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Photo-induced Electrochemical Reduction of Water to Hydrogen at Ruthenium-modified Polysulphur Nitride Electrodes

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Summary Ruthenium redox couples have been immobilized on the perpendicular surface of polysulphur nitride, $(SN)_x$, single-crystals which were used as electrodes, and which, when maintained at about $-0{\cdot}10$ V *vs.* the saturated calomel electrode in H_2SO_4 solution and illuminated with visible light, evolve hydrogen gas continuously.

THE photoinduced splitting of water to its elements and also the photoinduced reduction of water to hydrogen using visible or near-u.v. light is the subject of intensive investigation. Recently DeLaire *et al.* reported that the photoreduction of certain ruthenium(II) complexes in the presence of triethylamine results in the production of hydrogen from water.[1] However, their results showed that in the process of water reduction the external reductant (triethylamine) was consumed.

To circumvent this limitation, immobilizing a photoactive ruthenium(II) complex on to an electrode surface would prove advantageous, as it would result in a photoelectrochemical cell for the reduction of water to hydrogen. Light energy would transform the ruthenium species into one capable of reducing water to hydrogen, with the electrode providing the ruthenium with a very large source of electrons at a very small applied bias potential capable of sustaining the reaction indefinitely.

Previously it had been shown that polymeric sulphur nitride, which is a 'metallic' conductor,[2] interacts with metal cations to bind them to the $(SN)_x$ surface.[3,4] These immobilized metal ion surfaces can be used as electrodes to catalyse the heterogeneous electron transfer between the electrode and solution redox systems.[4] In the present paper we report that such a polysulphur nitride single-crystal electrode which has been pretreated with a ruthenium complex will generate hydrogen gas for a sustained period of time in an aqueous supporting electrolyte solution on irradiation of the electrode surface with visible light. Only a small applied bias potential is needed.

High purity single crystals of $(SN)_x$ were prepared from S_4N_4 by a published method[2] and gave satisfactory elemental analyses.† The crystals were cemented to the end of a silver wire (0·04 cm radius) sealed in an L-shaped glass tube with conducting silver paint (GC Electronics). All but the crystal face (*ca.* 0·5 to 0·10 mm geometric area) of interest was masked off with Torr Seal (Varian Associates). In this way electrodes can be constructed which have the $(SN)_x$ fibre bundles[3] parallel or perpendicular to the electrode–solution interface, and we shall refer to these as 'parallel' or 'perpendicular'.[3a] The L-shaped mounting leaves the exposed electrode surface in a vertical orientation which allows evolving gas to bubble freely from the surface. A small-bore tube with a flared open end, initially filled with solution, was placed over the electrode to collect the evolved gas. All apparatus and procedures for the electrochemical experiments were the same as previously described.[3] The complexes (**1**)—(**3**) used here were synthesized by published

$[Ru(bipy)_2(MeOCH_2CH_2OMe)](PF_6)_2$
(**1**)
$[Ru(NH_3)_5Cl]Cl_2$
(**2**)
$[Ru(NH_3)_5(H_2O)](PF_6)_2$
(**3**)
bipy = 2,2′-bipyridyl

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† We thank Galbraith Laboratories, Inc., Knoxville, Tennessee for performing these experiments.

methods.[5] The $(SN)_x$ electrodes were dipped into either a stirred 1·0 mM solution of (**1**) in N_2-de-aerated dimethoxyethane for 10 min or 3·5 mM aqueous solutions of the other penta-ammine complexes. The dipped electrodes were washed thoroughly with distilled water after treatment. All chemicals were of reagent grade and used without further purification. Solutions were prepared with distilled water which was passed through ion-exchange and activated-carbon columns. Solutions were deoxygenated with high purity nitrogen. All potentials were measured with respect to the saturated calomel electrode (SCE).

Cyclic voltammograms of untreated perpendicular $(SN)_x$ electrodes in a 0·2 M solution of tetrabutylammonium tetrafluoroborate in tetrahydrofuran (THF) show no current peaks between 0·00 and +1·00 V *vs.* SCE. However, perpendicular electrodes dipped into the solution of (**1**) described above exhibit a well developed redox couple at about +0·70 V *vs.* SCE. The differential pulse polarograms of such modified electrodes also exhibit a well defined symmetric peak in the same voltage region. It was found that the redox peaks persisted on prolonged cycling. Electrodes cycled over 1000 cycles (20 mV s^{-1}) still retained 40 to 50% of the initial peak currents. This long term stability of these redox peaks, a linear dependence of peak current on scan rate, and the symmetric shape of the pulse polarograms all suggest that the redox couple observed is immobilized on the $(SN)_x$ surface.[6] Parallel electrodes dipped into the solution of (**1**) exhibited cyclic voltammograms that were exactly the same as those for the untreated perpendicular electrodes. No surface redox couple was observed. Thus, although the chemical composition of the surface redox system produced on dipping the 'perpendicular' electrodes into a solution of (**1**) is unknown at this time, the above results suggest that it would be some type of ruthenium-containing complex.[3,4] An estimate of the surface concentration of this species from the electrochemical experiments (assuming a one-electron process and geometric electrode surface area) is about 10^{-10} mol cm^{-2}.

When such a ruthenium-treated perpendicular $(SN)_x$ electrode was immersed in an acidic aqueous solution and illuminated by visible light, gas bubbles began to evolve from the electrode surface at potentials of about 0·00 V *vs.* SCE. The gas evolved was colourless and odourless. Quantitatively, it was found that for 10 electrodes maintained at −0·1 V *vs.* SCE and illuminated for 6 h using a 498 nm filter with the described light source,‡ an average of 0·2 ml of gas per electrode was collected. This gas would not ignite when sparked in a nitrogen atmosphere but burned on ignition after slow release into air. The product of this combustion was a liquid which was collected on a cold tube above the flame and which on mass spectral analysis was identified as water. No mass spectral peaks corresponding to sulphur- or nitrogen-oxides or ammonia were observed. This indicates that the gas evolved in the experiment is hydrogen. On prolonged illumination with unfiltered light under the above conditions it was found that the rate of production of hydrogen decreased as a function of time. The half-life of individual electrodes varied between 6 and 9 h. Examination of the cyclic voltammograms of electrodes after prolonged photo-induced hydrogen evolution showed that the peak currents of the +0·70 V *vs.* SCE redox couple had also decreased. Re-dipping of the degenerated electrodes into the solution of (**1**) returned the hydrogen evolution rates to approximately the initial rates. No gas evolution, with or without illumination, has ever been observed for either untreated electrodes or electrodes treated with other transition metal cations within the potential limits of 0·00 and −1·00 V *vs.* SCE.

Control experiments showed that the instantaneous current in the cell flowed and ceased to flow as the incident light was turned on and off. Furthermore, the decrease in the current observed correlates directly with the decrease in the rate of hydrogen evolution on prolonged electrolysis, and the total charge passed also correlates with the quantity of hydrogen produced. Identical illumination experiments using 'perpendicular' electrodes (either untreated electrodes or electrodes immersed in THF alone) showed no evidence of hydrogen evolution and no change in the background current. Neither treated nor untreated 'parallel' electrodes exhibited hydrogen evolution or current increase on illumination. Nor did illuminated $(SN)_x$ electrodes dipped into solutions of (**2**) or (**3**) exhibit hydrogen evolution at any potential. Furthermore, both parallel and perpendicular untreated $(SN)_x$ electrodes exhibit cathodic breakdown current at potentials more negative than −1·0 V *vs.* SCE in acidic (pH = 0) solution and no significant gas evolution was then observed.[4] The breakdown process is corrosion of $(SN)_x$ and produces water-soluble ammonium ion and H_2S in 0·5 M H_2SO_4. Pretreatment of the electrodes with transition metal cations shifts this corrosion process to even higher negative overpotentials.[4]

Qualitatively, the rate of hydrogen evolution decreases with increasing pH at a fixed potential. Also, the onset of H_2 evolution shifts to a more negative potential as the pH increases. This negative shift of gas evolution is exactly the opposite found for the shift of breakdown potential with pH.† At any fixed pH, the rate of H_2 evolution increases with increasing negative potential and reaches a potential-independent limiting rate at about 100 mV beyond the onset potential. Breakdown potentials were unaffected by the illumination.

It would be expected that an excited state of any ruthenium complex directly attached to a 'metal' would not have a long enough lifetime[7] to effect the photo-induced splitting of water to oxygen and hydrogen. It is not surprising that oxygen was not found However, it is surprising that at the most a monolayer of an immobilized complex would have a sufficient efficiency of light absorbance to give a measurable rate of hydrogen evolution.

One possible alternative explanation of the above results is that the incident light energy results in a temperature increase at the interface and that $(SN)_x$ at higher temperatures is unstable in the presence of water and reacts to produce hydrogen. However, previous studies have shown that $(SN)_x$ electrodes are stable at 70 °C over long periods of time.[8] No degradation or gas evolution was observed at any temperature. As the perpendicular crystal face is essentially black and therefore strongly absorbs light throughout the whole visible region of the spectrum,[9] the presence of the ruthenium complex will not significantly increase the total light energy absorbed at the surface or, hence, any heating effect produced.

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‡ Illumination was provided by a movie projector light source (power rated at 0·4 mV cm^{-2}) which was placed 25 cm from the glass electrochemical cell.

The observation of some microscopic surface change of the $(SN)_x$ surface on prolonged electrolysis suggests that $(SN)_x$ might also act as a chemical reducing agent in the same manner as triethylamine in the homogeneous process demonstrated by Delaire *et al.*[1] However, the addition of various amounts of triethylamine (0·01 to 0·1 M) had no effect within experimental error on the rate of hydrogen evolution. Also, the homogeneous photoinduced production of hydrogen required the presence of a platinum oxide catalyst (Adam's catalyst).[1] However, addition of the catalyst did not affect the rate of hydrogen evolution and had, at most, only a slight effect on prolonging the half-life of an electrode. Decomposition products as previously found are ammonium ion and elemental sulphur,[3,4] and electrodes showed no measurable weight loss during the time scale of these experiments.

The above results indicate that an approximate 0·20 V underpotential for H_3O^+ reduction is achieved by the photoinduced action on the immobilized ruthenium complex on the $(SN)_x$ surface. However, since the system is not completely stable, the chemical nature of the surface is unknown, and the efficiency of light energy–hydrogen conversion is not yet known, we are not certain that a truly thermodynamically uphill reaction is achieved here.

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