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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:

$$SC + h\nu \rightarrow SC(h^+_{VB}, e^-_{CB})$$ \hspace{1cm} (1)
$$2H_2O + 4h^+_{VB} \rightarrow O_2 + 4H^+$$ \hspace{1cm} (2)
$$2H_2O + 2e^-_{CB} \rightarrow H_2 + 2OH^-$$ \hspace{1cm} (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$_2$O$_3$ (E$_g$ ca. 2.2 eV, threshold absorption < 565 nm) and WO$_3$ (2.6 eV, threshold absorption = 475 nm). However, both Fe$_2$O$_3$ 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$_2$O$_3$, 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$_2$O$_3$ photoanode surfaces with IrO$_2$ nanoparticles, deposited by means of an electrochemical process [6, 7].

1 Experimental

Fe$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$, 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$_2$O$_3$ in 0.1 M NaOH. In the dark, the current remains in a range ±2 μA 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$_2$O$_3$ films with different SnCl$_2$ doping levels (0.05 to 0.6% in precursor solution) and thicknesses (200-500 nm) Fe$_2$O$_3$ 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).
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 IrO₂ for 10 ms at +1.4 V vs. SCE onto the surface of the Fe₂O₃. The limiting photocurrent increased and there was a -0.2 V shift in the photocurrent onset potential when IrO₂ was present on the Fe₂O₃ surface. This indicated that the deposited IrO₂ catalysed the water oxidation reaction (2) by photogenerated holes in the Fe₂O₃. The catalytic effect of the IrO₂ was also highlighted by the decrease in the photocurrent for the IrO₂-decorated Fe₂O₃ 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$_2$O$_3$: 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ electrodes in 0.1 M NaOH. a) undecorated Fe$_2$O$_3$ (squares); b) Fe$_2$O$_3$ after IrO$_2$ deposition for 10 s at +1.4 V vs. SCE.

Further analysis of Fe$_2$O$_3$ 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$_2$O$_3$, before and after coating with IrO$_2$. For the undecorated Fe$_2$O$_3$, the flat band potential was found to be -0.35 V (QRE), in the range of previously determined values for Fe$_2$O$_3$. 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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.

References