Supporting Information for:

**The Effects of Ultrasound on the Electro-Oxidation of Sulfate Solutions at Low pH**

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**SI-1:** General Experimental Remarks: Ammonium sulfate (98+%), sodium metavanadate (96%), potassium iodide (99%) and Naphthol Blue-Black (also known as Amido Black 10B) were obtained from Alfa Aesar. Sulfuric acid (95%) was obtained from Fisher. Ammonium persulfate (≥98%), sodium sulfite (≥98%) and potassium permanganate (≥99%) were obtained from Sigma Aldrich. Hydrogen peroxide (30% by volume) and potassium chloride (analytical grade) were obtained from VWR Chemicals. Titanium oxysulfate (technical grade) was obtained from Riedel-de Haën. Potassium Ferricyanide (ACS grade) was obtained from Acros Organics. All aqueous solutions were prepared using ultrapure grade water (18.2 MΩ cm) obtained from a Sartorius Arium comfort combined water system. UV-Vis spectra were recorded on a JASCO V-670 spectrophotometer using 1 cm pathlength cuvettes.

Electrochemical studies were performed in a three-electrode configuration in single chamber cells unless otherwise stated. The working electrode used was either a boron doped diamond button electrode of surface area 0.071 cm2 (supplied by Windsor Scientific Ltd., UK), or a boron doped diamond foil (surface area = 0.88 cm2) also supplied by Windsor Scientific Instruments. Unless otherwise stated, the reference electrode used was a platinum wire and the counter electrode was a graphite rod (99.9999%, Sigma Aldrich) with a surface area far greater than that of the working electrode.

For sonication experiments, a Fisher Scientific FB15050 ultrasonic bath (frequency = 37 kHz) was employed, always filled with 2.2 L of water. A 100 mL beaker (open to the atmosphere) was used as the reaction vessel, and this was always submerged to the same depth (1 cm) and clamped in exactly the same position in the bath for each experiment. For all configurations, the distance between the working electrode and the base of the cell was 1.8 cm and the distance between the working electrode and the base of the ultrasound bath was 8.2 cm. The volume of solution submerged was 12.5 cm3 and the total surface area of the beaker exposed to the bath was 25 cm2. Using this set-up, the consistent temperature rise recorded during the sonication of 25 mL of pure water over 30 minutes (7 °C) could be used to gauge the acoustic power dissipated during sonication as 443 ± 83 mW, by the calorimetric method of Margulis and Mal’tsev. Using the volume quoted, an ultrasonic intensity of around 35 mW cm−3 is obtained.

**SI-2:** Electrochemical Methods: General: Electrochemical studies were performed in a three-electrode configuration in single chamber cells unless otherwise stated. The working electrode used was either a boron doped diamond (BDD) button electrode of surface area 0.071 cm2 (produced by chemical vapour diffusion and used as grown after polishing by the supplier, supplied by Windsor Scientific Ltd., UK), or a boron doped diamond foil (surface area = 0.88 cm2) also supplied by Windsor Scientific Instruments (produced by chemical vapour diffusion and used as grown with the nucleation side exposed). For the ultrasound bath calibration with [Fe(CN)6]3−, a glassy carbon electrode with surface area 0.071 cm2 (CH Instruments) was used. Unless otherwise stated, the reference electrode used was a platinum wire and the counter electrode was a graphite rod (99.9999%, Sigma Aldrich) with a surface area far greater than that of the working electrode. Working electrodes were polished with alumina powder and washed with water. Both working and counter electrodes were then washed with isopropyl alcohol and deionized water prior to use.

Controlled Current Electrolysis of Sulfate Solutions: Controlled current electrolysis at high current density was carried out using a CHI760d potentiostat version 14.05 or a Palmsens4 potentiostat on a boron doped diamond (BDD) button electrode of surface area 0.071 cm2. 25 mL of 3.62 M ammonium sulfate solution in 1 M H2SO4 was subjected to a current of 100 mA (current density of 1.41 A cm−2) for 15 minutes. This corresponds to 90 C of charge passed. Using Faraday’s Law of Electrolysis, a theoretical yield of 0.466 mmol of persulfate (assuming a 2-electron process and a 100% Faradaic efficiency) was thus obtained. This experiment was performed in the presence and absence of applied ultrasonic fields (37 kHz, see below). The effect of the observed temperature rise during sonication was also probed. This data is summarized in Table 1 in the main text (entries 1 and 2).

Controlled current electrolysis at low current density (23 mA cm−2, Table 1, entries 3 and 4) was carried out in a similar manner, except that the working electrode was now a boron doped diamond foil (surface area = 0.88 cm2) and the electrolyte was 0.5 M ammonium sulfate solution in 1 M H2SO4.

All potentials are reported uncorrected for cell resistances, which were found to be around 10 Ω.

Controlled Current Electrolysis in the Presence of Naphthol Blue-Black: 25 mL of 0.5 M ammonium sulfate and 3.2 µM naphthol blue-black in 1 M H2SO4 was subjected to a current density of 23 mA cm−2 for 5 minutes. Temperatures were initially 18 °C in all cases. When samples were stirred, they were stirred with a magnetic stir bar at 500 rpm. Some of the solutions subjected to controlled current electrolysis were also sonicated at 37 kHz, whilst others were not as described in the main text.

Naphthol Blue-Black Oxidation using Ammonium Persulfate: To 25 mL of 0.5 M ammonium sulfate in 1 M H2SO4 was added 0.106 g (0.466 mmol) of ammonium persulfate. The ammonium persulfate fully dissolved. The solution was then made to a concentration of 3.2 µM in naphthol blue-black and left to stir at room temperature for 5 minutes.

**SI-3:** Sonochemical Methods: A Fisher Scientific FB15050 ultrasonic bath (frequency = 37 kHz) was employed, always filled with 2.2 L of water. A 100 mL beaker was used as the reaction vessel, and this was always submerged to the same depth (1 cm) and clamped in exactly the same position in the bath for each experiment. The volume of solution submerged was 12.5 cm3 and the total surface area of the beaker exposed to the bath was 25 cm2. Using this set-up, the consistent temperature rise during sonication of 25 mL pure water over 30 minutes (7 °C) could be used to gauge the acoustic power dissipated during sonication as 443 ± 83 mW.

**SI-4:** **Total Oxidation Determination and Colorimetric Tests**

To determine the total amount of oxidants made during electrolysis, iodometric titration was used according to general procedures reported by Deadman et al. (B. J. Deadman, K. Hellgardt, K. K. Hii, React. Chem. Eng. 2017, 2, 462). To the solution to be tested, 200 equivalents of KI were added (relative to the theoretical maximum yield of ammonium persulfate calculated using Faraday’s law). This turned the solution dark orange. Sodium thiosulfate of known concentration was then added until the solution became colourless. To aid with detecting the endpoint, starch solution may be added, which reacts with any remaining iodide ions to give a dark blue colour. This method allowed the total amount of oxidants present in the analyte solution to be obtained on the basis of the amount (and concentration) of the sodium thiosulfate used in the titration.

**Determination of Caro’s Acid**

100 mM vanadyl sulfate solution was prepared by mixing sodium metavanadate with 1:3 diluted sulfuric acid to produce a yellow solution. A molar equivalent amount of sodium sulfite was added forming the blue vanadyl sulfate solution. This solution was then degassed to remove sulfur dioxide and used as below.

1 mol equivalent of VOSO4 (relative to the theoretical maximum amount Caro’s acid that could be made based on the charge passed in the electrolysis) was added to the solution to be tested. The vanadyl ion (VO2+) is selectively oxidised by Caro’s acid to the pervanadyl ion (VO2+). The absorption at 360 nm was measured and was compared to a calibration graph to determine the concentration of pervanadyl. Knowing the concentration of pervanadyl allows the calculation of the concentration of Caro’s acid that was in the solution and thus, the amount of Caro’s acid made during a particular experiment.

To produce the calibration curve, known amounts of KMnO4 were added to the VOSO4 solution to produce known amounts of pervanadyl, and then the absorption at 360 nm was measured.

**Determination of Hydrogen Peroxide**

To determine the concentration of hydrogen peroxide present, the analyte solution was mixed with titanium oxysulfate (TiOSO4) (a 1 mole equivalent relative to the theoretical maximum amount of hydrogen peroxide that could be made based on the charge passed). The TiOSO4 solution was made by dissolving TiOSO4 in 2 M H2SO4 (aided by sonication). When hydrogen peroxide reacts with TiOSO4, titanic acid is formed, turning the solution yellow. Absorption at 407 nm was taken and compared with a calibration curve to determine the amount of hydrogen peroxide made. To produce the calibration curve, known amounts of H2O2 were added to the TiOSO4 solution and then absorption at 407 nm was measured.