

Photosynthesis of Peroxodisulphate with Visible Light at Polycrystalline WO_3 Anodes

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Polycrystalline WO_3 electrodes, when illuminated with visible light in acid hydrogen sulphate solutions, have been shown to produce peroxodisulphate with 85% current efficiency.

Tungsten trioxide is known to be a fairly stable semiconducting anode material for the photoinduced formation of oxygen from aqueous solutions.¹⁻³ Investigations so far have involved single crystals^{2,4,5} and polycrystalline WO_3 prepared by direct oxidation of tungsten metal,^{1,3,6,7} by a chemical vapour deposi-

tion technique,^{1,3} and by sputtering of WO_3 .⁶ Apart from the photo-oxidation of water, anodic processes studied on illuminated WO_3 electrodes comprise oxidation of halogenides, $\text{Fe}(\text{CN})_6^{4-}$, and hydroquinones.⁵⁻⁸ In this paper we report unambiguous evidence that the visible light driven oxidation

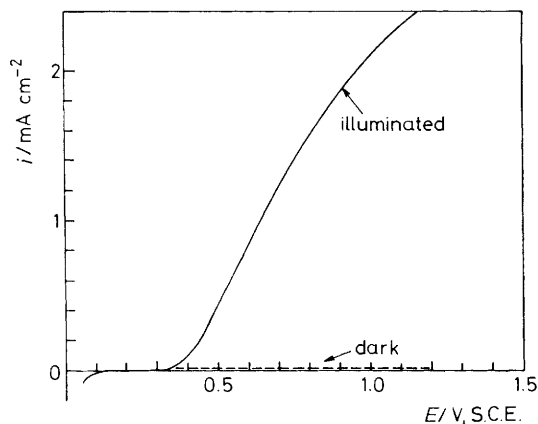


Figure 1. Photocurrent and dark current as a function of potential (S.C.E.) for the polycrystalline WO_3 electrode in 3 M KHSO_4 ; scan rate 5 mV/s. Illumination with visible light, $\lambda > 400$ nm.

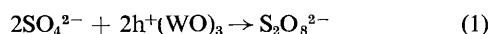
of sulphate to persulphate can be performed with high efficiency on polycrystalline WO_3 .

WO_3 was obtained from Fluka (puriss. grade) in powdered form. Polycrystalline electrodes were prepared *via* a procedure elaborated recently for preparing CdS and other chalcogenide electrodes.^{9,10} A paste of WO_3 was made by mixing 50 mg of WO_3 with 50 μl of an aqueous Triton X-100 solution (5% v/v). This was painted onto a Ti sheet (typical size 1 cm^2) which previously had been etched for 30 s in an aqueous solution of HF (4% wt/wt) and HNO_3 (30% wt/wt). After air drying the coating for 10–15 min the electrode was heated at 670 $^\circ\text{C}$ for 10 min in an Ar stream (flow rate 10–15 ml/min, 30 p.p.m. of O_2). Thus a polycrystalline coating of WO_3 , distinguished by a yellowish green colour, was obtained.

Electrochemical measurements were carried out with a Tacussel Potentiostat PRT 20-10 X and a three-compartment cell with suitable accessories for deoxygenation and product analysis. Potentials were measured and quoted, unless otherwise indicated, against the standard calomel electrode (S.C.E.). Illuminations were performed with a 250-W halogen lamp. I.r. and u.v. radiation was removed by a water jacket and a 400 nm cut-off filter, respectively. The light beam was focused on the WO_3 electrode.

Figure 1 shows the current–voltage characteristics of the WO_3 electrode both in the dark and under illumination in 3 M KHSO_4 (pH *ca.* 0.7). The anodic onset of the photocurrent occurs at 0.32 V. This is slightly more positive than the reported flatband potential of WO_3 in 0.1 N H_2SO_4 (–0.05 V to 0.2 V, depending on preparation).⁶ The photocurrent rises steeply upon anodic polarization, values exceeding 2 mA/cm^2 at potentials more positive than 1 V. Dark currents in the potential domain from 0.4 to 1.2 V are smaller than 1 $\mu\text{A}/\text{cm}^2$. Cathodic polarization leads to significant dark current corresponding to reduction of WO_3 to a blue material which is either a substoichiometric oxide¹¹ or a hydrogen bronze.^{12,13}

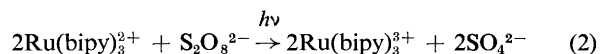
Careful analysis of the products resulting from potentiostatically controlled photoelectrolysis ($E = 0.8$ V) showed that oxygen formation accounts only for a very small portion of the anodic photocurrent. Instead, the dominant pathway of photoelectrolysis was discovered to be synthesis of peroxydisulphate *via* equation (1) where $h^+(\text{WP}_3)$ stands for a hole



in the valence band of WO_3 .

First qualitative evidence for the formation of $\text{S}_2\text{O}_8^{2-}$ was obtained *via* its characteristic oxidation of Ni^{II} hydroxide to form brown–black Ni^{IV} oxyhydrate.¹⁴ This reaction is not given by hydrogen peroxide, which reduces the Ni^{IV} precipitate

readily. A further indication that $\text{S}_2\text{O}_8^{2-}$ was formed was the observation of very effective photo-oxidation of $\text{Ru}(\text{bipy})_3^{2+}$,¹⁵ equation (2). Thus addition of $\text{Ru}(\text{bipy})_3^{2+}$ (10^{-4} M) to the

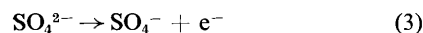


anode compartment after photoelectrolysis and exposure to the room light of fluorescent tubes leads to bleaching of the $\text{Ru}(\text{bipy})_3^{2+}$ spectrum and appearance of the characteristic spectrum of $\text{Ru}(\text{bipy})_3^{3+}$ within a few minutes.

Quantitative analysis of $\text{S}_2\text{O}_8^{2-}$ was carried out by addition of an excess of iodide solution and spectrophotometric analysis of the I_3^- at pH 6.8 as previously described.¹⁶ When the amount of peroxydisulphate produced under illumination is plotted as a function of the electric charge passed through the circuit a straight line is obtained from the slope of which one calculates that 85% of the current corresponds to SO_4^{2-} oxidation, the remainder being oxygen formation. $\text{S}_2\text{O}_8^{2-}$ photosynthesis continues to occur in a linear fashion even when significant amounts of it have been accumulated.†

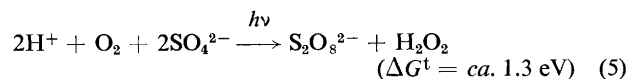
The following experiments allowed the exclusion of O_3 or H_2O_2 generation as possible alternatives to $\text{S}_2\text{O}_8^{2-}$ photoelectrosynthesis (both are also known to oxidize I^- to I_3^-). Flushing the solution with Ar during and after photoelectrolysis does not affect the analytical results. Also tests for H_2O_2 with TiCl_4 which result in the formation of yellow peroxotitanic acid¹⁷ were negative. Thus there remains no doubt that peroxydisulphate is the principal oxidation product in the photoelectrolysis of aqueous HSO_4^- solutions.

This result has important mechanistic implications. The formation of $\text{S}_2\text{O}_8^{2-}$ from sulphate occurs in two steps, *i.e.* (3) and (4), the one electron oxidation of SO_4^{2-} requiring



a standard potential E° (N.H.E.) = *ca.* 3.4 V (N.H.E. = normal hydrogen electrode).¹⁸ From the observation that $\text{S}_2\text{O}_8^{2-}$ is the main reaction product it may be concluded that reaction (3) occurs in preference to water oxidation despite the fact that the latter process requires a less anodic potential than the former. From the present data, it appears that the reaction pathway is controlled by kinetic rather than thermodynamic factors. The rate of hole transfer from the WO_3 valence band depends on the overlap of electronic states of the redox system in the electrolyte with the valence band edge of the semiconductor. In the case of WO_3 the latter is located at *ca.* 3 V (N.H.E.) matching approximately the Fermi level of the $\text{SO}_4^{2-}/-$ couple in solution and therefore favouring high hole transfer rates. The overlap may be less good with occupied states of the OH^-/OH redox systems ($E^\circ = 2.8$ V, N.H.E.) which explains why water oxidation occurs only to a small extent.

Our findings suggest the design of a two half-cell system, separated by a membrane, in which the illuminated WO_3 electrode is connected to a cathode where O_2 reduction to H_2O_2 or H_2O occurs. From the photocurrent *vs.* potential function displayed in Figure 1 and the characteristics of currently available O_2 electrodes, it is apparent that such a cell could operate at reasonably high current densities. A light driven process such as reaction (5) could store almost 50%



of the photon energy necessary to excite the WO_3 electrode. Furthermore, the process may find applications in powdered

† A total charge of 35 C was passed through the cell.

or colloidal WO_3 solutions which are presently being investigated.¹⁹

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