Electronic Supplementary Information (ESI)

Defining the origins of electron transfer at screen-printed graphene-like and graphite electrodes: MoO_2 nanowire fabrication on edge plane sites reveals electrochemical insights

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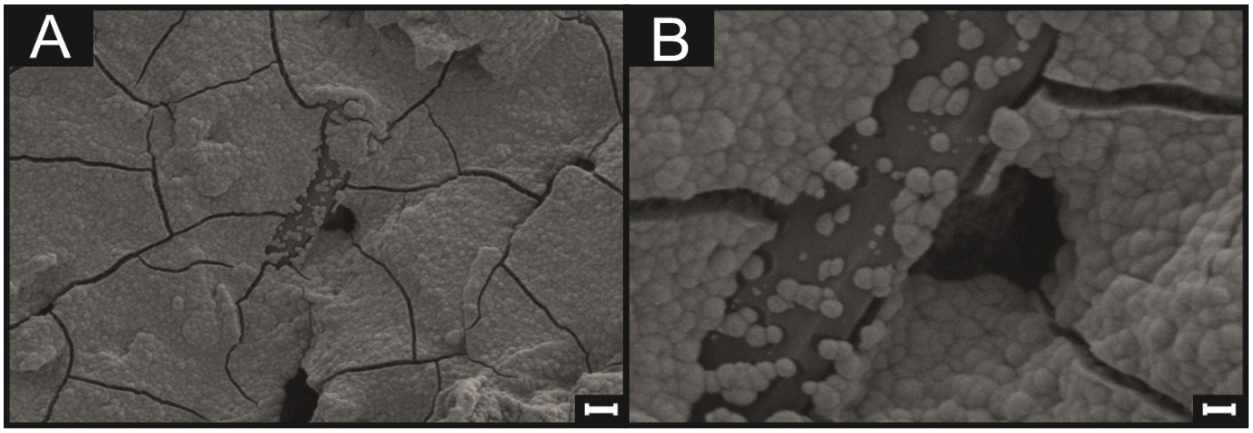
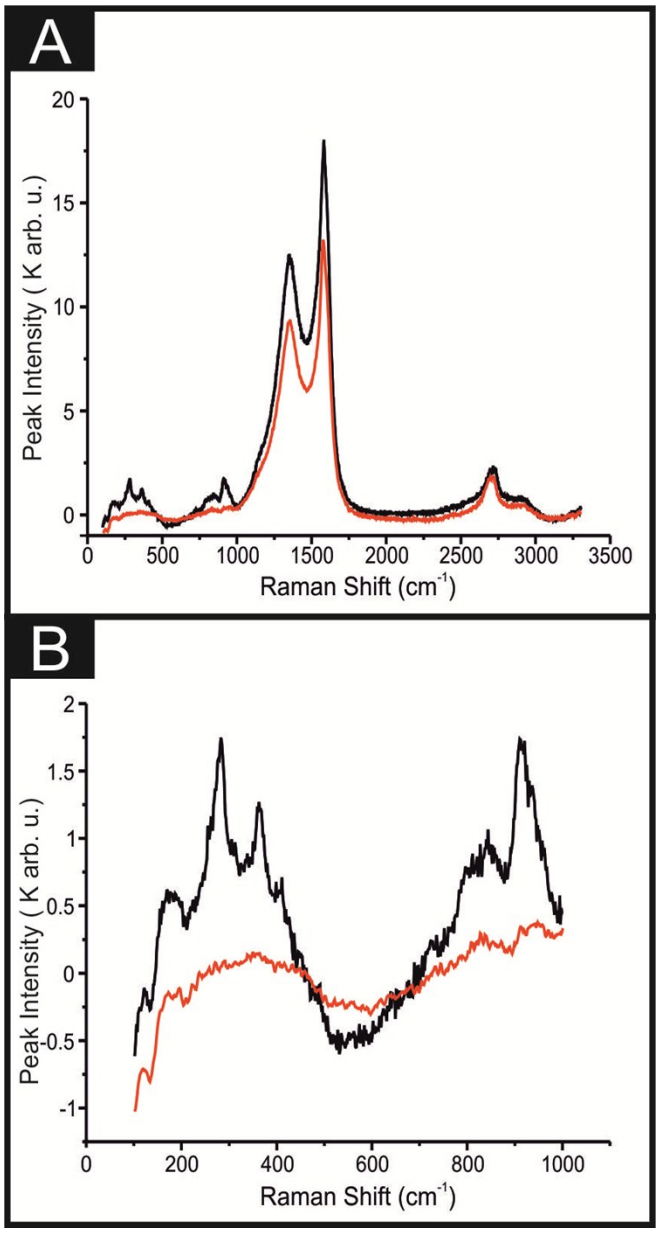
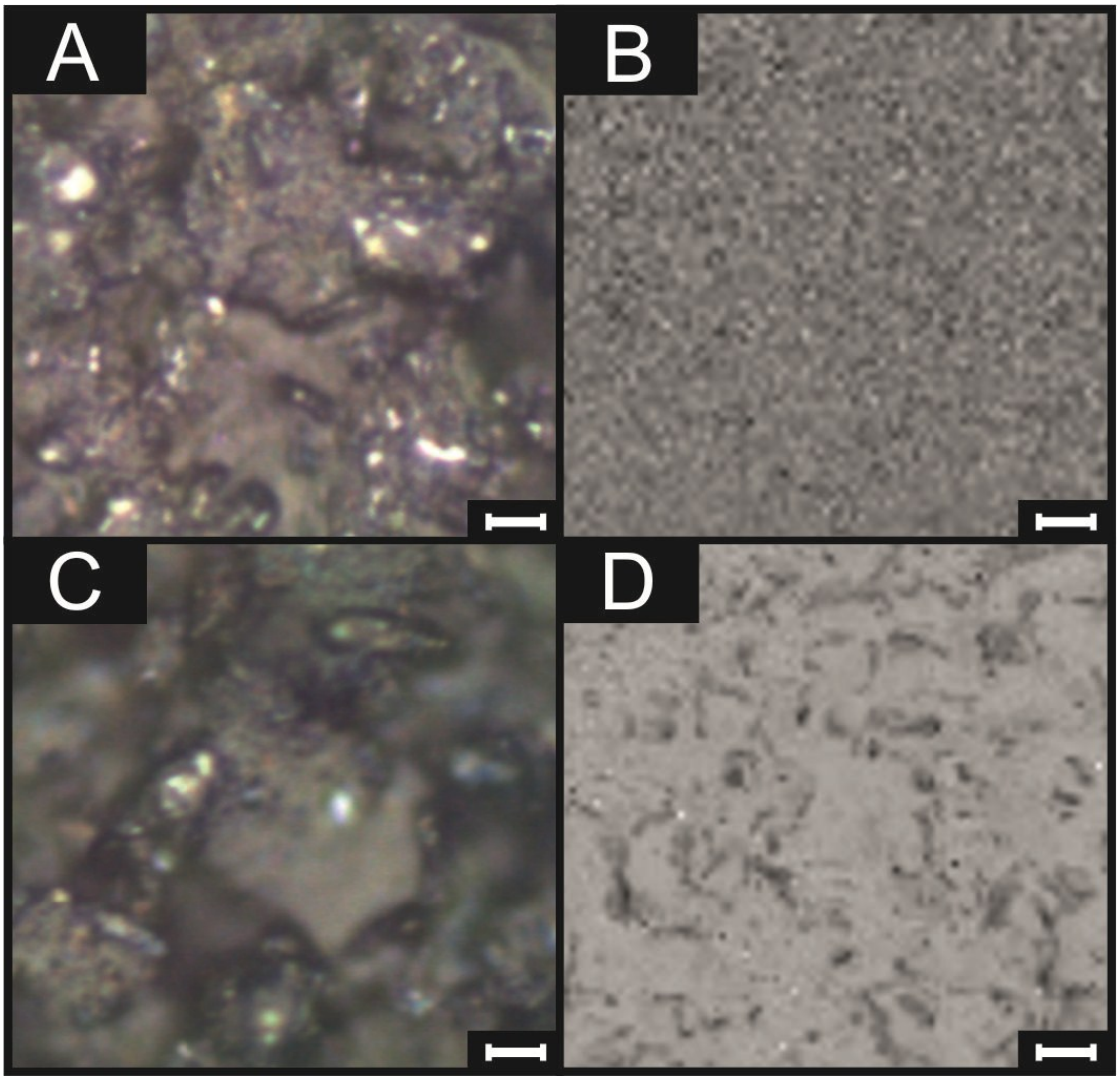
ESI Fig. 1 SEM images of the ESPE surface (using a pH 8.5 coating solution of 1 mM Na_2MoO_4, 1 M NaCl and 1M NH_4Cl) following the electrodeposition procedure at –0.92 V for 512 seconds. Image shows complete MoO_2 deposition over/across the electrode surface, with cracks visible in the electrodeposited film/covering. (A) ×10k magnification (scale bar: 1 μm), (B) ×60k magnification (scale bar: 300 nm).



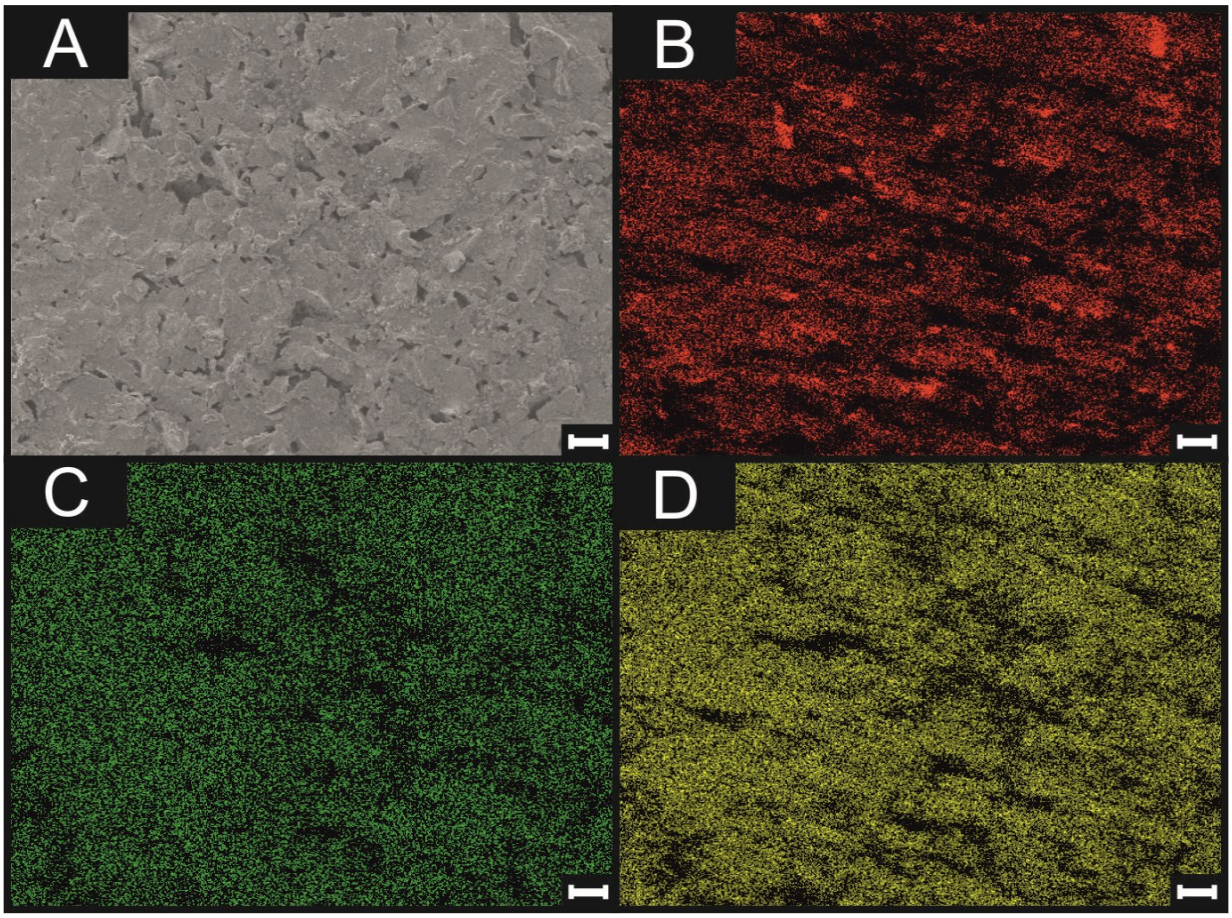
ESI Fig. 2 Raman spectra of an unmodified ESPE (red) and an ESPE (black) following MoO_2 electrodeposition onto its surface (chronoamperometry for 256 seconds at –0.92 V). Utilising the ranges 100 to 3300 cm^{-1} (A) and 100 to 1000 cm^{-1} (B).



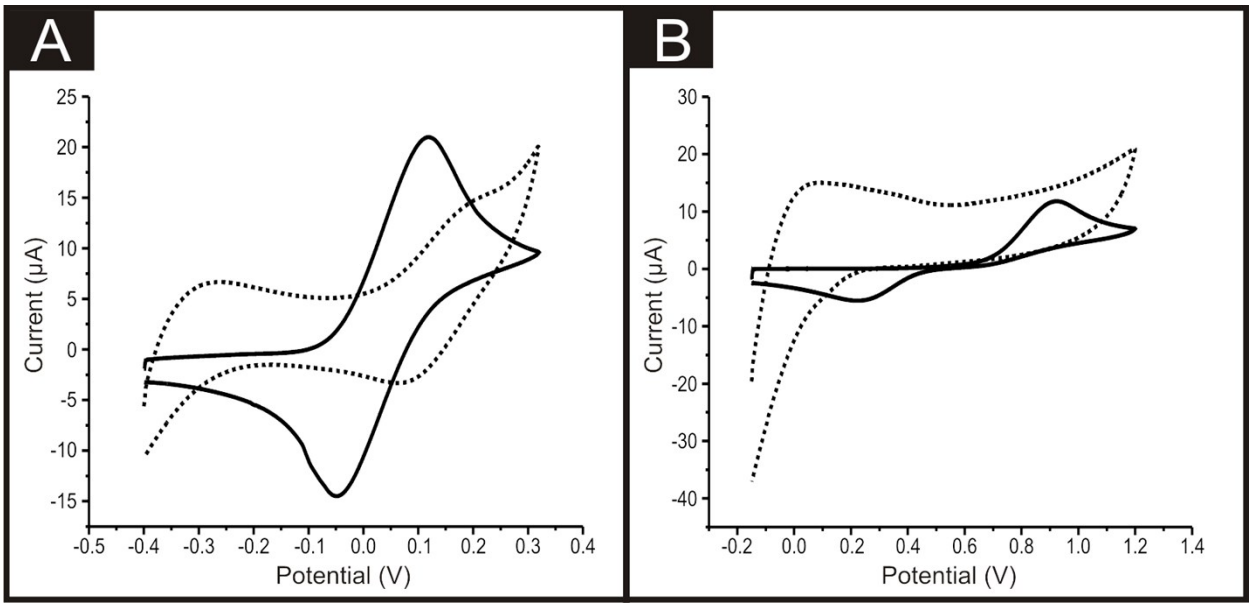
ESI Fig. 3 Optical images and Raman maps of; a bare/unmodified ESPE ((A) and (B) respectively) and an ESPE following MoO_2 electrodeposition for 256 seconds at –0.92 V ((C) and (D) respectively). Raman intensities recorded at 871 cm^{-1}, scale bar representing 10 μm, 400 point maps utilised.



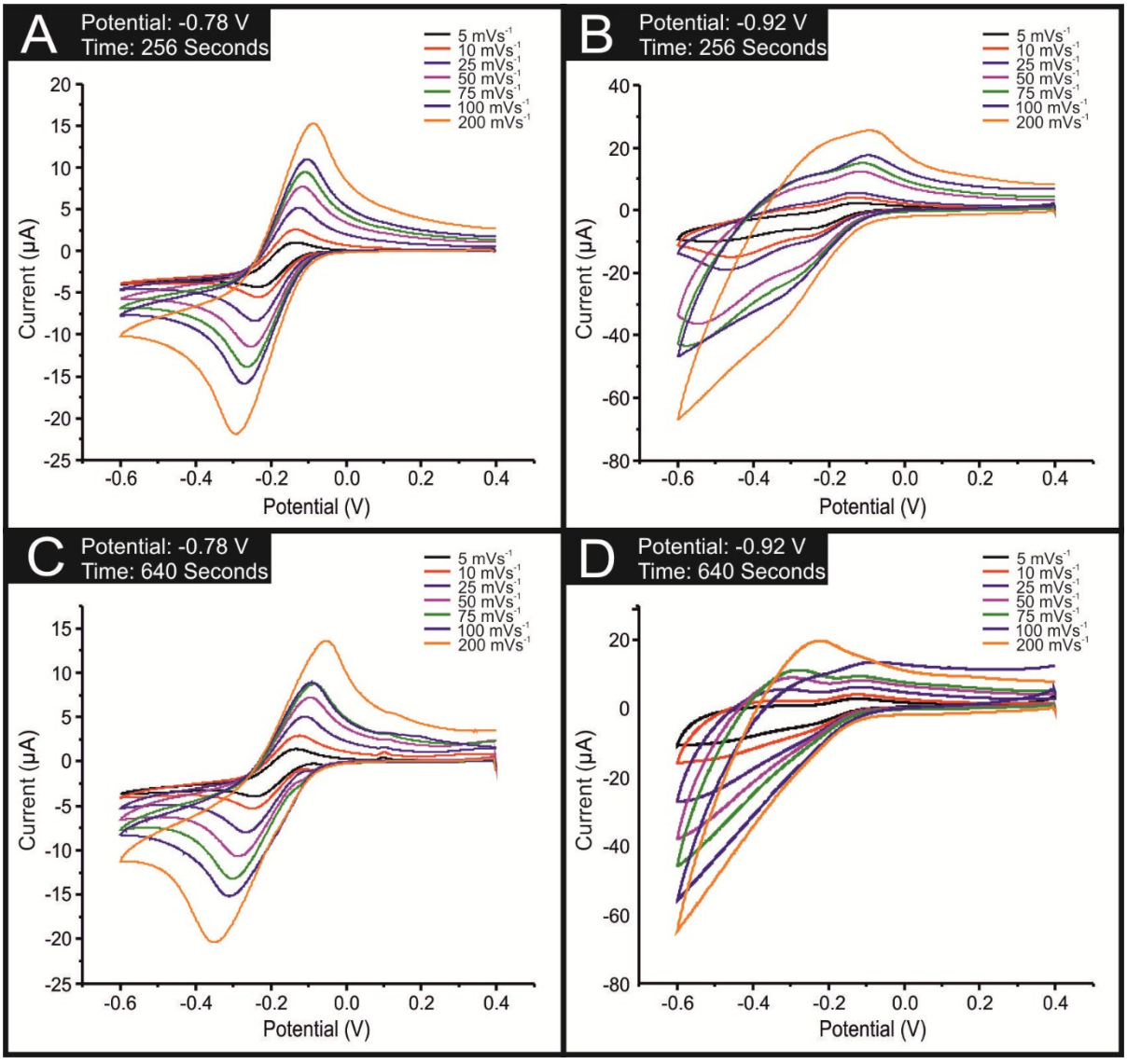
ESI Fig. 4 SEM image of an ESPE following MoO_2 electrodeposition for 384 seconds, with EDS analysis highlighting the underlying carbon (B, in red), Molybdenum (C, in green) and Oxygen (D, in yellow) coverage of the original SEM image presented in A (scale bars: 10 µm).



ESI Fig. 5 Cyclic voltammetric response utilising a bare/unmodified ESPE (solid line) and an ESPE following MoO_2 deposition *via* chronoamperometry at –0.92 V for 640 seconds (dotted line), (A) towards TMPD in 0.1 M KCl, and (B) towards 1 mM $Fe_{aq}^{2+/3+}$ in 0.2 M $HClO_4$. Scan rate: 100 mVs^{-1} (*vs.* SCE).



ESI Fig. 6 Cyclic voltammetric profiles recorded in 1 mM $[Ru(NH_3)_6]^{3+/2+}$ (0.1 M KCl) at ESPEs following various MoO_2 deposition protocols. 1 mM Na_2MoO_4, 1 M NaCl, 1 M NH_4Cl (adjusted to pH 8.5) was used as the coating solution *via* chronoamperometry. Individual electrode preparation conditions are indicated within the figure. The scan rate studies presented are a representative range of electrode conditions utilised to extract the k^o data that is tabulated in Table 1 (*vs*. SCE).



ESI Fig. 7 SEM images of a bare/unmodified ESPE (A) and at ESPEs following MoO_2 deposition *via* chronoamperometry utilising various conditions (B, C, D and E, parameters noted within the figure) in 1 mM Na_2MoO_4, 1 M NaCl, 1 M NH_4Cl (adjusted to pH 8.5) (*vs*. SCE). Scale bar: 1 μm, ×30k magnification.