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The effect of methyl viologen ion on photocurrent and stability of Cu_2O photocathodes in I^-/I_3^- redox electrolyte

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Abstract

The photocurrent and stability of a photoelectrochemical cell with a Cu_2O cathode in I^-/I_3^- redox electrolyte are enhanced by trace quantities of methyl viologen added to the electrolyte. It is suggested that methyl viologen ions adsorbed on the Cu_2O surface act as a relay to transfer electrons to the I_3^- ion.

Keywords: Methyl viologen ion; Photocurrent; Stability; Cu_2O Photocathodes; Redox electrolyte

1. Introduction

Photoelectrochemical cells (PECs) and related studies on the photoeffects at the semiconductor–electrolyte interface continue to be an active area of research [1–8]. The main advantage of PECs is the ability to use polycrystalline films prepared by simple deposition techniques. In a solid state photovoltaic cell, the applicability of polycrystalline films is largely limited by the recombination of the photogenerated carriers before separation by the barrier electric field. However, in a PEC, the intimate semiconductor surface–electrolyte contact creates a more effective charge separation environment. The chief disadvantage of PECs is the instability resulting from photocorrosion. The cause of photocorrosion is generally due to the inefficiency of the redox couple for minority carrier scavenging. Thus thermodynamically favourable photodegradative processes remain unsuppressed. Photogenerated minority carriers, instead of reacting with redox species in the solution, react with the semiconductor material. More efficient redox couples reduce photocorrosion and also increase the photocurrent. Several workers have studied PECs made from cuprous oxide [9–11], which is a highly photo- unstable material, susceptible to corrosion. Although cuprous oxide is unlikely to be suitable for practical systems, studies on PECs based on this material can contribute to an understanding of the methods of improvement of PECs.

The photocurrent and stability of a cuprous oxide photocathode in an I^-/I_3^- electrolyte is significantly improved by the addition of trace quantities of methyl viologen dichloride ($MVCl_2$). This has been explained by the surface adsorption of MV^{2+} ions, which act as an electron relay.

2. Experimental details

Copper plates (1.5 cm×2 cm) were mechanically polished and ultrasonically cleaned with detergent. Cleaned plates were brushed with soap solution, washed with distilled water and dried by blowing with a warm current of air. Brushing with the soap solution keeps the copper surface coated with a thin protective film (probably stearic acid) which prevents staining of the surface due to atmospheric oxidation. Cuprous oxide was thermally grown by heating the plate in an oven to 650 °C for approximately 5 min. The simple procedure of brushing with soap solution and washing gives uniform cuprous oxide films of improved quality. Plates not subjected to this treatment are generally non-uniform and patchy in appearance.

PECs were constructed using the cuprous oxide-coated plate as the photocathode and a Pt mesh as the counter-electrode. The electrolyte used was 0.01 M KI containing 0.001 M I_2. The cuprous oxide electrode was biased at −30 mV vs. an Ag/AgCl electrode to obtain a zero dark current. A Nikon Monochromator Auto Scanner AS-C101 was used to record the pho-

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tocurrent action spectrum after amplification (Stanford Research Systems SR 530 lock-in amplifier). The time development of the photocurrent under white light illumination (40 W tungsten filament lamp) was monitored with an *XY/t* recorder.

3. Results and discussion

Fig. 1 shows the action spectra of cuprous oxide photocathodes in electrolytes of composition KI (0.01 M) + I_2 (0.001 M) (a), KI (0.01 M) + I_2 (0.001 M) + MV (100 μM) (b) and Na_2SO_4 (0.01 M) + MV (100 μM) (c). It can be seen that the photocurrent in the presence of MV^{2+} and KI + I_2 is much higher than that in the presence of KI + I_2 or MV^{2+} alone. MV^{2+} in the supporting electrolyte Na_2SO_4 gives only a minute photocurrent. The time variation of the photocurrent under white light illumination (40 W tungsten filament lamp) is shown in Fig. 2. A significant improvement in stability is noted when the electrolyte contains both MV^{2+} and KI + I_2.

The above observations can be understood on the basis of the following arguments. Cuprous oxide is a p-type semiconductor (band gap, approximately 2.3 eV); on illumination, photogenerated electrons (minority carriers) tunnel into the solution; these electrons are scavenged by I_3^- ions to yield I^- ions, i.e.

$$I_3^- + 2e^- \longrightarrow 3I^- \tag{1}$$

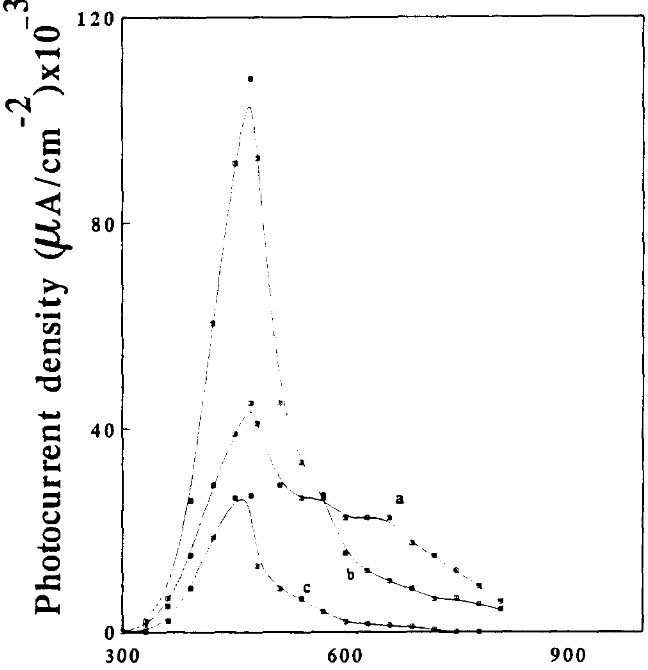

Fig. 1. Photocurrent action spectrum of Cu_2O photocathode in: (a) KI (0.01 M) + I_2 (0.001 M); (b) KI (0.01 M) + I_2 (0.001 M) + MV (100 μM); (c) MV (100 μM) + Na_2SO_4 (0.01 M).

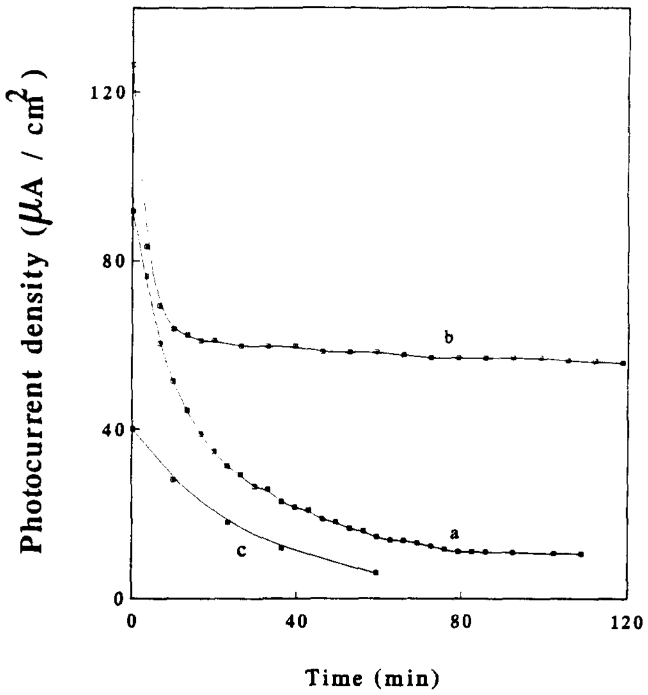

Fig. 2. Time development of the photocurrent of the Cu_2O/Pt PEC when the composition of the electrolyte is: (a) KI (0.01 M) + I_2 (0.001 M); (b) KI (0.01 M) + I_2 (0.001 M) + MV (100 μM); (c) MV (100 μm) + Na_2SO_4 (0.01 M).

The counter-electrode accepts electrons from I^- to regenerate I_3^- ions, i.e.

$$2I^- - 2e^- = I_2 \tag{2}$$

$$I^- + I_2 \longrightarrow I_3^- \tag{3}$$

The photocurrent quantum efficiency and stability of the cathode against corrosion depend largely on the rapidity of reaction (1). Competitive reactions that cause photocorrosion are as follows

$$I_3^- + e^- + Cu_2O \longrightarrow CuI + CuO + 2I^- \tag{4}$$

and

$$2H^+ + 2e^- + Cu_2O \longrightarrow 2Cu + H_2O \tag{5}$$

Of the above two reactions, the single electron transfer (reaction (4)) is predominant and the main products of Cu_2O photocorrosion in KI + I_2 are found to be CuO and CuI [10]. It is known that the methyl viologen ion (MV^{2+}) can act as an electron relay [12–14] by accepting electrons to form MV^+ and $MV^\cdot$; MV^+ and/or $MV^\cdot$ then transfers electrons to I_3^-, i.e.

$$I_3^- + 2MV^+ \longrightarrow 2MV^{2+} + 3I^- \tag{6}$$

$$I_3^- + MV^\cdot \longrightarrow 3I^- + MV^{2+} \tag{7}$$

As MV^+ and $MV^\cdot$ are powerful electron acceptors, Eqs. (6) and (7) are the most plausible intermediate steps. Unfortunately, we are not in a position to provide direct evidence to support the occurrence of Eqs. (6)

and (7). The high transient photocurrent and rapid decay to the stable value (Fig. 2, curve b) could result from the initial acceptance of electrons by MV^{2+} to form metastable MV^+ adsorbed at the Cu_2O surface.

Thus MV^{2+} facilitates the transfer of electrons to I_3^- enhancing the photocurrent and stability. The variation of the initial photocurrent (after the decay of the transient) with MV^{2+} concentration in the electrolyte is shown in Fig. 3. Saturation is noted after a slightly elevated peak. We have not succeeded in explaining the shape of the curve; the competition between the adsorption of MV^{2+} and I_3^- and/or the polymerization of adsorbed MV^{2+} [12] are possible reasons for this peculiar shape.

Singly reduced methyl viologen (MV^+) is unstable in aqueous solution. However, it is known that adsorbed MV^+ is relatively stable [15–17]. The photocurrent enhancing effect undoubtedly depends on the ability of adsorbed MV^{2+} and MV^+ to accept electrons. The photocurrent spectra (Fig. 1) probably provide evidence for the existence of surface adsorbed MV^+. When curves a and b are compared (Fig. 1), it can be seen that, in curve b, the photocurrent is significantly suppressed in the wavelength region 600–650 nm. Light absorption by MV^+ peaks at 602 nm [12] and in adsorbed species red shifts are observed. The absorption spectrum of the adsorbed species cannot be obtained as the steady state concentration of this species is small. The difference in the shapes of curves a and b may be explained as originating from the light cut-off by MV^+. However, alternative more complex mechanisms cannot be ruled out.

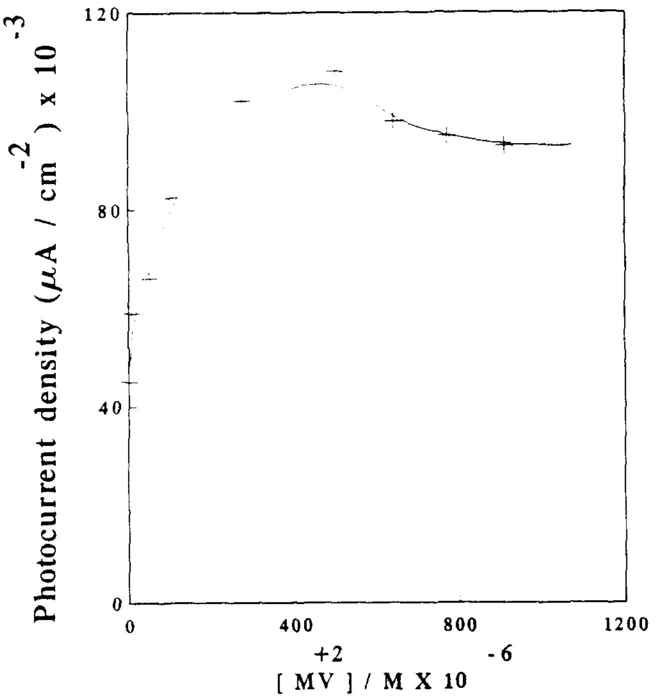

Fig. 3. Variation of the stabilized photocurrent with the MV concentration; KI (0.01 M) and I_2 (0.001 M) kept constant.

4. Conclusions

In semiconductor photocatalysis, it is well known that electron relays (notably MV^{2+}) facilitate electron transfer [12–14]. This investigation demonstrates that the same effect can be adopted in PECs to enhance the photocurrent quantum efficiency and stability.

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