Supporting Information

Water Oxidation Intermediates on Iridium Oxide Electrodes Probed by *In Situ* Electrochemical SHINERS

Experimental section:

The procedure for Au@SiO_2 shell-isolated nanoparticle synthesis is laid out in detail by Tian et al.[1] All glassware must be thoroughly cleaned prior to use. New glassware is initially washed with Piranha solution (5 parts H_2SO_4 to 1 part 40% H_2O_2) to remove traces of organic compounds. After rinsing thoroughly with Milli-Q water, the glassware is boiled in Milli-Q water 3 times prior to use. After use glassware is washed with Aqua Regia (1 part HNO_3 to 3 parts HCl) and stored in water, reserved only for SHINs synthesis.

55 nm Au nanoparticles are prepared by a method previously reported.[2] 7 ml of $HAuCl_4$ (9.8 mM) is added to 200 ml Milli-Q water in a round bottom flask and refluxed at 200 °C with stirring. Trisodium citrate solution (1.4 ml, 1 wt.%) is added and refluxed for 40 minutes. The initial yellow solution turns red/purple by the end of the reflux. This solution is returned to room temperature and stored in the dark.

0.4 ml (3-Aminopropyl)trimethoxysilane (APTMS) solution (22 µL in 100 ml Milli-Q water) is added to a sample of the gold nanoparticle suspension (30 mL) with vigorous stirring at room temperature for 20 minutes to allow the APTMS to exchange with citrate ligands. 3.2 ml sodium silicate (adjusted to pH 10.3 with HCl) is then added to the nanoparticle/APTMS suspension and left to stir at room temperature for 5 minutes. It is then transferred to a preheated water bath at 93 °C and left stirring. The time left stirring at this stage controls the thickness of the SiO_2 shell, with 20 minutes stirring at 93 °C giving a shell thickness of 2 nm, measured previously by TEM.[3] Every 10 minutes 2 samples (1 ml each) are taken and cooled in ice to halt shell growth. Once cool, the samples are centrifuged at 5500 RPM for 15 minutes and the supernatant is removed. The particles are then resuspended in 1 ml water and centrifuged again at 5500 RPM for 15 minutes. The supernatant is removed again and resuspended in water. Half the samples (1 from each time step) are stored, while the other half are centrifuged again for another washing step. The first set of SHINs (that were only washed once) are kept in case the nanoparticles in the second set aggregate. The SHINs are kept refrigerated (2 °C) in the dark and used within a few weeks. The SHINs used in this study strike a good balance between inertness, enhancement and ease of synthesis, figure S2, S3. Further increases in signal size can be achieved using a thinner silica shell, however, at the cost of introducing more pinholes potentially leading to electrochemical contributions from the gold core. Alternatively, larger Au cores can provide a greater electric field enhancement, however the synthetic procedures are more complex.[4]

Anodically deposited IrO_x films were prepared on glassy carbon electrodes based on the procedure reported by Mallouk *et al.*[5] An aqueous solution of $[Ir(OH)^6]^{2-}$ was prepared by dissolving 0.2 mmol K_2IrCl_6 in 100 ml NaOH (0.1 M) and heating to 70 °C, where an immediate colour change from yellow to colourless was observed. The solution was then rapidly cooled in ice and could be stored in the refrigerator (2.5 °C) for several weeks. Electrodeposition was carried out with a diluted $[Ir(OH)^6]^{2-}$ solution (15ml, 0.8 mM) in a 3-neck pear shaped electrochemical cell. The solution was adjusted to pH 8 with HCl and held at 1.5 V (vs Ag/AgCl) for 500 s with a Pt flag counter electrode. After each set of Raman experiments the electrodes were consecutively mechanically polished with 1 & 0.05 µm alumina slurries and sonicated in water for 30 s before the next deposition was carried out.

In situ Raman experiments were carried out in a custom-made spectroelectrochemical cell (developed by researchers in Xiamen University) with a Pt wire counter electrode and a silver wire pseudo-reference electrode. 2 µl of the SHINs suspension is dropped onto the IrO_x working electrode and allowed to dry in air and then the electrode is mounted and screwed in to position approximately 50 µm away from the front window. The exact distance between the front window and electrode surface could be measured using the computer controlled micrometer stage within the Raman microscope. The z- coordinate axis of the stage can be calibrated to µm by focussing on either face of the front window (of known thickness) of the Raman cell. The difference in the z-axis coordinates when the inner face of the front window and when the electrode surface are in focus can then be converted to a distance in µm. Due to the non-uniform distribution of SHINs from the drop-casting, a quick Raman peak-intensity-map of the electrode surface was carried out prior to experiments to identify spots that gave a more enhanced signal. It should be noted that a significant “coffee-ring” effect was observed in this drop casting, where the edges of the drop had thick layers of SHINs that block the Raman signal of the underlying IrO_x surface; all SHINER spectra were taken from spots away from this ring, towards the centre of the drop. Typical experiments involved 20 s exposure time to a 633 nm laser in the Renishaw InVia system during voltammetry experiments controlled by the Biologic SP200 potentiostat.

Supplementary figures:

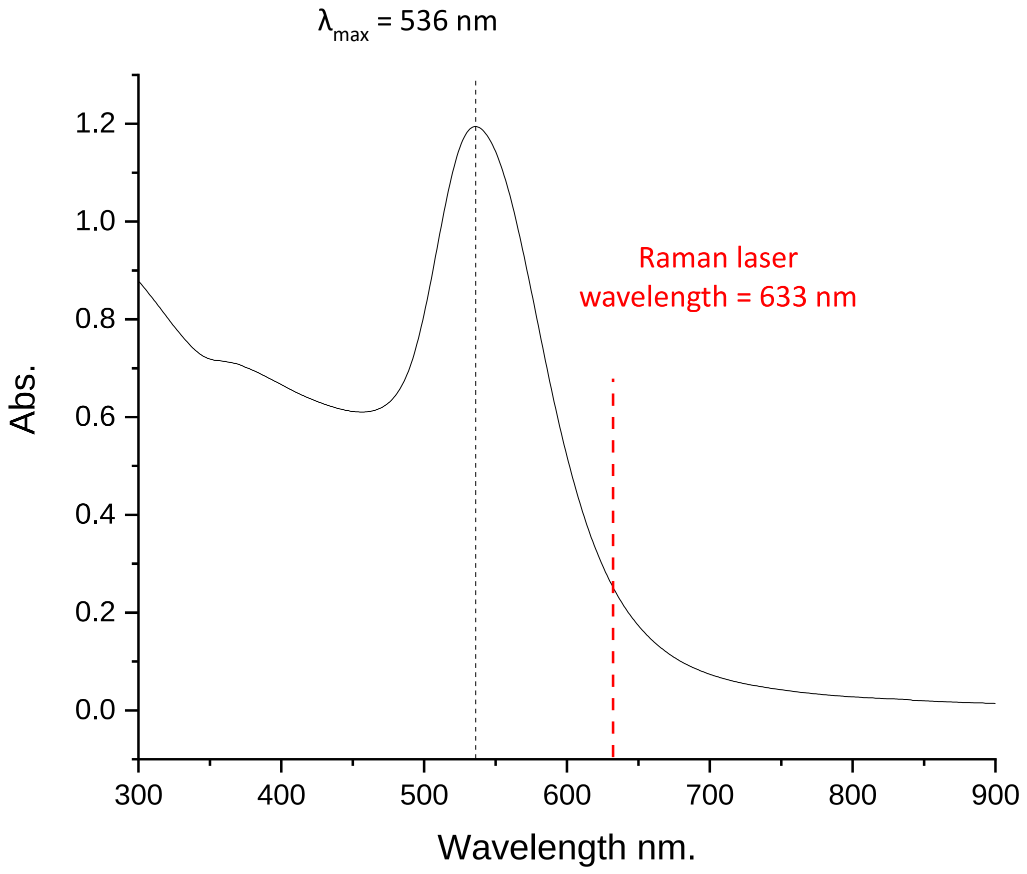

Figure S1: UV-Vis spectrum of $Au@SiO_2$ SHINs used in this report. SHINs suspended in Milli-Q water in 1 cm pathlength cuvette with Milli-Q water background. The maximum wavelength is in-line with gold nanoparticles of around 55 nm.[6]

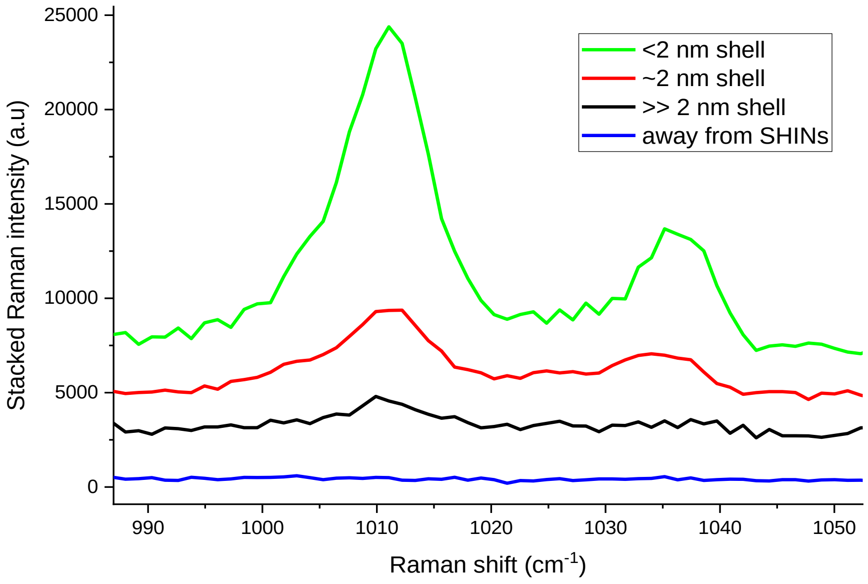

Figure S2: SHINs enhancement test. 2 µl of the SHINs suspension is dropped onto a clean gold wafer and allowed to dry in air. A drop of aqueous pyridine solution (10 mM) is sandwiched onto the gold wafer with a microscope slide cover slip and the Raman spectrum is recorded. The intensity of the ring breathing modes of pyridine adsorbed on a gold surface at 1012 and 1036 cm^{-1} are used as a test of the enhancement factor of the SHINs, where thinner shells give a larger enhancement.

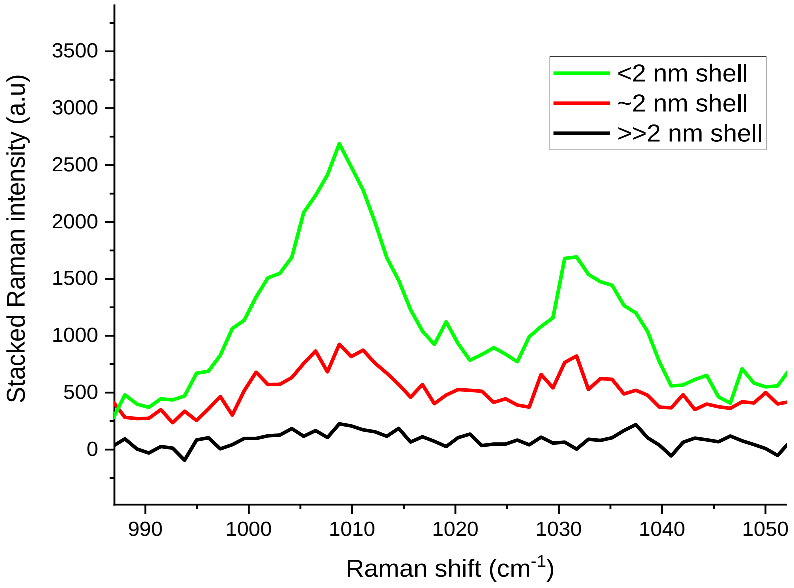

Figure S3: SHINs pinhole test. 2 µl of the SHINs suspension is dropped onto a clean silicon wafer and allowed to dry in air. A drop of aqueous pyridine solution (10 mM) is sandwiched onto the silicon wafer with a microscope slide cover slip and the Raman spectrum is recorded. Here the presence of the ring breathing modes of pyridine adsorbed on a gold surface can only be present if the pyridine can reach the gold surface of the SHINs, indicating the presence of pinholes in the SHINs. It should be noted that the presence of pinholes does not indicate that the SHINs are electrochemically active. SHINs with a 2nm shell were used for the rest of the data in this report and there is no evidence of gold oxidation or reduction in Figure S7.

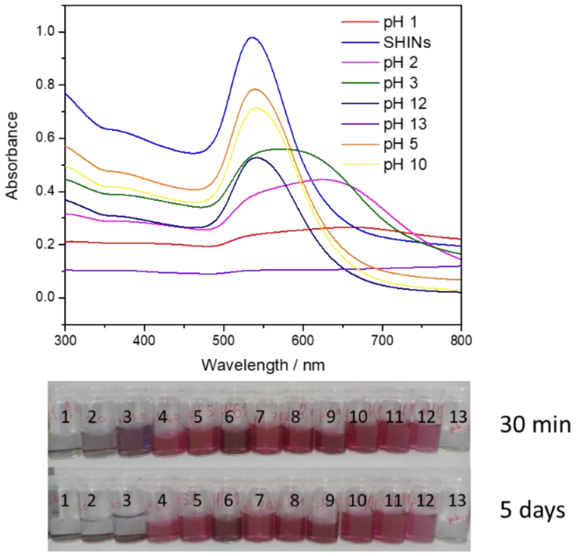

Figure S4: UV-vis spectra of Au@SiO$_2$ SHINs suspended in solutions of various pH (adjusted with NaOH or HCl) after 30 minutes and photographs of the suspensions after 30 minutes and 5 days. These experiments are used as a test of the stability of the SHINs at different pH values, where aggregation indicates that the conditions are unsuitable for the SHINs. The absorbance maximum remains constant at 536 nm between pH 5 and pH 12, with spectra above and below these pH values clear signs of aggregation (broadening and red-shifting). The UV/Vis data shows the SHINs are stable at up to pH 12 for > 30 minutes. Our experiments are conducted in pH 10 electrolyte, with typical experiments lasting around 12 minutes, though the SHIN-coated electrode may have been immersed in the electrolyte for up to 2 hours.

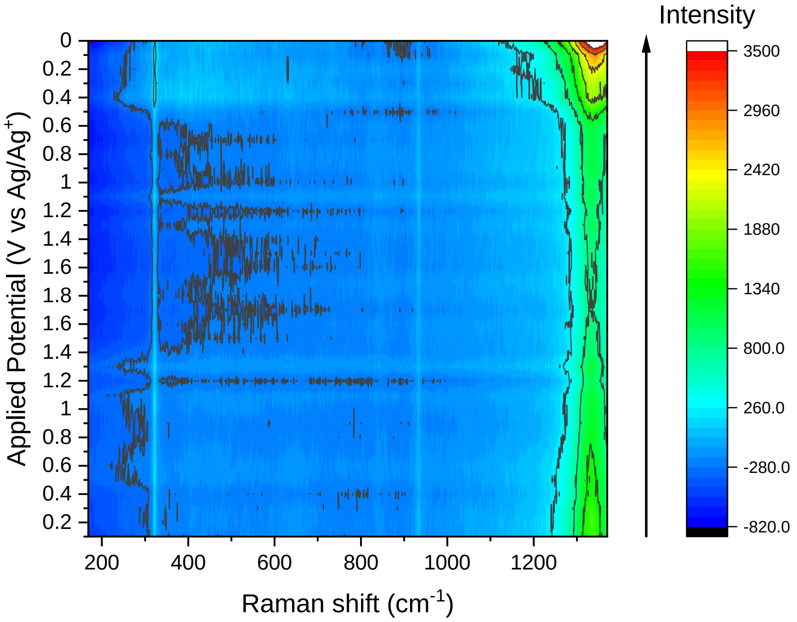

Figure S5: In situ SHINERS of SHINs/GCE system in 1 M $NaClO_4$ during a CV scanned at 5 mV s^{-1}, arrow indicates scan direction. The edge of the D-band of the glassy carbon surface can be seen around 1300 cm^{-1}. Showing a significant decrease with applied potential. This should not affect the results discussed here as it is outside of the spectroscopic region displayed in the main text.[6]

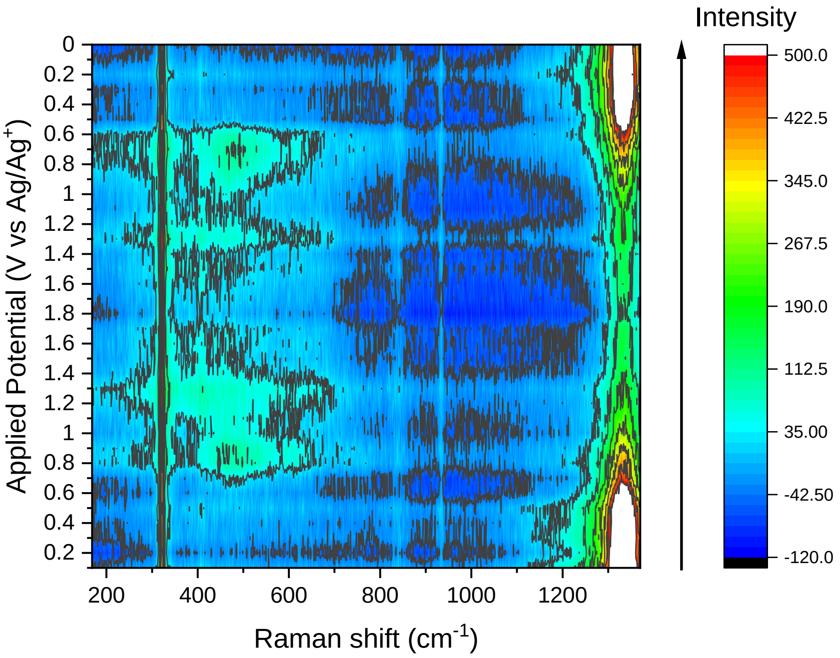

Figure S6: In situ Raman of IrO_x/GCE without any SHIN particles on the surface in 1 M $NaClO_4$ during a CV scanned at 5 mV s^{-1} (note the much smaller range in intensity), arrow indicates scan direction.

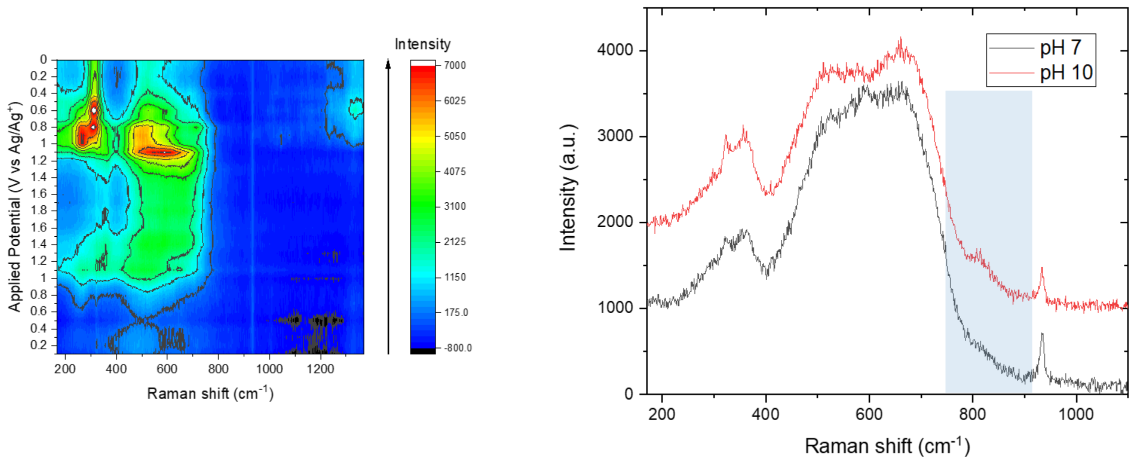

Figure S7: (Left) In situ SHINERS of SHINs/IrO_x/GCE in 1 M $NaClO_4$ (pH ~7) during a CV scanned at 5 mV s^{-1}, arrow indicates scan direction. (Right) Spectra recorded at 1.8 V at pH 7 (from experiment on the left) and at pH 10 (full experiment in figure 2 main text). Both spectra show the presence of η at a similar wavenumber, however at higher pH we measure a stronger Raman band for this species. The similarity between the two pH's reinforces the assignment of η.

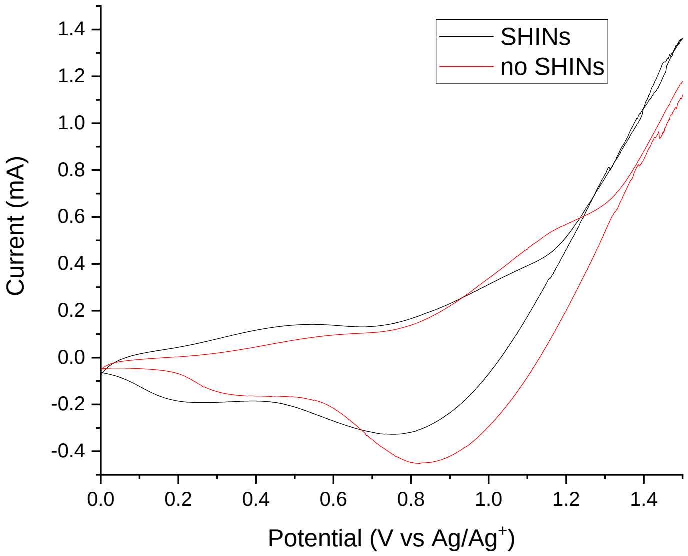

Figure S8: Comparative CVs of the IrO_x/GCE system with and without SHINs drop-cast on the surface, scanned at 50 mV s^{-1} in 1 M $NaClO_4$ in the spectroelectrochemical cell used for Raman. Potential values are slightly shifted due to the use of a Ag wire pseudo-reference electrode, but no additional features are present.

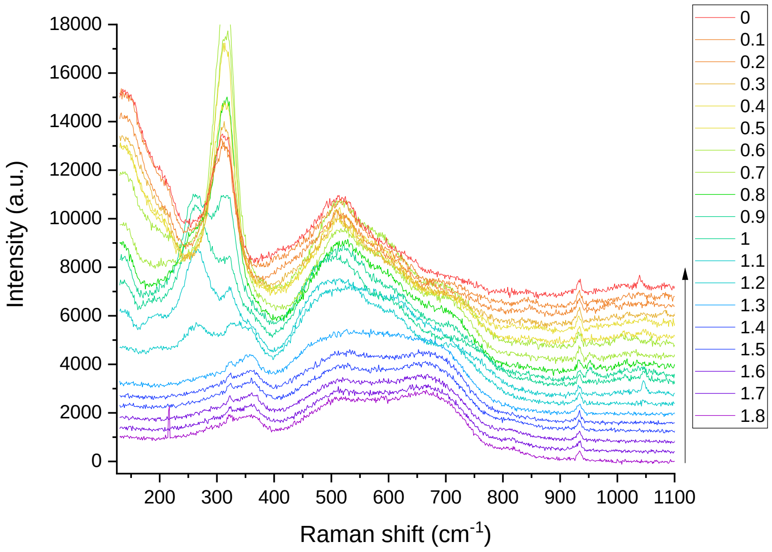

Figure S9: Reverse scan at 5 mV s^{-1} of Figure 2 (a) from the main text in 1 M $NaClO_4$ adjusted to pH 10 with NaOH, arrow indicates scan direction. Certain features are significantly more intense on the reverse sweep, possibly due to the initially mixed valence surface being forced through the different individual oxidation states as the potential is scanned negatively. These changes in relative intensity are not permanent and the spectrum by the end of the scan is decreasing in intensity, approaching the appearance of the initial spectrum.

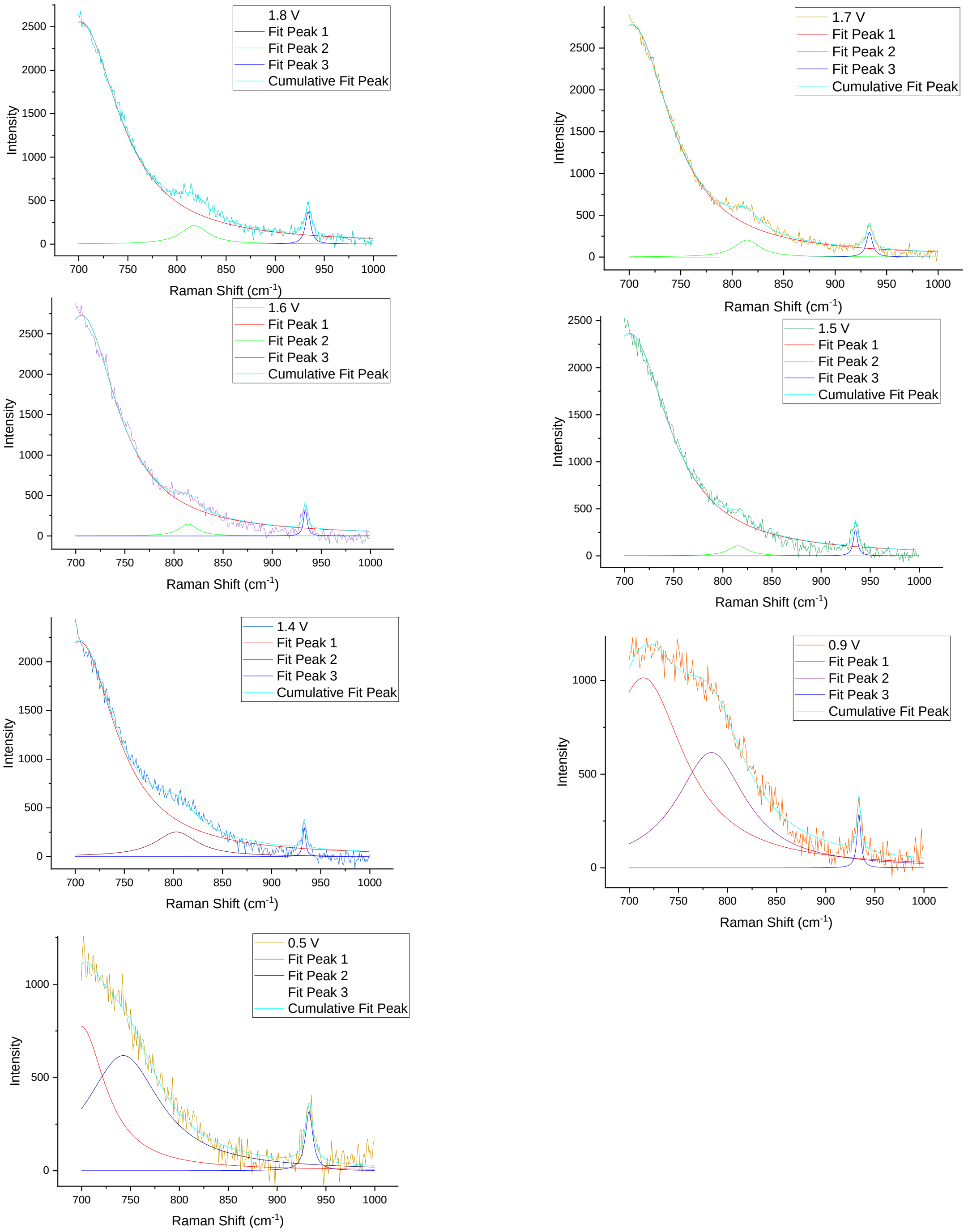

Figure S10: Lorentzian peak fitting between 700 and 1000 cm^{-1} focussing on η peak around 815 cm^{-1}. Fitting of the main feature between 400 and 850 cm^{-1} involves deconvolution of at least 5 features at each potential. To avoid unnecessary uncertainty, the fitting is restricted to between 700 and 1000 cm^{-1} and we fit the broad response up to 750 cm^{-1} to a single Lorentzian to focus on monitoring the potential dependent behaviour of the η peak at 815 cm^{-1}, which is only present during catalytic oxygen evolution between 1.5 and 1.9 V vs Ag/Ag^{+}. Below 1.4 V, a new feature, centred at 803 cm^{-1} (assigned to ζ in the main text), better fits the spectrum instead of η. This feature is redshifted at lower potentials (see spectrum at 0.9 V) to around 743 cm^{-1} (in the spectrum at 0.5 V), where it corresponds to the peak labelled ε in the main text. The purpose of this fitting is solely to monitor changes in the η peak; while the fitting of ε and ζ may not be accurate, it is shown here to indicate that a peak around 815 cm^{-1} (η) no longer fits the spectrum.

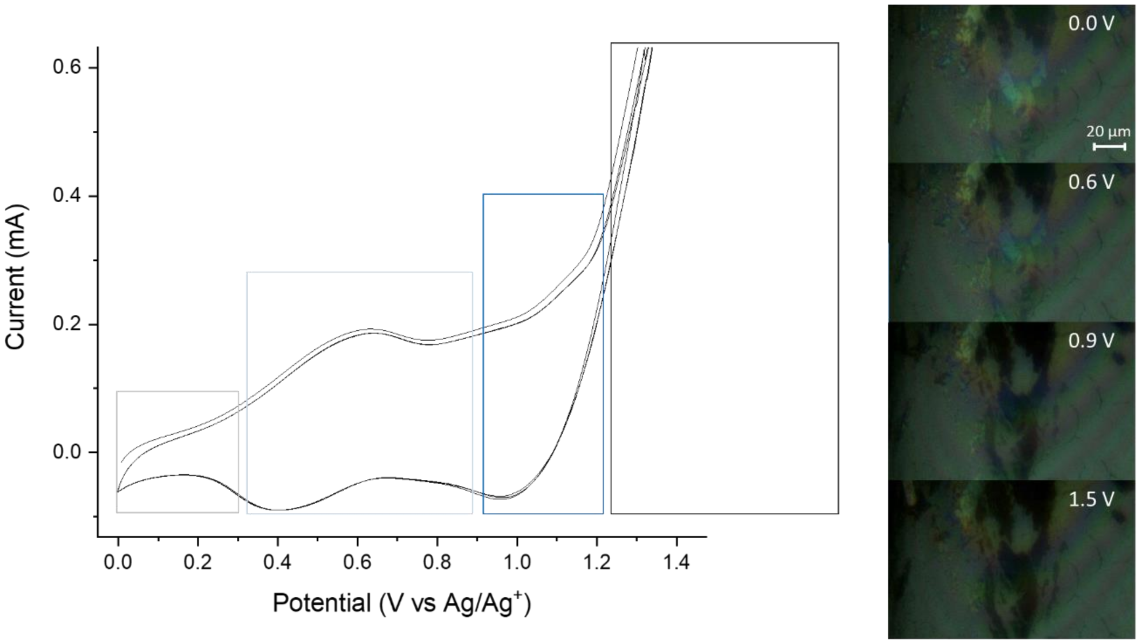

Figure S11: Electrochromic effect of IrO_x/GCE system displayed by optical microscope images of the electrode surface in the Raman microscope at the stated potentials (V vs Ag wire). Note that the Raman laser spot is focussed to a 1.5 µm spot at the centre of each image, where the colour change is most obvious. During cycling, the electroactive material changes from almost transparent in region I to a deep blue/black colour in region IV. Thus, depending on the proportion of electroactive material within the laser spot, the Raman spectrum can be significantly more intense at higher potentials. Often (as in Figure 2 in the main text) some amount of electro-inactive material is present within the laser spot, giving a relatively large signal at lower potentials too. This phenomenon slightly complicates the comparison of peak positions at the low potential region across datasets; the assignments shown in Table 1 are taken from spectra held above 0.9 V to overcome this.

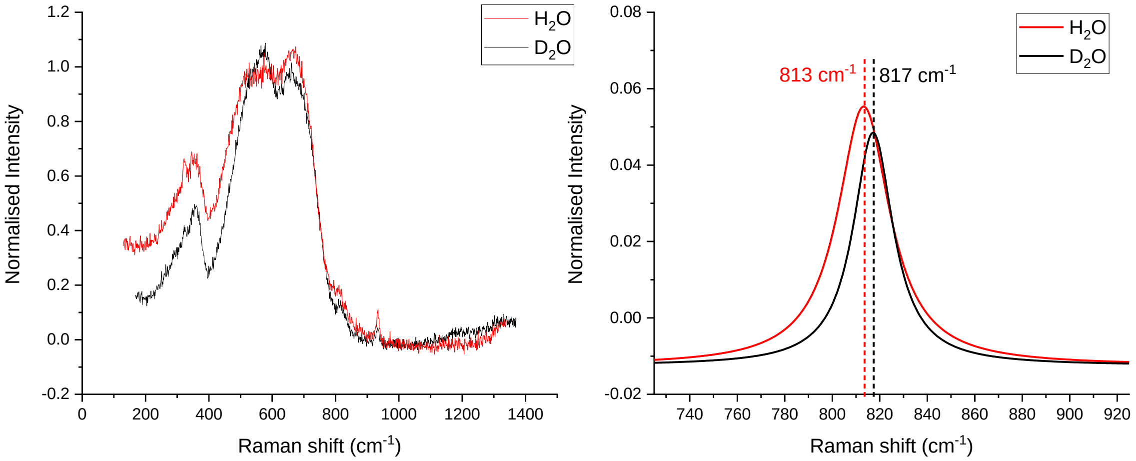

Figure S12: Comparison of normalised SHINER spectra at 1.8 V vs Ag wire in H_2O and D_2O-based 1 M $NaClO_4$, adjusted to pH (or pD) 10. Lorentzian peak fitting of η peak in both electrolyte systems (right) displays only a minor shift in position, supporting the assignment to an Ir=O stretching mode solvated by H_2O/D_2O. Both the timescale of our experiment (20 s per spectrum) and the lack of a significant shift (4 cm^{-1}) upon deuteration suggest this mode is not the O-O stretch of the surface IrOOH observed by Sivasankar *et al.*,[7] which did not persist in spectra after 610 ms following initiation and blueshifted by 30 cm^{-1} upon deuteration.

References:

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