Photocurrent enhancement in a cadmium sulphide anode coated with Prussian blue

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Abstract

The photocurrent quantum efficiency of a polycrystalline cadmium sulphide anode in a $KI + I_2$ solution is found to increase on the deposition of a thin film of Prussian blue. It is suggested that the Prussian blue film traps holes generated in cadmium sulphide and efficiently transfers to the redox species in solution.

1. Introduction

Photoeffects at the polycrystalline semiconductor thin film/electrolyte interface has attracted a great deal of attention from applied as well as fundamental points of view [1-7]. In solid-state photovoltaic cells, the applicability of polycrystalline films is largely limited by the recombination of photogenerated carriers before separation by the barrier electric field. However, in a photoelectrochemical cell (PEC), the intimate semiconductor surface/electrolyte contact, creates a more effective charge separation barrier, increasing the photocurrent quantum efficiency [1-7]. Again, efficient redox species in the electrolyte, which could scavenge the minority carriers tunnelling into the solution, also enhance the photocurrent quantum efficiency. In experiments with semiconductor particles, it has been concluded that certain materials, when deposited on the semiconductor surface, act as agents which promote transfer of either electrons or holes into the species in solution [8]. Plantinum or other noble metals deposited on semiconductor particles are known to act as electron transfer agents. Similarly, ruthenium dioxide or manganese dioxide behave as hole transfer agents [8]. It is known that coating of semiconductor photocathodes with thin layers of platinum enhance the photocurrent quantum efficiency by promoting electron transfer to the acceptors in the electrolyte [9]. There are also reports in literature which suggest that Prussian blue and related compounds act as hole transfer agents in photoelectrochemical processes [10]. As expected, we found that the photocurrent quantum efficiency of a polycrystalline cadmium sulphide photoanode is enhanced by deposition of a thin film of Prussian blue.

2. Experimental details

Cadmium sulphide was deposited on indium-tin oxide-coated glass by the following chemical deposition technique [11]. Indium-tin oxide-coated glass plates $(1 \times 3 \text{ cm}^2)$ were ultrasonically cleaned in a detergent solution. Then 20 cm³ 0.5 M CdSO₄ solution and 100 cm³ 1 M ammonia solution were mixed and maintained at a temperature of 85 °C. Glass plates were kept rotating in the bath for 30 min and a 0.5 M solution of thiourea was added dropwise. The film thickness depended on the concentration of the reactants, deposition time, temperature of the bath, speed of rotation, etc. All coated plates were made by keeping the above conditions constant. The film thickness was estimated by weighing the plates before and after deposition and found to be ~0.2 µm.

Prussian blue was deposited on cadmium sulphide electrodes by the following method [12]. The oxidized form of Prussian blue (i.e. Berlin green) in the watersoluble form was prepared by mixing 0.05 M ferric chloride (acidified with H_2SO_4) with 0.05 M potassium ferricyanide. This solution was subjected to electrolysis after deoxygenation, with cadmium sulphide-coated plate as the cathode and platinum foil as the anode. The working electrode was biased -0.5 V vs. Ag-AgCl electrode, which is the optimum condition for coating Prussian blue [12]. One electron reduction of Berlin green yields Prussian blue and molar thickness (corresponding to the stoichiometric composition $Fe_4[Fe(CN)_6]_3$) can be estimated from the duration of electrolysis and the current density. As the electrolyte is photosensitive, the above coating process has to be carried out in the dark.

Photoelectrochemical cells were constructed with Prussian blue-coated CdS plates (and also bare CdS plate for comparison) and platinum foil as the cathode.

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In all experiments, the anode was biased to give zero dark photocurrent. The electrolyte used was 0.1 M KI containing 10^{-3} M iodine. The photocurrent action spectrum was recorded using a set-up consisting of a monochromator (Nikon Monochromator AS-C101) light chopper and a lock-in amplifier (Standford Research systems SR 530).

3. Results and discussion

Photocurrent action spectrum of CdS/Prussian blue and CdS plates are compared in Fig. 1. The photocurrent initially increases with an increase in the thickness of the Prussian blue layer; it reaches an optimum and then decreases as illustrated in Fig. 2. Curve b of Fig. 1 corresponds to optimum surface concentration which is $\sim 9.6 \times 10^{16}$ units of Fe₄[Fe(CN)₆]₃. The Prussian blue crystal structure is made up from Fe^{2+} and Fe³⁺ cations arranged in a face-centered cubic lattic of unit cell length ~ 10 A [13]. Cyanide ions lie along edges of the cube coordinated to metallic ions on either side. In the coating process, the production of one unit cell of Prussian blue requires the reduction of 14 Fe³⁺ ions. Consequently the unit cell thickness of the film of optimum surface concentration is \sim 70 (*i.e.* thickness of the film $\sim 7 \times 10^{-6}$ cm). A film of this thickness increases the photocurrent quantum efficiency by a factor of ~ 3 (Fig. 1). Figure 3 shows the absorption spectrum of Prussian blue. The peak absorption here is in the vicinity of ~ 650 nm and an absorption minimum occurs around 450 nm, which is close to the band-gap wavelength of cadmium sulphide (~ 510 nm).



Fig. 1. Photocurrent action spectrum of (a) CdS, (b) CdS coated with PB film of thickness \sim 70 unit cells, (c) CdS coated with PB film of thickness \sim 98 unit cells.



Fig. 2. Variation of photocurrent density with surface concentration of PB.



Fig. 3. Absorption spectrum of PB.

The enhancement of photocurrent by the Prussian blue film can be explained on the assumption that it acts as an efficient hole-accepting agent. Photocurrent generated in the cell is limited by the recombination of carriers. Efficient transfer of holes to Prussian blue, trapping there and transfer to redox species, greatly reduces the combination probability. Holes accumulating in Prussian blue is subsequently removed by electron donors in the electrolyte. Two reactions involved are represented below.

$$\begin{array}{cccc} hv & \longrightarrow e^{-} & + & h^{+} \\ & \downarrow & & \downarrow \\ conduction \ band \ CdS & valence \ band \ CdS & (1) \\ & h^{+} + PB \longrightarrow (PB)^{+} \\ & \uparrow \\ valence \ band \ CdS & (2) \end{array}$$

$$(PB)^{+} + I^{-} \longrightarrow I \tag{3}$$

$$I^- + I_2 \longrightarrow I_3^- \tag{4}$$

where PB denotes Prussian blue. I_3^- accepts electrons at the counterelectrode to generate I^- .

The structure and properties of Prussian blue have attracted much attention [13]. It represents a prototype mixed valence compound of stoichiometric composition, $Fe_4^{3+}[Fe^{2+}(CN^{-})_6]^3$. A soluble form of composition $KFe[Fe(CN)_0]$ is also known; films deposited by the present method are known to have former composition. A Prussian blue lattice has alternate ferrous-ferric anions (Fe²⁺-Fe³⁺). As evident from cyclic voltammograms of the coated films [12], Fe^{2+} sites could get easily oxidized to Fe³⁺. Presumably, easy oxidation is responsible for the ability to accumulate holes. The fact that the optimum surface concentration corresponds to several unit cell thicknesses indicates that the hole accumulation is a bulk property of Prussian blue. The hole-scavenging property increases with an increase in the thickness of the film. However, as light cut-off increases, there exists an optimum surface concentration.

4. Conclusion

A factor limiting photocurrent quantum efficiency of photoelectrochemical cells is recombination of photo-

generated carriers. Recombinations are reduced if the tunnelling of minority carriers into the solution is facilitated. This in turn depends on the rate of removal of the minority carrier by the redox species in the solution. Prussian blue film acts as an intermediate which assists transfer of holes to the solution (*i.e.* transfer of holes to I^- in the present case).

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