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IrO_2 Nanoparticle-decorated Water Oxidation Catalysts for Semiconductor Photoanodes

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Hydrogen has applications as a fuel for both vehicle and stationary power generation. It is very conveniently, if expensively, produced by electrolysis of water. If electrolysis could be driven by solar energy, hydrogen becomes the ultimate “green” fuel, with low environmental impact in both production and consumption.

Solar photoelectrolysis of water, in which one or both electrodes in an electrolyser are powered by solar photons to split water into hydrogen and oxygen, has been investigated intensively, since the original publication [1] using a TiO_2 photo-anode. Most photoelectrochemical studies in water splitting have focused, for stability reasons, on the development of oxygen evolving photoanodes. These operate according to the reaction scheme (1-3) below:

$$SC + h\nu \rightarrow SC(h^{+}{}_{VB}, e^{-}{}_{CB}) \qquad (1)$$

$$2H_2O + 4h^{+}_{VB} \longrightarrow O_2 + 4H^{+} \qquad (2)$$

$$2H_2O + 2e^{-}_{CB} \longrightarrow H_2 + 2OH^{-} \qquad (3)$$

The absorption of a photon of energy greater than the band gap energy of the semiconductor generates an electron-hole pair in process (1). The space charge field in the semiconductor causes separation of the generated charge carriers. Holes are driven to the electrode surface, where they oxidise water to oxygen by reaction (2). Conversely, electrons are driven via an external circuit to a cathode at which water is reduced to hydrogen by reaction (3).

The photoanode should be an oxide in order to withstand the strongly oxidising conditions of oxygen evolution. However, most oxides are wide band gap semiconductors, and thus not well-matched to the solar spectrum. Advances in materials engineering have enabled materials better matched to the solar spectrum, but intrinsically less efficient, to be considered as potential photoelectrodes [2-4]. Their absorption of visible light has attracted interest in Fe_2O_3 (E_g ca. 2.2 eV, threshold absorption < 565 nm) and WO_3 (2.6 eV, threshold absorption = 475 nm). However, both Fe_2O_3 and WO_3 are poor oxygen evolution catalysts, which limit the overall kinetics and therefore the efficiency of water splitting. One approach to improve the water splitting efficiency is to modify the semiconductor with suitable electrocatalysts that increase oxygen evolution kinetics. Recently, this has been achieved with Fe_2O_3, using a cobalt-phosphate (Co-Pi) catalyst [5]. Transition metal oxides, such as IrO_2 and RuO_2 are known to be active oxygen electrocatalysts [6] and can be produced as nanoparticles, which would enable decoration of surfaces with catalyst layers sufficiently thin to permit unhindered photon absorption by the semiconductor.

We report results of decorating Fe_2O_3 photoanode surfaces with IrO_2 nanoparticles, deposited by means of an electrochemical process [6, 7].

1 Experimental

Fe_2O_3 thin films, doped with tin, were deposited by spray pyrolysis from an ethanol solution of $FeCl_3$ and $SnCl_2$ (Sn/Fe = 0.05-0.6%) onto fluorine-doped tin oxide-coated glass heated to 450 °C on a hotplate. Details of the spray pyrolysis process and film growth will be described elsewhere [8]. IrO_2 was electrodeposited onto the Fe_2O_3 films from two solutions:

1. Oxalate-stabilised IrO_2 at +1.4 V vs. SCE [7].
2. Hydroxide-stabilised IrO_2 at +1.0 and +1.4 V vs. SCE [6].

Electrodeposition was carried out for times ranging from 1 ms to 100 s to achieve a range of IrO_2 coverage. The photoelectrochemical behaviour of Fe_2O_3, before and after IrO_2 decoration, was measured in 0.1 mol dm^{-3} NaOH, using standard techniques. A silver wire was used as a quasi-reference electrode (QRE) in the photoelectrochemical experiments. The QRE potential was regularly measured against a saturated calomel (SCE) as +0.125 V (SCE) to determine the stability of the QRE potential. All electrochemical measurements were made using an Eco Chemie Autolab 320N potentiostat.

2 Results and Discussion

Fig. 1 shows the typical response of untreated Fe_2O_3 in 0.1 M NaOH. In the dark, the current remains in a range ±2 $\mu A\ cm^{-2}$, for potentials between -0.5 and +0.5 V (QRE). At potentials > +0.5 V (QRE) a rapid increase in current occurred due to oxygen evolution by reaction (2). This behaviour was observed for a range of Fe_2O_3 films with different $SnCl_2$ doping levels (0.05 to 0.6% in precursor solution) and thicknesses (200-500 nm) Fe_2O_3 was stable when cycled to potentials above +1.4 V (QRE), resulting in a significant rate of oxygen evolution. However, they were very sensitive to the negative potential limit of the potential cycle, undergoing irreversible reduction at potentials below approximately -0.6 V (QRE).

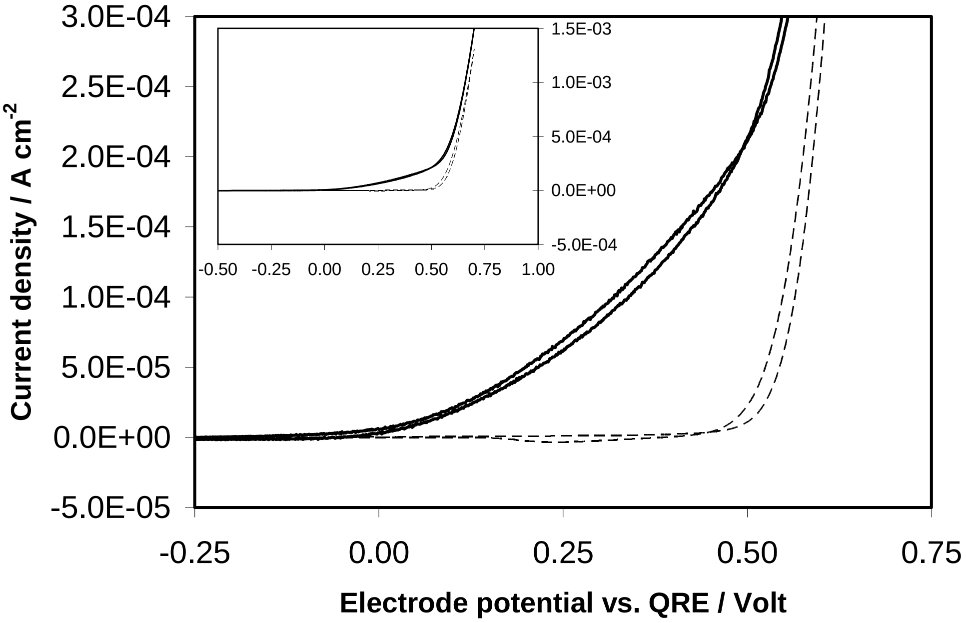

Figure 1: **Current-potential response for a Fe_2O_3 electrode in 0.1 M NaOH: dashed line: dark current; solid line: white light illumination (20 W m^{-2}). Potential scan rate: 0.01 V s^{-1}. Inset shows the full response between -0.5 and +0.75 V (QRE).**

Upon illumination with white light, the photocurrent onset potential was ca. 0 V (QRE). Under continuous illumination, the photocurrent did not reach a limiting value before the onset of light-independent oxygen evolution occurred. However, using chopped light and phase-sensitive detection, the photocurrent-potential response shown in Fig. 2, exhibiting a plateau. These reflect more closely the expected form of the photocurrent-potential behaviour for a semiconductor-electrolyte interface.

Fig. 2 also shows the effect of depositing ca. 0.2 monolayer of IrO_2 for 10 ms at +1.4 V vs. SCE onto the surface of the Fe_2O_3. The limiting photocurrent increased and there was a -0.2 V shift in the photocurrent onset potential when IrO_2 was present on the Fe_2O_3 surface. This indicated that the deposited IrO_2 catalysed the water oxidation reaction (2) by photogenerated holes in the Fe_2O_3. The catalytic effect of the IrO_2 was also highlighted by the decrease in the photocurrent for the IrO_2-decorated Fe_2O_3 at +0.5 V (QRE). This was due to an increase in the light-independent oxygen evolution reaction rate, which increased rapidly and prevented accurate subtraction of the photocurrent.

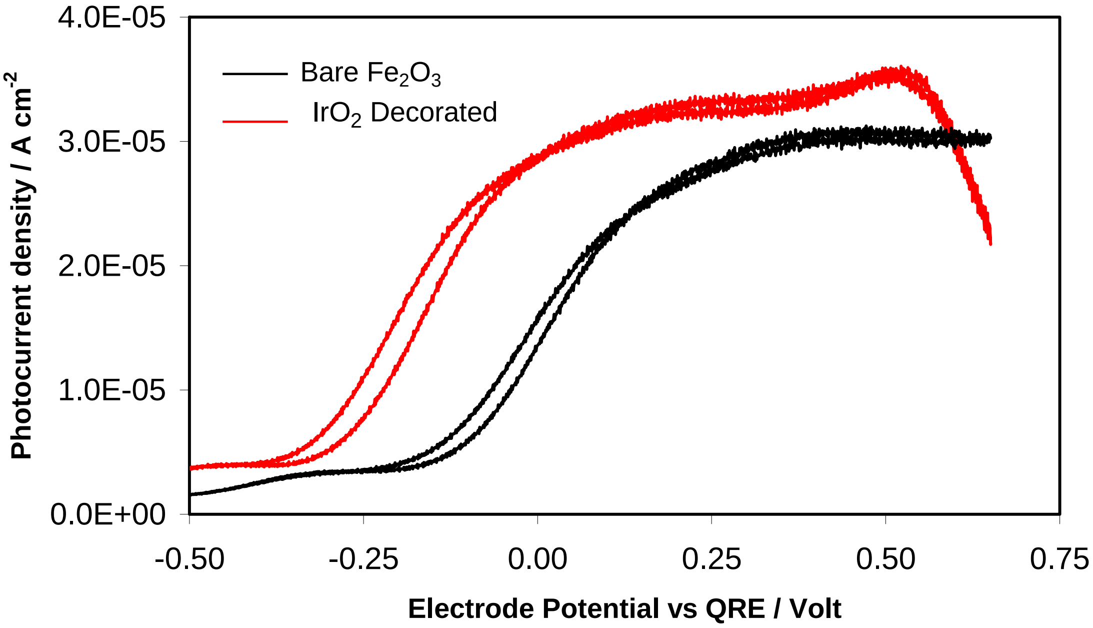

Figure 2: **Photocurrent-potential response of Fe_2O_3: no IrO_2 (black); after 10 ms IrO_2 deposition at +1.4 V vs. SCE (red). Light chopped at 87 Hz; potential scan rate: 0.01 V s^{-1}.**

The coverage of the Fe_2O_3 by IrO_2 deposited in the 10 ms was estimated to be ca. 0.2 of a monolayer of IrO_2, assuming that each IrO_2 had a molecular radius of 135 pm and required 1 electron per molecule for deposition. The effect of IrO_2 coverage on the photocatalytic activity was investigated further by depositing IrO_2 for both shorter and longer times. During these experiments, it was evident that, although there was an initial enhancement of the Fe_2O_3 photo-response, this was quite short-lived. In the case of short deposition times (0.1-100 ms), the enhanced activity due to IrO_2 persisted for only 2 - 3 potential cycles under illumination. Following these cycles, the photo-response returned to the same level as before IrO_2 deposition.

The IrO_2 deposition was investigated further using a hydroxide-stabilised solution of IrO_2 nanoparticles. Although the current density – potential behaviour of this deposition process was different, the same result was observed, with initial enhancement of photo-response decreasing over three potential cycles to that observed before IrO_2 deposition. However, if IrO_2 was deposited for 100 s, an initial decrease in photo-response was observed. Further potential cycling resulted in a slight increase in photo-response, which gradually tended towards that before IrO_2 deposition.

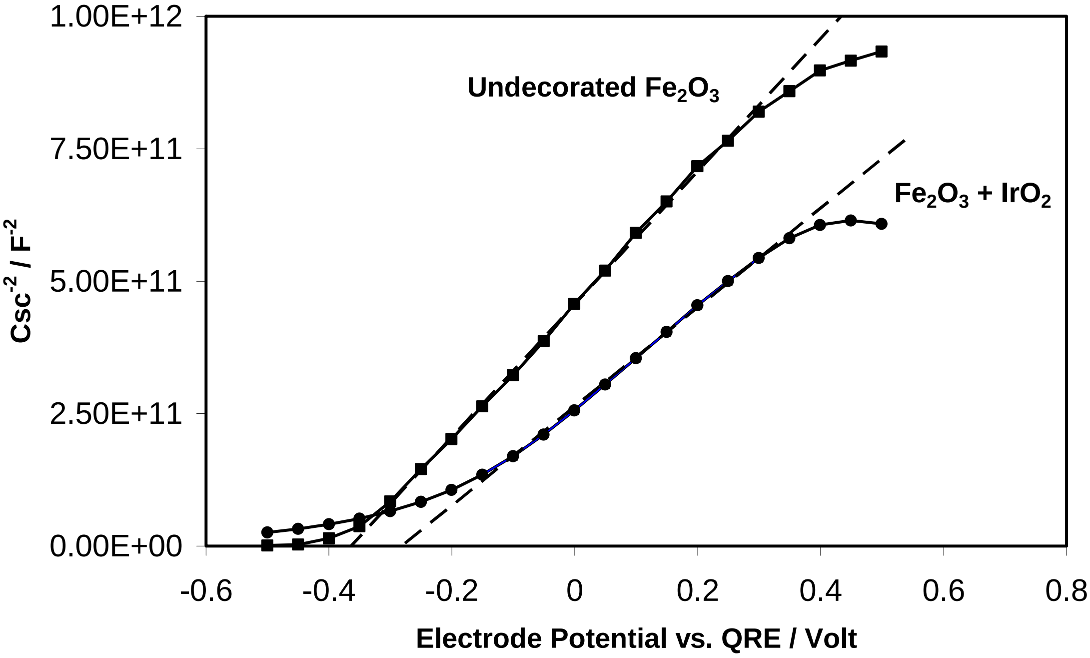

Figure 3: **Mott-Schottky plots of Fe_2O_3 electrodes in 0.1 M NaOH. a) undecorated Fe_2O_3 (squares); b) Fe_2O_3 after IrO_2 deposition for 10 s at +1.4 V vs. SCE.**

Further analysis of Fe_2O_3 before and after IrO_2 deposition was carried out using electrochemical impedance spectroscopy to determine the flat band potential and dopant density of the semiconductor, using the Mott-Schottky relationship. Fig. 3 shows Mott-Schottky plots for Fe_2O_3, before and after coating with IrO_2. For the undecorated Fe_2O_3, the flat band potential was found to be -0.35 V (QRE), in the range of previously determined values for Fe_2O_3. On depositing IrO_2, the flat band potential shifted slightly to ca. -0.3 V (QRE), apparent doping density increased, corresponding to a lower gradient in Fig.3, and no irreversible damage to the semiconducting properties of the Fe_2O_3 was apparent.

These results show that the photocurrent onset potential was very close to the flat band potential. This shows that the catalysis was efficient for as long as the IrO_2 catalyst persisted on the surface, since photocurrent was generated under conditions of low band bending. IrO_2 deposition on Fe_2O_3 enhanced the usually slow surface kinetics [9], decreasing photocurrent onset potentials by several tenths of a volt.

Analysis of the electrolyte for dissolved iridium species is being undertaken to determine whether loss of photocatalytic activity was (improbably) due to dissolution of the IrO_2.

3 Conclusions

These results demonstrated that IrO_2, at sub-monolayer coverage, enhanced the photo-response of Fe_2O_3 photoanodes, lowering the onset potential for photocurrent (oxygen evolution) by 0.2 V compared to the un-catalysed surface. However, the effect of the IrO_2 deposit was transient, usually persisting for only a few minutes on potential cycling. The deposition of IrO_2 did not appear to affect Fe_2O_3 irreversibly, suggesting that this approach to enhancing photo-response should be extended to other photoanode materials.

Further work is required to determine why the effect of IrO_2 lasts only for a short time, since it is known to be stable to oxygen evolution under similar conditions on metallic electrodes.

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