Supporting information

Amperometric micro pH measurements in oxygenated saliva

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SI1 Voltammetric surface waves at carbon fibre microelectrode without chemical modification

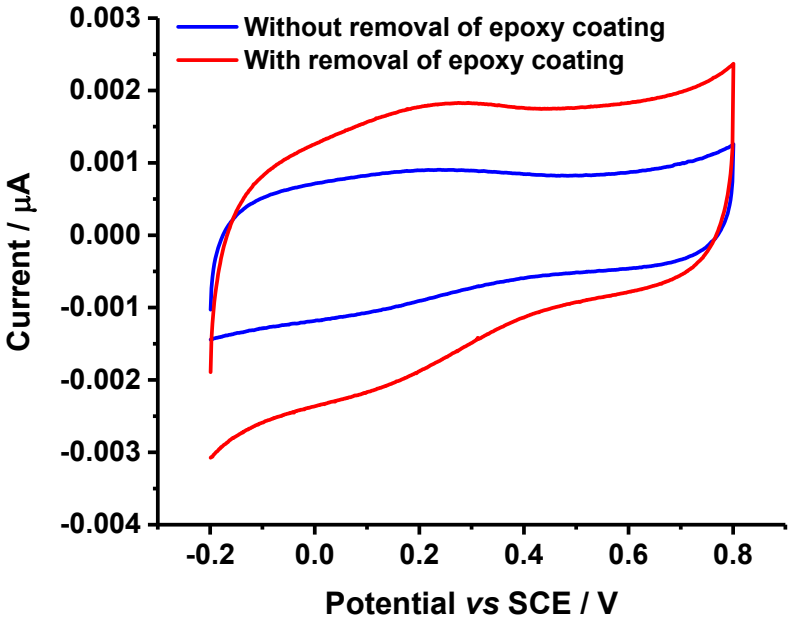

Fig. SI 1 CVs of pitch-based carbon fibre (micro-wire electrode) in 0.01 M HNO_3 + 100 mM KCl supporting electrolyte, used as received (blue line) and removed epoxy coating (red line) carbon fibre.

SI2 Chemical modification of carbon fibre surface in 0.03 M $KMnO_4$ prepared in sulfuric acid

Chemical modification of carbon fibre procedure

The carbon fibre was boiled in acetone for 1 hour to remove the sizing and expose the carbon surface. After boiling in acetone, the treated carbon fibre was immersed in normal temperature acetone and then left to dry.

Chemical modification of carbon fibre surface was carried out. For the optimisation of oxidising time, 0.03 M potassium permanganate solution was prepared in 10 mM sulfuric acid. This solution was used to oxidise carbon fibre at 85°C for 5, 10, 20, and 40 minutes. The samples were washed thoroughly with distilled water and then dried in oven at 60°C for 2 hours. For the optimisation of sulfuric acid concentration, 0.03 M potassium permanganate solutions were prepared in 5, 10, and 20 mM sulfuric acid. The carbon fibre was oxidised in the solutions at 85°C for 10 min. Again, the samples were washed thoroughly with distilled water and then dried in oven at 60°C for 2 hours. After that, the modified carbon fibres made into micro-wire electrodes and tested.

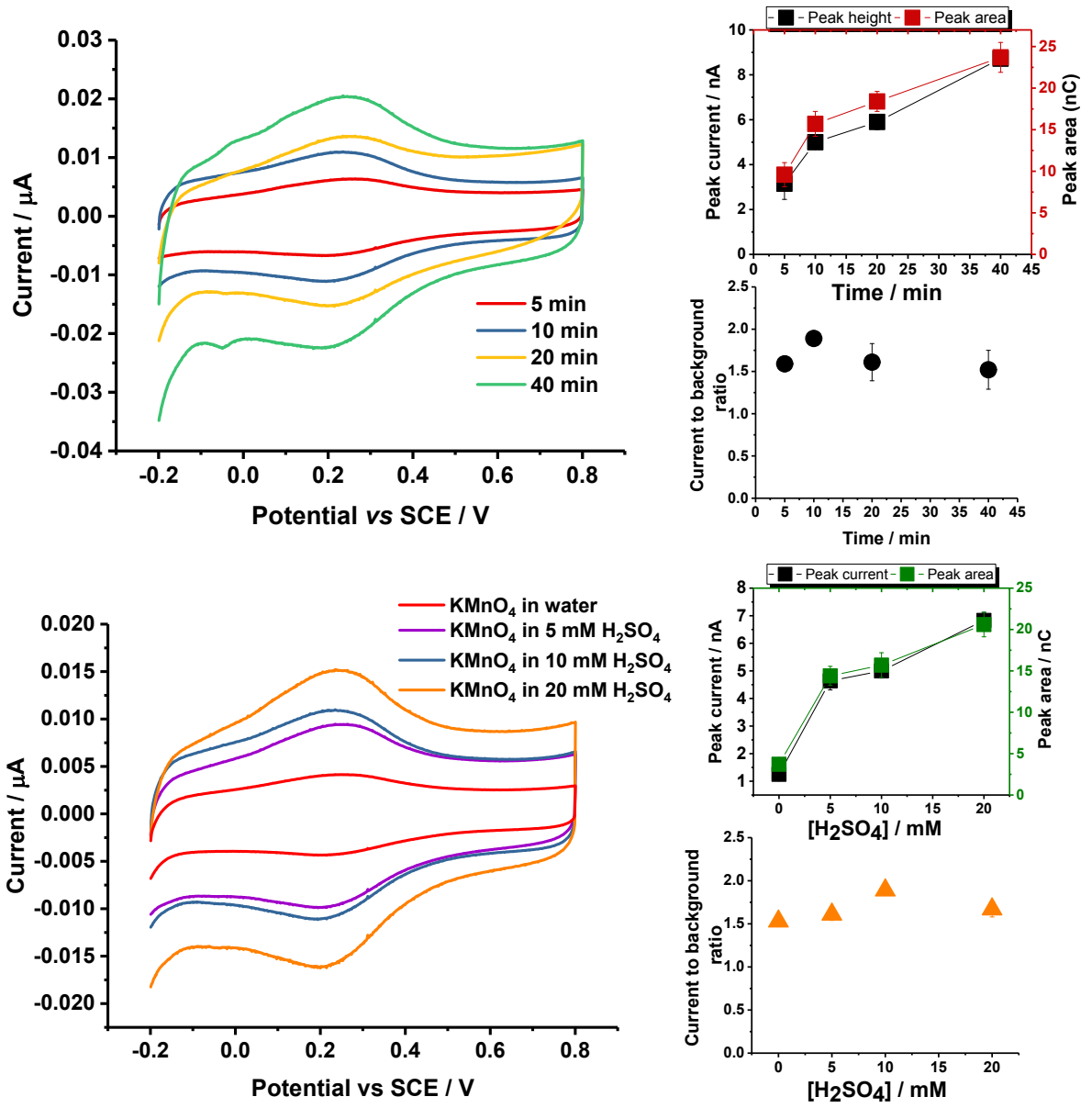

Fig. SI2 Optimisation of (A) modification time and (B) sulfuric acid concentration in 0.03 M $KMnO_4$ prepared in 5, 10, and 20 mM sulfuric acid.

SI 3 Reproducibility and stability of micro-wire electrodes

The reproducibility of the micro-wire pH sensors was investigated by preparing three electrodes. Cyclic voltammetry of *literature synthetic saliva* (pH 5.0) at scan rate of 4 V s^{-1} was recorded on three different micro-wire electrodes (Fig. SI3). The oxidation potential, reduction potential, and midpoint potential were 0.102±0.006 V, 0.041±0.006 V, and 0.072±0.006 V vs SCE respectively. The small standard deviation indicates that sensing performance of micro-wire electrode-to-electrode shows the good reproducibility.

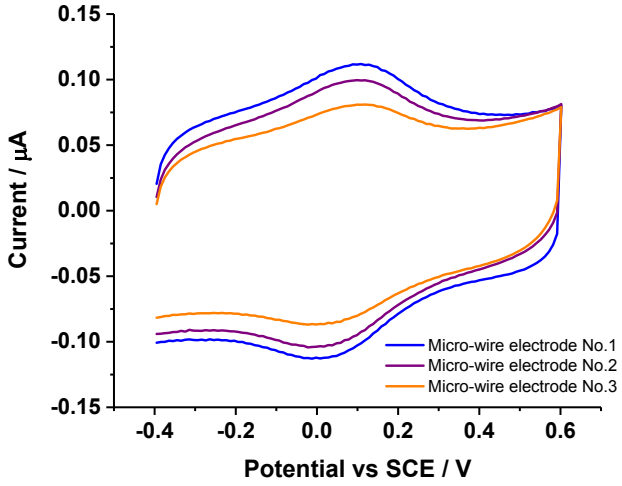

Fig. SI3 Cyclic voltammograms in *literature synthetic saliva* (pH 5.0) at different micro-wire electrodes at scan rate of 4 V s^{-1}.

The stability of the micro-wire pH sensor was determined by using the same electrode with multiple scans in 0.01 M HNO_3 solution (pH 2.2) at scan rate of 0.1 mV s^{-1}. The voltammetric responses to the repeated scans showed a stable voltammograms (Fig. SI4). The oxidation potential, reduction potential, and midpoint potential remained at 0.235 V, 0.206 V, and 0.221 V vs SCE respectively.

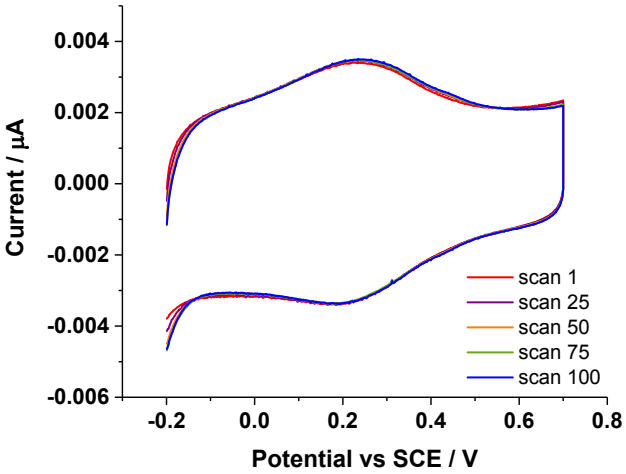

Fig. SI4 Cyclic voltammograms in 0.01M HNO_3 (pH 2.2) at the same micro-wire electrode with multiple scans at scan rate of 0.1 V s^{-1}.