The lack of an artificial system that mimics elemental sulfur (S\(_8\)) oxidation by microorganisms inhibits a deep mechanistic understanding of the sulfur cycle in the biosphere and the metabolism of sulfur-oxidizing microorganisms. In this article, we present a biphasic system that mimics biochemical sulfur oxidation under ambient conditions using a liquid|liquid (L|L) electrochemical cell and gold nanoparticles (AuNPs) as an interfacial catalyst. The interface between two solvents of very different polarity is an ideal environment to oxidise S\(_8\), overcoming the incompatible solubilities of the hydrophobic reactants (O\(_2\) and S\(_8\)) and hydrophilic products (H\(^+\), SO\(_3^{2-}\), SO\(_4^{2-}\), etc.). The interfacial AuNPs provide a catalytic surface onto which O\(_2\) and S\(_8\) can adsorb. Control over the driving force for the reaction is provided by polarizing the L|L interface externally and tuning the Fermi level of the interfacial AuNPs by the adsorption of aqueous anions.
Mimicking the Microbial Oxidation of Elemental Sulfur with a Biphasic Electrochemical Cell

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Abstract

The lack of an artificial system that mimics elemental sulfur (S₈) oxidation by microorganisms inhibits a deep mechanistic understanding of the sulfur cycle in the biosphere and the metabolism of sulfur-oxidizing microorganisms. In this article, we present a biphasic system that mimics biochemical sulfur oxidation under ambient conditions using a liquid|liquid (L|L) electrochemical cell and gold nanoparticles (AuNPs) as an interfacial catalyst. The interface between two solvents of very different polarity is an ideal environment to oxidise S₈, overcoming the incompatible solubilities of the hydrophobic reactants (O₂ and S₈) and hydrophilic products (H⁺, SO₃²⁻, SO₄²⁻, etc.). The interfacial AuNPs provide a catalytic surface onto which O₂ and S₈ can adsorb. Control over the driving force for the reaction is provided by polarizing the L|L interface externally and tuning the Fermi level of the interfacial AuNPs by the adsorption of aqueous anions.
Introduction

Sulfur and its species are important geochemical agents, with the sulfur cycle vital to maintaining the natural equilibrium of the biosphere. Most sulfur redox reactions in the biosphere are thermodynamically allowed but kinetically sluggish, requiring catalysis by microorganisms capable of using inorganic sulfur compounds in their metabolism, either as electron donors or acceptors.[1] Indeed, the earliest organisms on Earth gained energy from the metabolism of sulfur compounds, including elemental sulfur.[2] Technologically, microbiological sulfur oxidation unpins many industrial processes such as mineral biotechnology,[1] microbial corrosion,[3] decreasing the pH of alkaline soils[4] and the development of fertilizers.[5] Plants assimilate mainly sulfate ions, but there are many commercial fertilizers that contain sulfur in elemental form. Their effectiveness depends on the rate at which elemental sulfur is oxidized to sulfate ions by microorganisms in the soil.[6]

The most stable allotrope of elemental sulfur is \( \alpha-S_8 \). This highly hydrophobic molecule is neither wetted nor dissolved by water. To oxidize \( \alpha-S_8 \), it has been proposed that microorganisms first dissolve it in the hydrophobic regions of their outer biomembranes. Subsequently, \( \alpha-S_8 \) can be transported inside the cell by surfactants or react at the biomembrane|water interface.[7] In this context, many fundamental questions remain concerning the sulfur oxidation reaction and associated kinetics. Why is this reaction almost exclusively driven by microorganisms in the biosphere? Can a chemical pathway be designed for this reaction with a low activation energy and without the need of a biomolecule?

Biochemical reactions at a biomembrane interface are typically coupled to ion transfer and electron transfer chain reactions that either increase the electric field across the membrane or drive thermodynamically uphill reactions, like ATP synthesis.[8] A powerful approach to mimic and model such processes, involving simultaneous ion and electron transfer reactions, is to electrochemically polarize an interface between two immiscible electrolyte solutions (ITIES).[9–11] Electrochemical reactions at such polarized liquid|liquid (L|L) interfaces may be complex due to the simultaneous coupling of not only interfacial ion and electron transfer reactions but also homogeneous chemical reactions, interfacial adsorption of ions or neutral species and the transport of solvent molecules across the interface by diffusion or facilitated by ion transfer.[12]

In the absence of a microorganism, the activation energy to form sulfate from \( S_8 \), molecular oxygen \((O_2)\) and water is prohibitively high at ambient conditions. Thus, a catalyst
is required to generate a new chemical pathway to oxidize S$_8$ with a low activation energy. Gold nanoparticles (AuNPs)$^{[13]}$ and nanoporous gold$^{[14]}$ are good catalysts for many oxidation reactions, despite the adsorption of O$_2$ on macroscopic gold surfaces being unfavoured.$^{[15]}$ In particular, supported AuNPs show unusually high catalytic activity for the oxidation of carbon monoxide and alcohols by O$_2$.$^{[16]}$ On the other hand, Tada et al.$^{[2]}$ reported that S$_8$ can be adsorbed on AuNP surfaces with cleavage of the S-S bond at a surface coverage ($\theta$) $<$ 1/3, while molecular adsorption takes place concurrently with atomic adsorption at $\theta$ $>$ 1/3.

Complications arise when using supported AuNPs, as the solid support is going to affect the electronic state of the NPs.$^{[17]}$ Therefore, determining the effect of solely the NPs size and electronic structure on the kinetics of a reaction, for example the O$_2$ reduction reaction (ORR), becomes difficult. In this sense, a polarized L|L interface functionalised with a film of AuNPs has some advantages when studying catalytic reactions. For example, there are two ways to change the Fermi level of NPs at a polarized L|L interface and tune their electronic state: by the adsorption of ions or in the presence of a redox pair in solution.$^{[18,19]}$ The past decade has seen a major increase in activity to functionalise the polarized L|L interface with various catalytic nanomaterials to study energy related reactions,$^{[20]}$ especially the ORR in the presence of AuNP films.$^{[21,22]}$

Herein, we describe a novel methodology to functionalise a polarized L|L interface with a film of AuNPs. This article provides the first experimental evidence of the physisorption of Cl$^-$ and OH$^-$ anions on such interfacial AuNPs. The oxidation reaction of elemental sulfur by O$_2$ at a polarized L|L interface catalysed by AuNPs is studied under ambient conditions and highlights the role of OH$^-$ anions to enhance this oxidation reaction.

Results and Discussion

**AuNP film growth at the polarized liquid|liquid interface.** The preparation of homogeneous and stable AuNP films at immiscible L|L interfaces is a major challenge.$^{[21,23,24]}$ Usually the surface is not homogeneously covered, significant aggregation of particles takes place at the interface and potential cycling can induce movement of the particles generating an interfacial convection (interfacial stirring).$^{[25]}$ Citrate ions are typically used to stabilize AuNP suspensions in bulk aqueous solutions.$^{[26]}$ However, such suspensions are very stable and, due to inter-particle electrostatic repulsion, the AuNPs rarely deposit in significant numbers at the L|L interface on contacting the aqueous phase with an immiscible organic solvent.$^{[27]}$ Various
approaches have been demonstrated to weaken the electrostatic repulsion between AuNPs and induce interfacial deposition while retaining the constituent properties of the individual AuNPs to the greatest extent possible. These include functionalizing the surfaces of charged colloidal NPs with charge-neutral organic “modifiers”\cite{28,29} or adding amphiphilic salts to the biphasic system\cite{30–32}. The latter act as “promoters” if the salts contain organic soluble ions of opposite charge to the NPs that screen inter-particle electrostatic repulsion\cite{23}.

Here, we replace the citrate buffer solution with a phosphate buffered saline (PBS) solution, pH 7.4, see electrochemical cell 1 in Scheme 1. The PBS-capped AuNP suspensions remain stable in the bulk aqueous phase. However, if these AuNPs come into proximity with a L|L interface formed by water and $\alpha,\alpha,\alpha$-trifluorotoluene (TFT) they lose their ionic solvation shells, induced by the electric field at the interface and/or by changes of the local solvent polarity. In other words, PBS gives the dynamic freedom necessary to avoid agglomeration in the bulk aqueous phase but, at the same time, facilitates a change of the AuNPs ionic and solvation cloud at the L|L interface.

\textbf{Scheme 1.} Four-electrode electrochemical cell configurations used to prepare the AuNP film at the polarized liquid|liquid (L|L) interface (electrochemical cell 1) and then use the formed interfacial AuNP film to oxidise sulfur biphasically (electrochemical cell 2). PBS is phosphate buffered saline solution at pH 7.4, BACl is bis(triphenylphosphoranylidene)ammonium chloride, BATB is the organic electrolyte salt bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate and the organic solvent is $\alpha,\alpha,\alpha$-trifluorotoluene (TFT). The experiments were carried out either under aerobic or anaerobic conditions, as detailed in the text.

Electrochemistry at polarized L|L interfaces both facilitates AuNP film formation and provides a novel method to monitor and control the AuNP films growth using cyclic
voltammetry (CV), see Figure 1A. The adsorption of aqueous anions on the AuNPs gives a well-defined reversible signal between −0.2 V and +0.2 V. With potential cycling, the amount of AuNPs at the interface increases and so too does the adsorption of anions. This electrochemically driven experimental approach yields a homogeneous film of AuNPs and provides an external control of the film thickness (Figure 1B). The experiment was performed under an argon (Ar) atmosphere as potential cycling in the presence of O₂ can slowly oxidise the AuNPs irreversibly (discussed vide infra) and change the active surface where anion adsorption takes place.

Figure 1. Inducing and monitoring AuNP film growth at a polarized L|L interface under anaerobic conditions. (A) Cyclic voltammetry (CV) as AuNPs deposit at the L|L interface over 100 potential cycles (solid lines). Every 10th CV is shown, starting with the first CV cycle, and the arrow shows the evolution with time. The dotted line shows a numerical simulation of the CV using a Frumkin isotherm (repulsive interaction factor of 13.5 kJ mol⁻¹, total surface charge 17.5 μC cm⁻²). The scan rate used was 25 mV·s⁻¹. The conditions in the glovebox were Ar (~1 bar) and O₂ (~1.5 ppm). The electrochemical cell used to prepare the AuNP film was as described by electrochemical cell 1 in Scheme 1 with x = 0. (B) Optical image of the AuNP film at the L|L interface after undeposited AuNPs in the bulk aqueous phase were removed by careful sequential washing with 10 mM LiCl. This image represents electrochemical cell 2 in Scheme 1 with x = 0 and X = Cl⁻.

Physisorption of aqueous anions on the interfacial AuNPs. The influence of the aqueous anion on the CV response of the interfacial AuNP film was probed by using either 10 mM LiCl or 10 mM LiOH as the aqueous phase under aerobic conditions (Figure 2A). For both aqueous electrolytes, the near symmetric shape of the CVs and their behaviour with scan rate, showing a linear increase in peak current with scan rate (Figure S1), indicate an interfacial adsorption/desorption process. Negatively charged AuNPs may attach and detach from the L|L interface with applied potential, but this process is very slow and does not yield symmetric
voltammetry signals. Therefore, the CV responses in Figure 2A are attributed to the adsorption of ions on the interfacial AuNPs, specifically OH\(^-\) and Cl\(^-\) anions. CV responses for the adsorption of these anions at the bare L|L interface do not give well defined peaks within the polarizable potential window. Figures 2A and 2B show that the adsorption strength of OH\(^-\) is much higher than that for Cl\(^-\), mirroring a trend observed for the electroadsorption of these ions on Au(111).  

Figure 2. Adsorption of aqueous anions on the interfacial AuNPs at the polarized L|L interface under aerobic conditions. (A) CVs with iR compensation at a scan rate of 200 mV s\(^{-1}\) and (B) differential capacitance curves for electrochemical cell 2 in Scheme 1 with \(x = 0\) and \(X\) either Cl\(^-\) (black line) or OH\(^-\) (red line). The dotted lines in (A) show a numerical simulation using a Frumkin isotherm. All electrochemical data in (A) and (B) were obtained using the same AuNP film at the L|L interface, and the experiments in the presence of LiCl were performed before those with LiOH. (C) CVs after the addition of 19 mM tetramethylammonium cation (TMA\(^+\)) to electrochemical cell 2, with \(x = 0\) and \(X = Cl^-\), at scan rates of 25 (black line) and 200 mV s\(^{-1}\) (red line). The CVs were taken with iR compensation. (D) Electrochemical impedance spectroscopy (EIS) spectra at +0.006 V (black circles) and +0.311 V (red squares) for the electrochemical cell described in (C). The solid lines show the fittings using the equivalent circuits depicted.
The dotted lines in Figure 2A show the results of computed numerical simulations of the CV profiles corresponding to an adsorption process following a Frumkin adsorption isotherm. The simulations solved the differential equation arising from the kinetics of the surface coverage in time upon potential cycling, the Python code is available in the Supporting Information (SI). The numerical simulations show that the maximum charge density associated with OH\(^-\) and Cl\(^-\) adsorption during the negative scan are 24 and 12 \(\mu\text{C}\cdot\text{cm}^{-2}\), respectively. The simulations also show that the adsorption of anions can be reasonably described by a Frumkin model, where the Gibbs adsorption energy increases with surface coverage, with a repulsive interaction factor of 14.5 kJ\cdot\text{mol}^{-1}. The total maximum charge associated with Cl\(^-\) adsorption is higher for AuNP films grown in an Ar atmosphere (17.5 \(\mu\text{C}\cdot\text{cm}^{-2}\), Figure 1A) than in air (12 \(\mu\text{C}\cdot\text{cm}^{-2}\), Figure 2A), and the CVs generated in an Ar atmosphere are more symmetric (Figure 1A, black lines) than those in air (Figure 2A, black line). The former suggests that the presence of \(\text{O}_2\) reduces the capacity of AuNPs to adsorb anions. On the other hand, the high value for the interaction factor, and the fact that it is almost the same for OH\(^-\) and Cl\(^-\), suggests that after adsorption the anions keep a significant negative charge. Thus, the anion-Au bond must be highly polar and the CVs in Figures 1A and 2A are due to the physisorption of anions, and not to their electro-adsorption. In conventional three-electrode electrochemical cells, it is electro-adsorption and not physisorption of anions that is observed.

Oxide formation on Au(111) electrodes has been reported to occur when OH\(^-\) adsorption reaches charge densities \(>35 \ \mu\text{C}\ \text{cm}^{-2}\), meaning that this is the maximum OH\(^-\) coverage that can be reached on Au\(^\text{[33]}\). Herein, the maximum coverage of OH\(^-\) reached on the interfacial AuNPs is ca. 24 \(\mu\text{C}\cdot\text{cm}^{-2}\). OH\(^-\) is adsorbed more efficiently on a polarized Au electrode as the Fermi level of Au decreases when the OH\(^-\) coverage increases with applied potential. In other words, the negative charge on adsorbed OH\(^-\) is screened by a net charge transfer from the adsorbed anion to the Au electrode. On the other hand, OH\(^-\) adsorption on the interfacial AuNPs increases their Fermi level. Thus, the AuNPs become more negatively charged, inhibiting the further adsorption of other OH\(^-\) anions.

The influence of the aqueous anion on the measured differential capacitance curves in the presence of the AuNP film was also investigated (Figure 2B). The capacitances in the presence of LiCl (black dots) and LiOH (red dots) were almost the same at potentials close to the potential of zero charge (PZC) around +0.3 V, confirming that the surface coverage of interfacial AuNPs was the same for both experiments and the AuNPs were stably attached to the interface. Furthermore, the well-defined peaks at potentials lower than the PZC confirm the
adsorption of negatively charged anions. To our knowledge, this is first experimental evidence that \( \text{Cl}^- \) and \( \text{OH}^- \) can be physisorbed, in their anionic form, on AuNPs at a polarized L|L interface.

The transparency of the interfacial AuNP film to ion transfer was investigated by monitoring the tetramethylammonium cation (TMA\(^+\)) transfer reaction using CV and electrochemical impedance spectroscopy (EIS) at a AuNP film functionalised L|L interface (Figure 2C). Considering that TMA\(^+\) transfers close to the PZC (compare Figures 2B and C), a low influence of the electrical double layer was expected as the impact of migration should be negligible.\(^{[9,34]}\) The interfacial AuNP film was found to have no significant effect on the TMA\(^+\) ion transfer kinetics as demonstrated by (i) the peak separation of the reversible TMA\(^+\) ion transfer response being 58 mV (Figure 2C), (ii) the ion transfer resistance being undetectable by EIS experiments (Figure 2D), and (iii) the Randles circuit accurately describing the EIS spectra at the TMA\(^+\) ion transfer potential of +0.311 V (Figure 2D).

The influence of scan rate on the signals associated with Cl\(^-\) and OH\(^-\) adsorption or TMA\(^+\) transfer is markedly different (Figure 2C and Figure S1). The peak current for the Cl\(^-\) and OH\(^-\) adsorption is proportional to the scan rate (Figure S1D) and increases much faster with scan rate than the TMA\(^+\) transfer signal, which is proportional to the square root of the scan rate (data not shown). Additionally, the EIS spectrum at +0.006 V (Figure 2D) shows that the AuNP film does not behave like an ideal capacitor and a constant phase element (CPE) with an \( n \) value of 0.91 is needed to fit the experimental data. Usually a CPE with an \( n \) value lower than 1 is associated with a capacitor comprising a very rough surface.\(^{[35]}\) Thus, this indicates that interfacial AuNP accumulation and agglomeration increases the roughness factor of the L|L interface. Previously, Younan \textit{et al.} showed that the capacitance of the L|L interface increases in the presence of an adsorbed monolayer of citrate coated AuNPs and attributed this to an increase of the interfacial charge density or by an increase of the interfacial corrugation.\(^{[36]}\)

**Adsorption of hydrophobic elemental sulfur on the interfacial AuNPs.** The presence of O\(_2\) changes the active surface area of the interfacial AuNPs for the adsorption of anions (discussed \textit{vide supra} when comparing Figures 1A and 2A). To further investigate this effect, the evolution of the CVs using electrochemical cell 2 with LiOH as the aqueous phase, see Scheme 1, under anaerobic conditions was probed (Figure 3A). Extensive potential cycling clearly decreases the peaks related to OH\(^-\) adsorption, generates a broad new signal between +0.1 V and +0.5 V and leads to the cathodic peak shifting to more positive potentials. Each of these changes are consistent with the CV obtained in air (red line in Figure 3A), suggesting
their origin as chemical reactions between O$_2$ and AuNPs upon potential cycling. It seems that O$_2$, even at very low concentrations (~1.5 ppm), slowly passivates the interfacial AuNPs surface, possibly by forming a layer of oxide upon extensive potential cycling.

![Figure 3. Redox reactions between sulfur and physisorbed OH$^-$ on the interfacial AuNPs at the polarized L|L interface under anaerobic conditions. CVs over 50 potential cycles using electrochemical cell 2 with $X = \text{OH}$ (see Scheme 1) in (A, C) the absence ($x = 0$) and (B, D) the presence ($x = 8.11$) of elemental sulfur in the organic phase. Every 10$^{th}$ CV is shown, starting with the first CV cycle, and the arrows show the evolution with time. The scan rate used was 25 mV·s$^{-1}$ in (A) and (B). The conditions in the glovebox were Ar (~1 bar) and O$_2$ (~1.5 ppm). For comparison, the red CV in (A) was obtained in air. The CVs shown in (C) and (D) were obtained after the 50$^{th}$ potential cycle in each case at scan rates of (C) 200 mV s$^{-1}$ and (D) 100 mV s$^{-1}$, respectively.

The introduction of dissolved elemental sulfur to the organic phase stabilises the CVs when the cell is inside the glovebox, with some signals increasing slightly upon potential cycling (Figure 3B). Interestingly, the CVs shown in Figure 3B are similar to those reported for aqueous solutions of Na$_2$S in alkaline media on Au electrodes$^{[37–39]}$ and, in our opinion, can be rationalized in a similar way. Firstly, previous studies have indicated that both atomic and molecular sulfur can be adsorbed on gold.$^{[38–40]}$ Secondly, the shape and behaviour of the CVs
with scan rate suggests that the peaks observed inside the potential window arise mainly from surface processes. Thirdly, the asymmetry of the CVs in Figure 3B, where the negative peaks are higher than the positive peaks, suggest that an irreversible chemical reaction is taking place during the potential scans. In this sense, we suggest that the following reactions are taking place in Figure 3B:

\[
\begin{align*}
OH^- (aq) & \rightleftharpoons OH^- (ad) \\
2OH^- (ad) + S(ad) & \rightleftharpoons 2OH(ad) + S^{2-} (ad) \\
2OH^- (ad) + S_x(ad) & \rightleftharpoons 2OH(ad) + S_x^{2-} (ad)
\end{align*}
\]

where (ad) means adsorbed on the interfacial AuNPs’ surface and (aq) means on the aqueous side of the interface.

The reduction of atomic (S) or molecular (S_x) sulfur adsorbed on the interfacial AuNPs can be promoted by the adsorption of OH⁻ (Equations (1) to (3)), leading to an additional negative peak between −0.15 and +0.2 V in the presence of sulfur (Figure 3D). The potential windows were reduced in Figures 3C and 3D to highlight (i) a reversible signal due to OH⁻ physisorption is seen in both CVs (red lines) and (ii) an irreversible signal is seen in the presence of either O₂ or sulfur (blue lines). The blue signals in Figure 3D can be attributed to a redox reaction between sulfur and adsorbed OH⁻.

Differential capacitance curves in the absence of sulfur in the organic phase further support the fact that O₂ modified the AuNP’s surface, with the capacitance under aerobic conditions being higher (Figure 4A). The AuNP’s surface is usually oxide-free under ambient conditions. However, in alkaline media, such as the LiOH aqueous phase used in Figure 4A, gold oxidation proceeds at lower potentials and therefore the formation of gold oxides upon potential cycling leads to higher capacitances. Another possibility for the origin of the gold passivation process can be an irreversible reaction between O₂ and unidentified contaminants present in the organic phase.
Figure 4. Adsorption of hydrophobic elemental sulfur on the interfacial AuNPs at the polarized L|L interface. Differential capacitance curves obtained at 80 Hz for electrochemical cell 2 (see Scheme 1) with $X = \text{OH}^-$ in (A) the absence ($x = 0$) and (B) the presence ($x = 8.11$) of elemental sulfur in the organic phase. The arrows show the scan direction. In (A) the influence of aerobic versus anaerobic conditions is probed in the absence of sulfur. The conditions in the glovebox were Ar (∼1 bar) and O$_2$ (∼1.5 ppm). In (B) the influence of the scan direction in the presence of sulfur is probed under aerobic conditions.

The differential capacitance curves change significantly with the scan direction in the presence of sulfur in the organic phase under aerobic conditions (Figure 4B). This demonstrates that the chemical composition of the AuNP’s surface at the same potential depends on the scan direction and that surface chemical reactions are taking place on this surface. The capacitances are near identical at the extremes of the potential window but, at potentials close to the PZC (ca. +0.3 V), the capacitances are lower for the negative scan direction than those for the positive scan direction. The adsorption of a hydrophobic and neutral species like S$_8$ is more likely close to the PZC because the gold surface is “clean” and more hydrophobic at the PZC. Therefore, we attribute the lower capacitance close to the PZC during the negative scan to the adsorption of atomic and molecular sulfur on the interfacial AuNPs (blue circles, Figure 4B). At negative or positive potentials, the AuNP’s surface is hydrophilic and the adsorption of S$_8$ is unlikely. Furthermore, S$_8$ does not adsorb on the interfacial AuNPs scanning positively as their surface has already been coated in adsorbed OH$^-$ species and is too hydrophilic.

The adsorption of S$_8$ scanning negatively agrees with the observation that the peak between −0.2 V and +0.2 V is higher for the negative scan direction curve (blue circles, Figure 4B). This behaviour may come from pseudo-capacitance currents due to the reduction of adsorbed sulfur, with the simultaneous oxidation of adsorbed OH$^-$, i.e., currents coming from reversible or quasireversible electron transfer reactions due to the simultaneous reduction of
adsorbed sulfur and oxidation of OH\(^-\) ions at the organic and aqueous sides of the AuNP film, respectively. Such changes were not observed with the scan direction in the absence of sulfur under aerobic conditions (data not shown).

**Biphasic oxidation of elemental sulfur catalysed by interfacial AuNPs at a polarised L|L interface.** The influence of the presence of sulfur in the organic phase on the evolution of the CVs as the AuNP film is formed with potential cycling under aerobic conditions is shown in Figure 5A. The presence of both AuNPs in the aqueous phase and sulfur in the organic phase (Figures 5A and 5B, black solid line) leads to an increase in current over the whole potential window in comparison to otherwise identical experiments either in the absence of the AuNPs (Figure 5B, red dash-dot line) or sulfur (Figure 5B, blue dashed line). The increase in current and irreversibility of the signal suggests an irreversible redox reaction between sulfur and dissolved O\(_2\), catalysed by the interfacial AuNPs, is taking place.

![Figure 5](image_url)

**Figure 5.** Redox reactions between sulfur and dissolved O\(_2\) on the interfacial AuNPs at the polarized L|L interface under aerobic conditions. (A) CVs over 50 potential cycles using electrochemical cell 1 in Scheme 1 with \(x = 8.11\) (i.e., in the presence of sulfur in the organic phase). Every 10\(^{th}\) CV is shown, starting with the first CV cycle, and the arrows show the evolution with time. (B) Comparison of the 50\(^{th}\) potential cycles for experiments using electrochemical cell 1 with \(x = 8.11\) and 4.95\(\times\)10\(^{13}\) AuNPs·ml\(^{-1}\) (black line), \(x = 0\) and 4.95\(\times\)10\(^{13}\) AuNPs·ml\(^{-1}\) (red dash-dot line), and without sulfur (blue dashed line) and AuNPs (black solid line). The arrows in (A) and (B) show the evolution of the CVs with time.
AuNPs·ml$^{-1}$ (blue dashed line), and $x = 8.11$ and 0 AuNPs·ml$^{-1}$ (red dash-dot line). (C) Comparison of the 50th potential cycles for electrochemical cell 2 in Scheme 1 with $x = 8.11$ and $X$ either Cl$^-$ (red line) or OH$^-$ (black line). (D) CVs over 100 potential cycles using electrochemical cell 2 with $x = 8.11$ and $X = \text{OH}^-$. Every 25th CV is shown, starting with the first CV cycle, and the arrows show the evolution with time. The insert shows a zoom of the positive scan of the 100th cycle. All CVs were obtained at a scan rate of 25 mV·s$^{-1}$ under aerobic conditions.

To study the oxidation of sulfur on a well-defined interfacial AuNP film, after the experiment shown in Figure 5A was complete, all suspended AuNPs were removed from the aqueous phase and replaced with pure 10 mM LiCl by sequential washing steps. The CV of this electrochemical cell is shown in Figure 5C (red line) and is identical to the CV shown in Figure 5B (black line). However, a remarkable increase of current over the whole potential window occurs when the LiCl aqueous phase was replaced by LiOH through a further sequential washing step (Figure 5C, black line). The OH$^-$ anions significantly enhance the redox reactions that are taking place, which we attribute to low temperature sulfur oxidation at a polarized L|$L$ interface in the presence of interfacial AuNPs. It is also noted that the CV in Figure 5C with LiOH (black line) under aerobic conditions is markedly different to the CVs in Figure 3B obtained under anaerobic conditions, using otherwise identical experimental conditions.

The signals $R$ and $O$ in Figure 5D are related to irreversible processes and grow upon potential cycling. The latter indicates that a redox reaction is taking place and the concentration of reactive intermediaries increases with time. This is the behaviour expected for biphasic S$_8$ oxidation, where intermediaries such as thiosulfate, sulfite and sulfate anions are formed and transferred irreversibly to the aqueous phase. The complexity of the processes taking place at the interface is highlighted by the many signals observed across the full potential window (see insert, Figure 5D), likely due to ion transfer of sulfur oxidation products to the aqueous phase such as polythionates, dithionate, dithionite, thiosulfate, etc. These ions transfer within the available potential window at the polarized L|$L$ interface due to their low charge densities and high solubilities in both the aqueous and organic phases. However, their analytical detection directly at the interface is extremely challenging due to their instabilities’ in low temperature aqueous systems with respect to sulfide, sulfate and elemental sulfur species.$^{[42]}$

The role of OH$^-$ to enhance the catalytic activity of AuNPs towards oxidation processes, such as the enhanced currents attributed to S$_8$ oxidation in Figures 5C and D when LiOH is the aqueous electrolyte, has precedent in the literature. For example, supported AuNPs have a
higher catalytic activity for the oxidation of carbon monoxide and alcohols at alkaline rather than acidic pHs. Adsorbed OH\(^-\) plays key roles in three processes critical to the oxidation process: the adsorption of O\(_2\) on the AuNPs, as an intermediary and as a source of oxygen atoms. Furthermore, Huang et al. reported that oxygen anions (O\(_2^\cdot\)) are preferentially adsorbed on AuNPs compared with O\(_2\). Thus, the adsorption of OH\(^-\), or Cl\(^-\), can promote the adsorption of O\(_2\) by charging the AuNP’s surface negatively. The latter increases the negative charge of O\(_2\) upon adsorption. This explanation is the same as that used to understand the adsorption of O\(_2\) on ionic solids, where charge transfer from the support to the AuNPs is required to enhance the ORR on gold.

Experimental evidence strongly suggests that the adsorption and reduction of O\(_2\) on AuNPs is more likely to occur through proton-coupled electron transfer (PCET) reactions. For example, using surface-enhanced infrared absorption spectroscopy (SEIRAS), Ohta et al. reported the presence of adsorbed O\(_2\) (O\(_2\)(ad)) and hydrogen superoxide (HO\(_2\)(ad)) during the ORR on Au(111) electrode in aqueous perchloric acid. Also, Shao et al. reported the presence of adsorbed HO\(_2^\cdot\) in the potential range where the ORR occurs in alkaline media.

**Tuning the Fermi level of the AuNPs by varying the interfacial Galvani potential difference.** The interfacial Galvani potential difference (\(\Delta_o \phi\)) affects both the thermodynamics and kinetics of all chemical reactions where ionic species are involved. For example, let’s consider the following reaction:

\[
\text{OH}^- (\text{aq}) + \text{O}_2 (\text{org}) \rightarrow \text{OH} (\text{ad}) + \text{O}_2^\cdot (\text{org}) \tag{4}
\]

The electrochemical potentials of the ionic species are:

\[
\tilde{\mu}_{\text{OH}^- (\text{ad})} = \mu_{\text{OH}^- (\text{aq})}^0 + RT\ln X_{\text{OH}^- (\text{aq})} - F\phi_{\text{aq}} \tag{5}
\]

\[
\tilde{\mu}_{\text{O}_2^\cdot (\text{org})} = \mu_{\text{O}_2^\cdot (\text{org})}^0 + RT\ln X_{\text{O}_2^\cdot (\text{org})} - F\phi_{\text{org}} \tag{6}
\]

In this sense, the change of free energy of reaction (4) is:

\[
\Delta \tilde{G} = \Delta G - F(\phi_{\text{org}} - \phi_{\text{aq}}) = \Delta G + \Delta_o \phi \tag{7}
\]

where \(\Delta G\) is the total change of the chemical potential. Equation (7) shows that interfacial polarization with a negative \(\Delta_o \phi\) makes reaction (4) more likely. The latter leads to an enhanced adsorption of OH\(^-\) on the AuNPs’ surface and, thus, an increase in the Fermi level of the interfacial AuNPs, \(E_F (\text{AuNPs})\). Furthermore, a negative \(\Delta_o \phi\) increases the molar fraction.
of OH\(^{-}\)(aq), \(X_{\text{OH}^{-}}\)(aq), thereby increasing the chemical potential of OH\(^{-}\) on the aqueous side of the interface and also increasing the driving force of reaction (4).

Under the approximation of Butler-Volmer equation, the electron transfer kinetic constant, \(k\), for the ORR:

\[
O_2(\text{org}) + e^- \rightarrow O_2^-(\text{ad}) \tag{9}
\]

is:

\[
k = k^0 \exp \left( \frac{\alpha F (E_F(AuNPs)-E^0)}{RT} \right) \tag{10}
\]

Taking into account that \(\Delta_{w}^\phi\) affects \(E_F(AuNPs)\), as discussed due to the adsorption of OH\(^{-}\), it is going to also affect the kinetics of the electron transfer reactions according to Equation (9).

Considering that \(E_F(AuNPs)\) increases at negative \(\Delta_{w}^\phi\) to favour reduction reactions in the organic phase, and the likely favoured PCET pathway for the ORR on the AuNPs surface, we propose that the irreversible signal \(R\) at a negative \(\Delta_{w}^\phi\) in Figure 5D is related to some or all the following reactions:

\[
O_2 + OH^-(ad) \rightarrow O_2^-(ad) + OH(ad) \tag{11}
\]

\[
O_2^-(ad) + H_2O(ad) \rightarrow HO_2^-(ad) + OH(ad) \tag{12}
\]

\[
HO_2^-(ad) + H_2O(ad) \rightarrow 2OH(ad) + OH^-(ad) \tag{13}
\]

These reactions can be seen in general as the electroadsorption of OH\(^{-}\) coupled to O\(_2\) reduction.

At positive \(\Delta_{w}^\phi\), \(E_F(AuNPs)\) lowers sufficiently due to the desorption of OH\(^{-}\) to favour oxidation reactions in the organic phase. Thus, we propose that the irreversible signal \(O\) in Figure 5D is related to sulfur oxidation. The first step of S\(_8\) oxidation can be the reaction:

\[
S_8(ad) + OH(ad) \rightarrow S_8^+(ad) + OH^-(aq) \tag{14}
\]

However, a more likely scenario is that adsorbed sulfur atoms can be oxidised as follows:

\[
S(ad) + OH(ad) + H_2O + O_2^-(ad) \rightarrow H_2SO_3 + OH^-(aq) \tag{15}
\]

To summarize the findings in this article succinctly, an overview of the individual steps in the electrochemically driven biphasic sulfur oxidation reaction catalysed by AuNPs deposited at a polarized \(L|L\) interface, under either aerobic or anaerobic conditions, is illustrated in Scheme 2.
Scheme 2. An overview of the electrochemically driven biphasic sulfur oxidation reaction under either aerobic or anaerobic conditions. The chemical reactions taking place at the surface of the AuNPs at the polarized L|L interface for electrochemical cell 2 under aerobic or anaerobic conditions in the presence of sulfur and OH\textsuperscript{−} ions (x = 8.11 and X = OH\textsuperscript{−}, see Scheme 1) are illustrated when the interfacial Galvani potential difference (\(\Delta_o^w \phi\)) is polarized negatively, positively or equal to the PZC.

Scheme 2 shows that the oxidation of adsorbed sulfur (S(ad)) and sulfide ions (S\(^{2−}\) (ad)) can take place under aerobic and anaerobic conditions, respectively. The driving force for these reactions is a positive polarization of \(\Delta_o^w \phi\) that can reduce \(E_F(AuNPs)\) to values lower than
either $E^0_{O_2/O_2}$ under aerobic conditions or $E^0_{SO_2^-/S^{2-}}$ under anaerobic conditions, respectively. Figures 5D and 3B, under aerobic and anaerobic conditions, respectively, both show positive current increases at positive $\Delta \phi_0$, supporting our hypothesis.

Whether sulfur oxidation by dissolved O$_2$ takes place heterogeneously or homogeneously remains a matter of debate. Smirnov et al. have previously shown, by means of a closed bipolar electrochemical cell, that the ORR takes place on the aqueous side of the interfacial AuNPs in the presence of an organic electron donor species.$^{[22]}$ However, it should be noted that there is no truly definitive experimental evidence in the literature as to whether the ORR mechanism is homogeneous or heterogeneous, or if the ORR takes place in the organic or aqueous phase in the presence of catalysts adsorbed at the L|L interface.$^{[45]}$ The standard reduction potentials and high O$_2$ solubility in organic solvents favour the hydrogen evolution reaction (HER) and ORR, via either the 2- or 4-electron pathway, taking place in the organic phase.$^{[45]}$ However, the concentration of protons in aprotic organic solvents is extremely low. Furthermore, while thermodynamically favoured, the kinetics of the HER and ORR in the organic phase may be slow as electrochemical reactions occur with higher rates in solvents with higher permittivity constants, i.e., aqueous solutions.

**Conclusions**

In this article, a novel methodology to form an interfacial film of AuNPs at a polarized L|L interface is developed. By employing PBS modified AuNPs, potential cycling yields a homogeneous film of interfacial AuNPs. Electrochemistry at a polarized L|L interface also provides a means of monitoring the adsorption of electrolyte species (herein Cl$^-$ and OH$^-$ anions) on the interfacial AuNPs and driving catalytic redox reactions at the AuNP’s surface (herein S$_8$ oxidation by O$_2$). Modelling of the CV data shows that the adsorption of anions can be reasonably described by a Frumkin model, the anion-Au bond must be highly polar and the anions are physisorbed on the interfacial AuNPs (a new insight). The homogeneous oxidation of S$_8$ at low temperatures is unlikely in a homogeneous phase as the reactants, intermediates and products have different solubility properties. Our biphasic system overcomes these solubility limitations, while simultaneously providing an electrochemically controlled catalytic interface. Importantly, differential capacitance measurements provide evidence that S$_8$ adsorbs on the interfacial AuNPs. The electrochemical signals attributed to S$_8$ oxidation by O$_2$ were enhanced when LiOH was used as the aqueous electrolyte. The OH$^-$ anions have multiple roles
in the mechanism, raising the Fermi level of AuNPs upon adsorption, enhancing O$_2$ adsorption on the AuNPs, and acting as an intermediary and source of oxygen atoms. To our knowledge, this is the first report of an artificial system that can mimic the microbial oxidation of elemental sulfur at ambient conditions.

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Keywords

Sulfur oxidation • polarized liquid|liquid interface • interfacial assembly • catalytic gold nanoparticles • anion physisorption

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The homogeneous oxidation of elemental sulfur at low temperatures is unlikely in a homogeneous phase as the reactants, intermediates and products have different solubility properties. A biphasic system overcomes these solubility limitations, while simultaneously providing an electrochemically controlled catalytic surface when the liquid-liquid interface is functionalised by a film of gold nanoparticles.

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Supporting Information

Mimicking the Microbial Oxidation of Elemental Sulfur with a Biphasic Electrochemical Cell

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S1. Experimental methods

S1.1 Materials. All chemicals were used as received without further purification. All aqueous solutions were prepared with ultrapure water (Millipore Milli-Q, specific resistivity 18.2 MΩ·cm). Bis(triphenylphosphoranylidene) ammonium chloride (BACl, 97%) and lithium tetrakis(pentafluorophenyl)borate diethyletherate ([Li(OEt₂)]TB) were obtained from Sigma-Aldrich and Boulder Scientific Company, respectively. Bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BATB) was prepared by metathesis of equimolar solutions of BACl and [Li(OEt₂)]TB in a methanol-water (2:1 v/v) mixture. The resulting precipitates were filtered, washed, recrystallised from acetone and finally washed 5 times with methanol-water (2:1 v/v) mixture. Lithium chloride (LiCl, ≥95%), lithium hydroxide (≥98%), tetramethylammonium chloride (TMACl, ≥98%), and elemental sulfur (analytical standard) were obtained from Sigma-Aldrich. The organic solvent α,α,α-trifluorotoluene (TFT, 99%) was obtained from Acros Organics. PBS-stabilised 5 nm colloidal AuNP suspensions were purchased from Sigma Aldrich.

S1.2 Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) at the ITIES. Electrochemical experiments were carried out at the water|α,α,α-trifluorotoluene interface using a four-electrode configuration (the geometric area of the cell was 1.60 cm²). To supply the current flow, platinum counter electrodes were positioned in the organic and aqueous phases. The potential drop at the L|L interface was measured by means of pseudo-reference silver/silver chloride (Ag/AgCl) electrodes, which were connected to the aqueous and organic phases, respectively, through Luggin capillaries. When 10 mM LiOH was used as an aqueous phase, a standard Ag/AgCl reference electrode separated by a porous junction was used to ensure the signal stability of the reference potential. The Galvani potential difference was attained by assuming the formal ion transfer potential of TMA⁺ to be 0.311 V.[1]

The water|TFT interface was functionalized with Au NPs film by means of cyclic voltammetry using electrochemical cell 1 (see Scheme 1 in the main text). Electrochemical impedance spectra were measured using an Autolab PGSTAT204 potentiostat with a frequency response analyzer module (FRA32M) and a four-electrode electrochemical cell. The AC amplitude was 10 mV and the frequency range was between 0.1 and 1000 Hz. Differential capacitances at different applied voltages were measured using potentiodynamic EIS at 80 Hz and assuming the cell behaves as a series R-C circuit. At this frequency, the contribution of faradic processes is insignificant in the working potential window.
S1.3. Numerical simulations. The CVs were simulated assuming a Frumkin isotherm, the kinetics given by the Butler-Volmer equation and the mass transport phenomena were neglected. In summary, the following two differential equations have to be solved simultaneously:[2,3]

\[ i_T = vC - R_sC_i_T' + nF\Gamma_{max}' \theta' \]  

(S1)

\[ \frac{d\theta}{dt} = k_0 \left[ \frac{C^*}{C^0} \left( 1 - \theta \right) e^{-\frac{\alpha nF}{RT}(\eta + g\theta + R_s i_T)} - \theta e^{-\frac{(1-\alpha)nF}{RT}(\eta + g\theta + R_s i_T)} \right] \]  

(S2)

where \( i_T \) is the current that crosses the interface, \( R_s \) the total resistance between the two reference electrodes, \( \theta \) is the surface fraction coverage, \( \Gamma_{max} \) is the maximum surface coverage (mol·m\(^2\)), \( C \) is the capacitance of the interface, \( C^* \) is the bulk concentration in the aqueous phase of the adsorbed specie and \( C^0 \) is the concentration at the reference state. The other symbols have their conventional meaning. The numerical solution of the kinetic differential equations was done using the following Python code:

```python
from scipy.integrate import odeint
from matplotlib.widgets import Slider, Button
import numpy as np
alpha = 0.5
g=0.5
n=1
F=96470
R=8.314
T=300
v=0.05
C=1e-5
gamma_max=2e-9
k0=100
C0=1e-3
E0=0.2
Ei=0.3
Ef=-0.3
p=n*F/(R*T)
tf=(Ei-Ef)/v

def sol(g,k0,C,Rs):
    def Adsorp(var,t):
        iT = var[0]
        theta = var[1]
        if t < tf:
            E = Ei - v*t
            s=1
        else:
            E = Ef
            s=0
        return np.array([iT, theta * s])

sol(g,k0,C,Rs)
```

S3
\begin{align*}
E &= Ef + v*(t-tf) \\
\eta &= E-E0 \\
\theta_d &= k0*(Cb*(1-\theta)*np.exp(-alpha*p*(\eta+g*\theta+Rs*iT))-\eta*np.exp((1-alpha)*p*(\eta+g*\theta+Rs*iT))) \\
id &= s/v*Rs-iT/(Rs*C)+(n*F*gamma_max*\theta_d)/(Rs*C) \\
\text{return } \{id, \theta_d\}
\end{align*}

\begin{align*}
t &= np.linspace(0,2*tf,1000) \\
var0 &= [0,0] \\
var &= \text{odeint}(Adsorp,var0,t) \\
E1 &= np.linspace(0.3, -0.3,500) \\
E2 &= np.linspace(-0.3, 0.3,500) \\
Ev &= \text{np.concatenate}((E1, E2), axis=0) \\
\text{return } Ev, \text{ var[:,0]*1e6}
\end{align*}

\begin{align*}
y &= \text{sol}(0,100,1e-5,1) \\
\text{import matplotlib.pyplot as plt} \\
\text{fig, ax = plt.subplots()} \\
\text{plt.subplots_adjust(left=0.15, bottom=0.35)} \\
L1, & = ax.plot(y[0], y[1]) \\
ax.set(xlabel='E (V)', ylabel='$i$ (\mu$A$)') \\
axcolor = 'lightgoldenrodyellow' \\
axg = plt.axes([0.15, 0.2, 0.65, 0.03], facecolor=axcolor) \\
sg = Slider(axg, 'g', -0.1, 0.5, valinit=0, valstep=0.05) \\
axk0 = plt.axes([0.15, 0.15, 0.65, 0.03], facecolor=axcolor) \\
sk0 = Slider(axk0, '$lg_{10} k^0$', -2, 2, valinit=2, valstep=0.5) \\
axC = plt.axes([0.15, 0.1, 0.65, 0.03], facecolor=axcolor) \\
sC = Slider(axC, '$Cx10^6$', 50, 1000, valinit=0, valstep=50) \\
axRs = plt.axes([0.15, 0.05, 0.65, 0.03], facecolor=axcolor) \\
sRs = Slider(axRs, 'R', 50, 1000, valinit=1, valstep=50) \\
\text{def update(val):} \\
\hspace{1cm}gv = sg.val \\
\hspace{1cm}k0v=sk0.val \\
\hspace{1cm}Rv=sRs.val \\
\hspace{1cm}Cv=sC.val \\
\hspace{1cm}k=\text{sol}(gv,10**k0v,Cv*1e-6,Rv) \\
\hspace{1cm}L1.set_ydata(k[1]) \\
\hspace{1cm}L1.set_xdata(k[0]) \\
\hspace{1cm}ax.set_ylim(k[1].min(), k[1].max()) \\
\hspace{1cm}ax.set_xlim(k[0].min(), k[0].max()) \\
\hspace{1cm}fig.canvas.draw_idle() \\
\hspace{1cm}sg.on_changed(update) \\
\hspace{1cm}sk0.on_changed(update) \\
\hspace{1cm}sC.on_changed(update) \\
\hspace{1cm}sRs.on_changed(update) \\
\hspace{1cm}resetax = plt.axes([0.8, 0.9, 0.1, 0.04]) \\
\hspace{1cm}button = Button(resetax, 'Reset', color=axcolor, hovercolor='0.975') \\
\end{align*}
def reset(event):
    sg.reset()
    sk0.reset()
    sC.reset()
    sRs.reset()
    button.on_clicked(reset)

plt.show()

S2. Supporting experimental data

Figure S1. Adsorption of aqueous anions on the interfacial AuNPs at the polarized \( \text{L|L} \) interface under aerobic conditions. CVs as a function of scan rate after the addition of 19 \( \mu \text{M TMA}^+ \) to electrochemical cell 2, see Scheme 1 main text, with (A) \( x = 0 \) and \( X = \text{Cl}^- \) and (B) \( x = 0 \) and \( X = \text{OH}^- \). (C) Plots of peak current (\( \mu \text{A} \cdot \text{cm}^{-2} \)) versus scan rate (\( \text{mV} \cdot \text{s}^{-1} \)) for the forward and reverse scans of the CVs shown in (A) and (B). (D) CVs after the addition of 19 \( \mu \text{M TMA}^+ \) to electrochemical cell 2, with \( x = 0 \) and \( X = \text{OH}^- \), at scan rates of 25 (black line) and 200 \( \text{mV s}^{-1} \) (red line). All CVs were taken with \( iR \) compensation.
S3. Supporting references

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