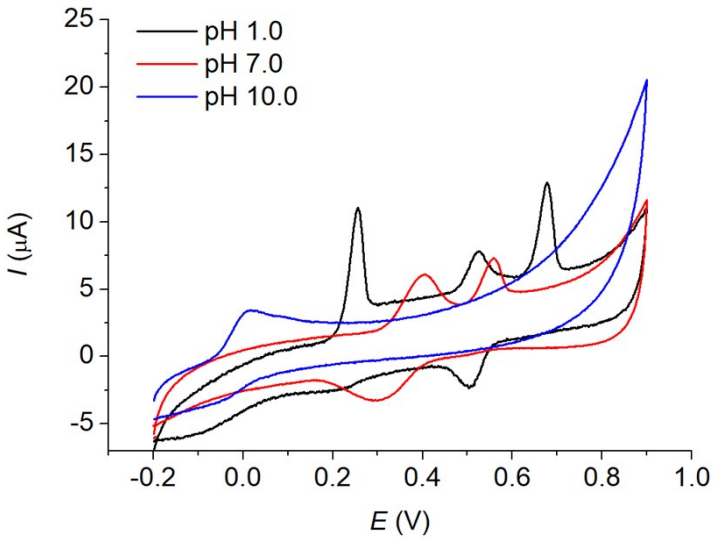

Figure S1: CV of 500 µM AA, 100 µM DA, and 100 µM UA at Nafion/MC/GCE electrodes at different pH. Scan rate: 10 mV s^{-1}. *E* vs. Ag/AgCl (saturated KCl) reference electrode.

S2 Characterization of working electrodes using hexaammineruthenium(III)

First, the bare glassy carbon electrode (GCE) was subjected to cyclic voltammetry measurements in 1.0 mM hexaammineruthenium(III) or RuHex in the presence of 0.10 M KCl supporting electrolyte (Figure S2). The scan rates were varied between 10 – 400 mV s^{-1}. The temperature was controlled at 25 °C (298 K). The diffusion coefficient of hexaammineruthenium(III) was calculated using the Randles-Sevcik equation (eqn. S1)[1] for an electrochemically reversible one-electron transfer process to yield the diffusion coefficient of RuHex of 8.61 x 10^{-10} ± 0.06 x 10^{-10} m^2 s^{-1}, close to the value reported in the literature (8.43 x 10^{-10} ± 0.03 x 10^{-10} m^2 s^{-1}).

$$I_p = 0.446FAc^* \sqrt{\frac{FDv}{RT}} \quad \text{(S1)},$$

where I_p is the peak current, F is the Faraday's constant (96,485 C mol^{-1}), A is the electrode surface area (m^2), c^* is the bulk concentration of the redox analyte, v is the voltage scan rate (V s^{-1}), R is the molar gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (K), and D is the analyte diffusion coefficient (m^2 s^{-1}).

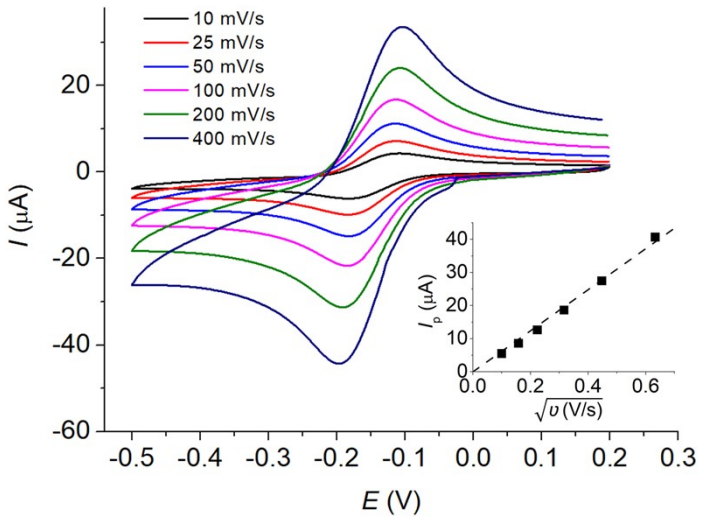

Figure S2: CV of 1.0 mM hexaammineruthenium(III) in 0.10 M KCl at a bare GCE at varied scan rates (10 – 400 mV s^{-1}). The inlay shows a plot of cathodic peak currents against square root of scan rates.

Next, the system of 1.0 mM hexaammineruthenium(III) in 0.10 M KCl supporting electrolyte was used to estimate the electroactive surface area of the MC/GCE electrodes immobilized with different amounts of microporous carbon. Figure S3 shows the plot of electroactive surface areas against the amount of immobilized microporous carbon. The electroactive surface areas were calculated using the reversible Randles-Sevcik equation (eqn. S1)[1] using the diffusion coefficient of RuHex of 8.61 x 10^{-10} m^2 s^{-1}. The results showed that the electroactive surface area increased with the amount of microporous carbon. However, the increase became less at large amounts s a large excess (multiple layers) of microporous carbon may hinder mass transport of the analytes to the electrode surface due to slow diffusion within the microporous structures, as also discussed in Section 3.3.5 in the main text.[2]

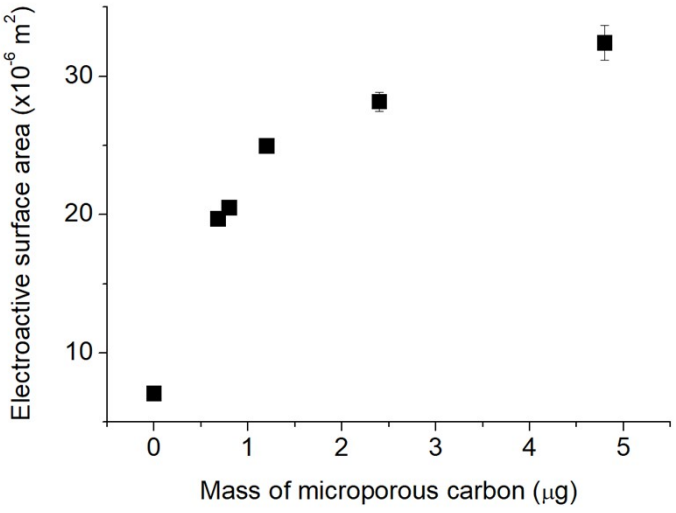

Figure S3: The plot of electroactive surface areas of MC/GCE electrodes against the amount of immobilized microporous carbon.

S3 Chronoamperometry of AA, DA, and UA

Figure S4 below shows chronoamperograms of AA, DA, and UA in 0.10 M HCl electrolyte at MC/GCE electrodes subjected to high overpotentials (0.8 V vs. Ag/AgCl [saturated KCl] for 60 seconds. Note that at longer times, the influence of natural convection becomes significant and was thus not evaluated further.[3]

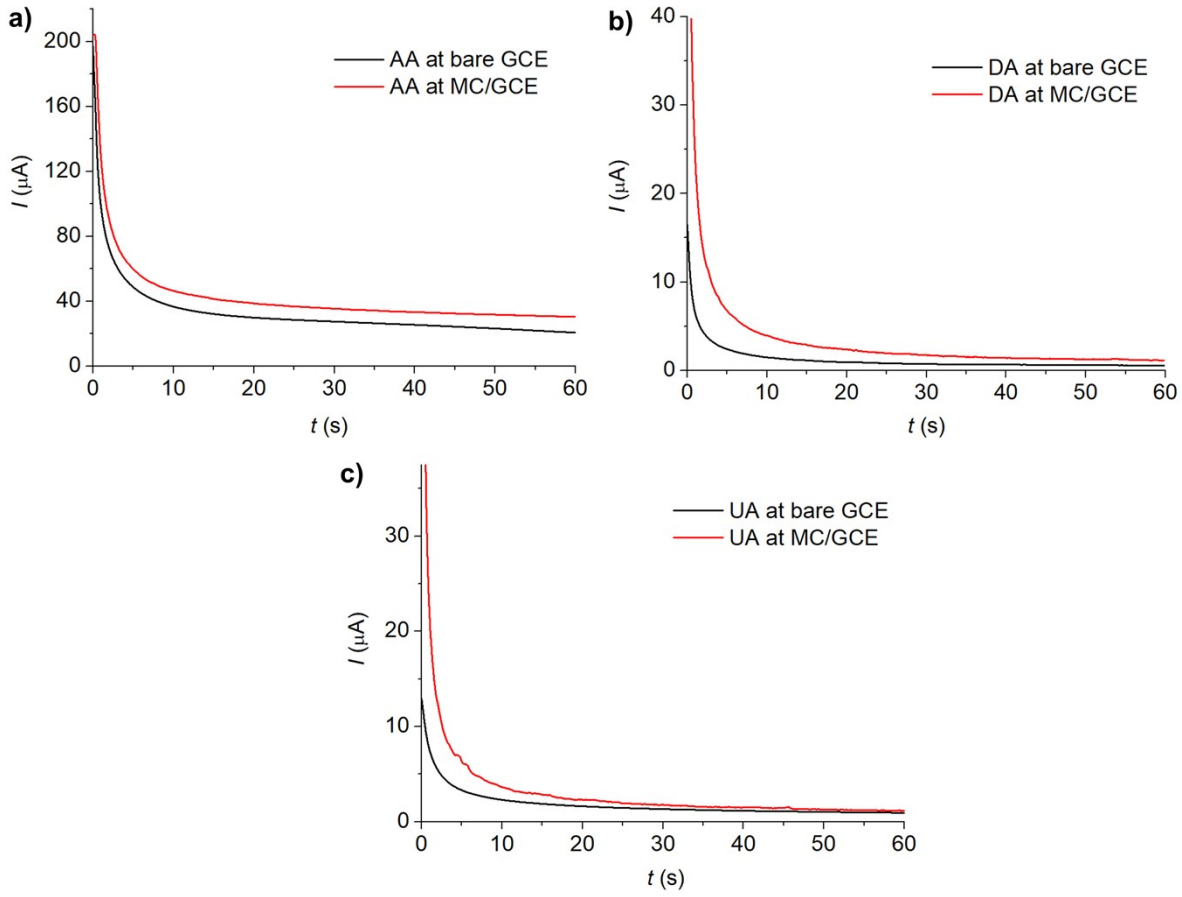

Figure S4: Chronoamperograms of **a)** 500 µM AA, **b)** 100 µM DA, and **c)** 100 µM UA. Working electrode: MC/GCE. Electrolyte: 0.10 M HCl. Applied potential: 0.8 V.

S4 Calibration curves: CV

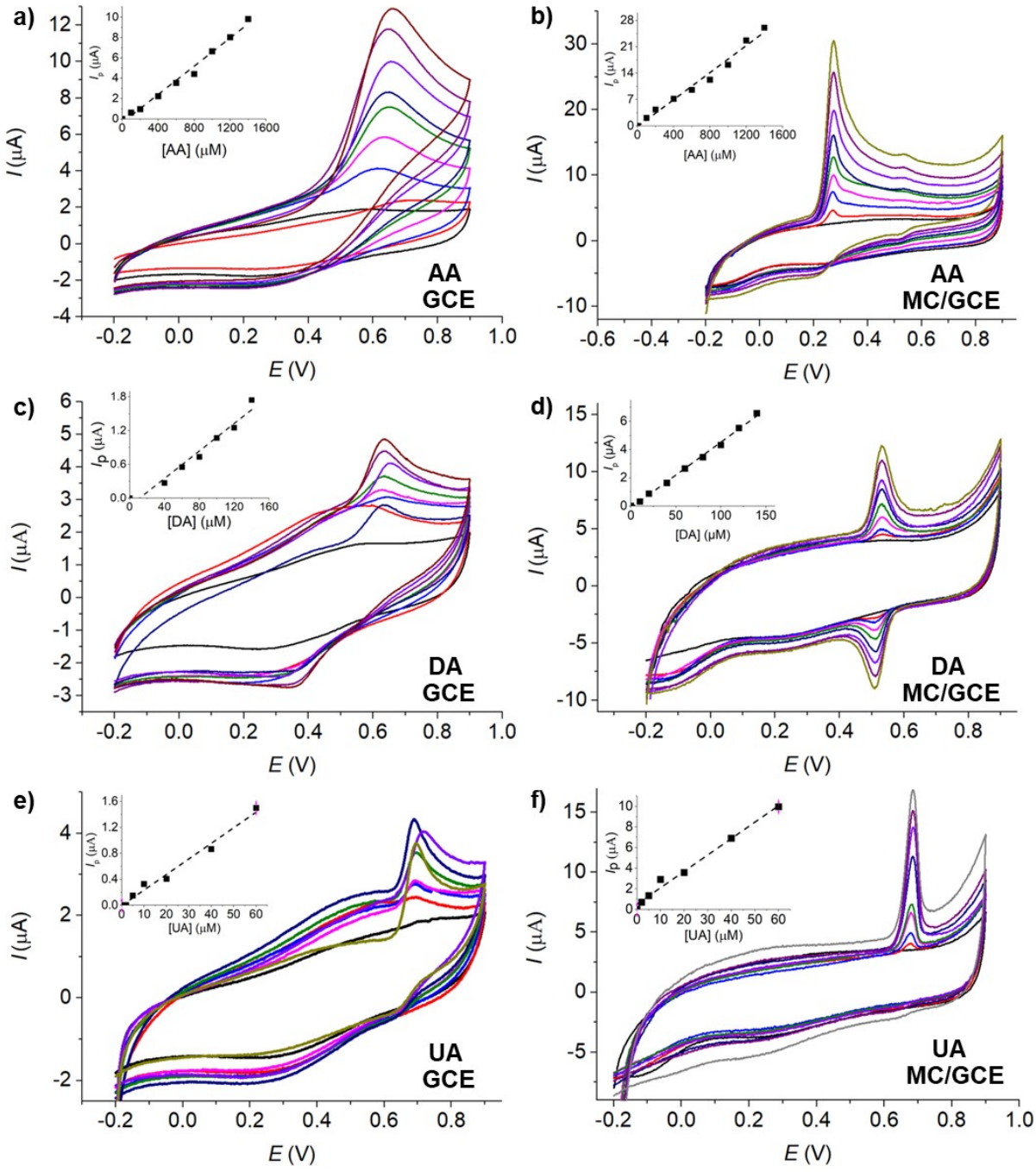

Figure S5: CV of varied [AA] at **a)** bare GCE and **b)** MC/GCE. CV of varied [DA] at **c)** bare GCE and **d)** MC/GCE. CV of varied [UA] at **e)** bare GCE and **f)** MC/GCE. Electrolyte: 0.10 M HCl. Scan rate: 10 mV s^{-1}.

S5 DPV of AA, DA, and UA in standard electrolyte vs. synthetic urine

Figure S6 compares the differential pulse voltammograms of 2,500 µM AA, 100 µM DA, and 200 µM UA in standard 0.10 M HCl electrolyte vs. in synthetic urine sample in the presence of 0.10 M HCl. The oxidation peaks of AA, DA, and UA in urine sample in the presence of 0.10 M HCl were not significantly altered compared with the responses in a standard 0.10 M HCl solution.

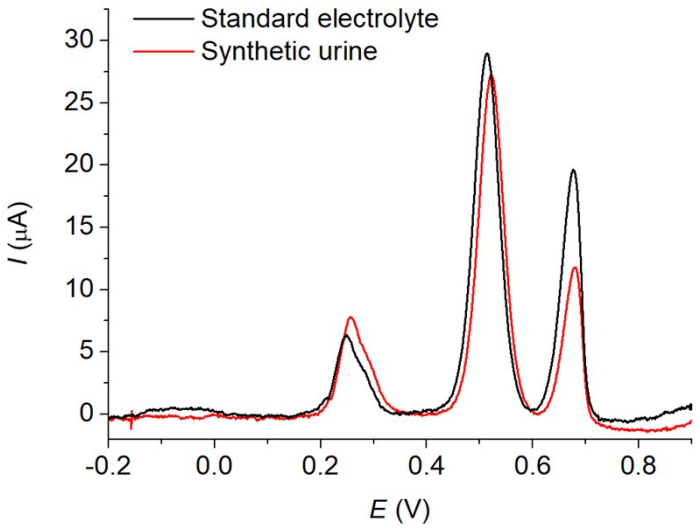

Figure S6: DPV at MC/GCE electrode in the mixture of 2,500 µM AA, 100 µM DA, and 200 µM UA in 0.10 M HCl standard electrolyte vs. in synthetic urine sample in the presence of 0.10 M HCl at the pulse amplitude of 10 mV, the pulse width of 50 ms, and the scan rate of 10 mV s^{-1}. *E* vs. Ag/AgCl (saturated KCl) reference electrode.

S6 Linear ranges: DPV

Figure S7 below demonstrates the DPV calibration plots of AA, DA, and UA beyond the linear ranges presented in Figure 7 in the main text.

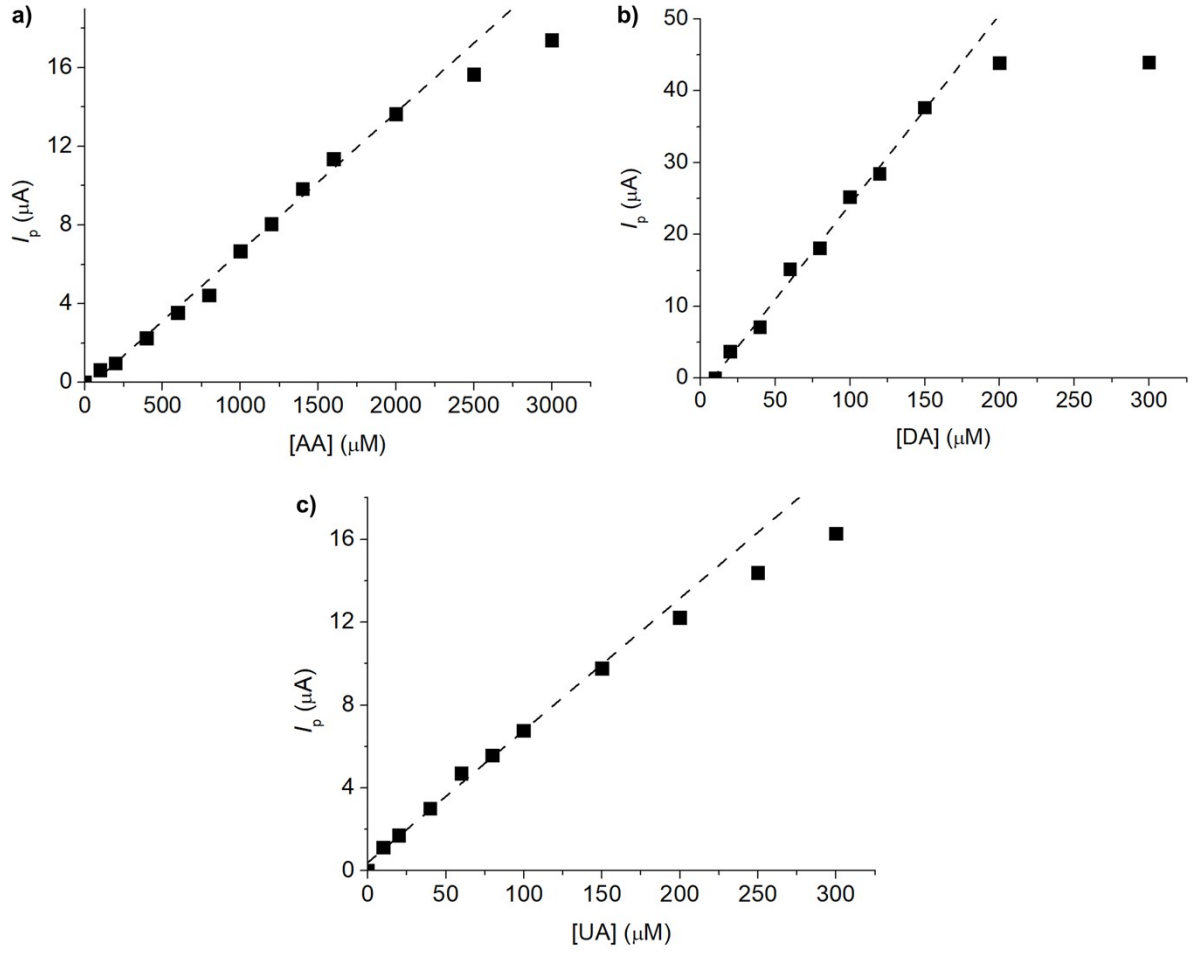

Figure S7: The calibration plots of DPV peak currents against the concentrations of **a)** AA, **b)** DA, and **c)** UA. Working electrode: MC/GCE. Electrolyte: 0.10 M HCl. Scan rate: 10 mV s^{-1}.

S7 UV-visible spectrophotometry vs. electrochemical responses of uric acid and H_2O_2

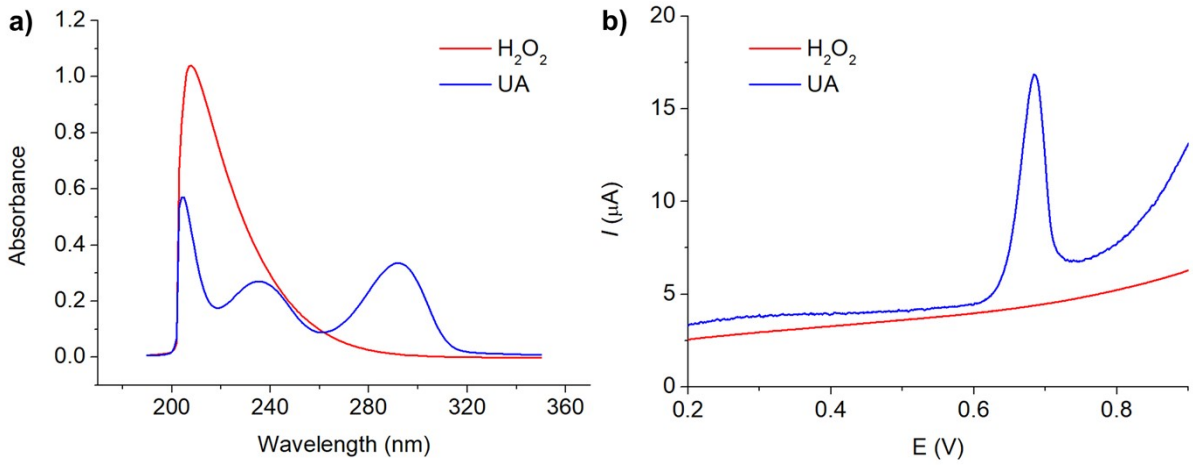

Figure S8: a) UV-visible spectra and **b)** voltammograms of **(red)** 30 mM H_2O_2 and **(blue)** 100 μM uric acid (UA)

References

1. Compton, R. G.; Banks, C. E., *Understanding voltammetry*. World Scientific: 2018.

2. Ngamchuea, K.; Tschulik, K.; Eloul, S.; Compton, R. G., In situ detection of particle aggregation on electrode surfaces. *ChemPhysChem* **2015,** *16* (11), 2338-2347.

3. Ngamchuea, K.; Eloul, S.; Tschulik, K.; Compton, R. G., Advancing from rules of thumb: quantifying the effects of small density changes in mass transport to electrodes. Understanding natural convection. *Analytical Chemistry* **2015,** *87* (14), 7226-7234.