

The enhancement of the photocurrent of a methyl violet sensitized cuprous iodide photocathode by β -cyclodextrin

K. Tennakone, G.R.R.A. Kumara, A.R. Kumarasinghe, P.M. Sirimanne

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

Received 25 May 1995; accepted 9 November 1995

Abstract

The photocurrent of a cuprous iodide photocathode sensitized with methyl violet is found to become enhanced if the cuprous iodide surface is previously coated with β -cyclodextrin. β -cyclodextrin forms an inclusion compound with methyl violet. Prevention of the formation of dye molecular aggregates by inclusion of dye molecules in β -cyclodextrin suppresses the formation of dye molecular aggregates that quench the photoexcitation.

Keywords: Methyl violet; Dye sensitization; Cuprous iodide; β -Cyclodextrin; Nanocrystallites

1. Introduction

The nanocrystalline TiO_2 photoelectrochemical cell (PEC) developed by Gratzel and coworkers [1–6] has aroused much interest in the dye sensitization of semiconductor electrodes and dye-sensitized (DS) devices. DS systems offer a way of extending the spectral response of photostable high band gap semiconductors to the visible spectrum. In a DS semiconductor surface, the photoexcited dye molecules injects electrons (holes) into the conduction (valence) band. As minority carriers, holes (electrons) are not encountered, the recombination losses from defects in the semiconductors are non-existent or minimal in DS semiconductor electrodes. However, the major drawback of DS PECs had been the low conversion efficiency. At monolayer or submonolayer coverage of the dye, the quantum efficiency of charge injection per molecule of the adsorbed dye approaches unity. A single monolayer coverage of the dye absorbs little light per unit area, in order to increase the energy conversion efficiency; the light absorption cross-section needs to be increased, by increasing the surface concentration of the dye. Attempts to do this encounter other problems that tend to decrease the quantum efficiency. Thick dye layers are insulating and also cut off light that should be incident on the dye molecules adsorbed at the surface of the semiconductor. Furthermore, when the surface concentration of the dye is increased, the probability of formation of dye molecular aggregates is promoted. In a dye molecular aggregate, excitation is rapidly quenched before charge carrier injection to

the bands. The above problems are cleverly circumvented in the DS microporous photoelectrode developed by Gratzel and coworkers [1–3]. In a DS microporous electrode, light intercepts many semiconductor particles thinly (e.g. monolayer) covered with sensitizer molecules. Consequently, the light absorption cross-section is increased, while maintaining a large effective surface area. Energy conversion efficiencies up to about 10% at solar intensities (about 1000 W m^{-2}) seem to be achievable with the nanocrystalline TiO_2 solar cell. This is still significantly below the efficiency of silicon solar cells. An important question is the ways in which the efficiency of the nanocrystalline cell can be further increased. Efficiency is limited by the slow kinetics of charge transfer by the redox couple. Again, even at monolayer or submonolayer levels of coverage of the dye, formation of dye molecular aggregates cannot be completely prevented. Such aggregates mutually quench the molecular excitations (concentration quenching) before carrier injection to the bands. Intermolecular contact responsible for the quenching of excitations can be prevented if the individual molecules are encapsulated or embedded in an inert matrix (it is interesting to note that, in natural photosynthesis, light-harvesting chlorophyll molecular units are embedded in protein matrix avoiding the mutual contact). The inclusion of a dye molecule (dye monomer) in cyclodextrin (CD) adsorbed on the semiconductor surface is an effective way to prevent the formation of dye molecular aggregates. In semiconductor colloids (TiO_2), it has been shown that, when the dye molecules are confined to the cavities of β -CD adsorbed on the TiO_2 surface,

the quantum efficiency of charge injection is enhanced [8]. Furthermore, surface adsorption of β -CD to semiconductor colloids has been found to improve the kinetics of charge transfer from the photoexcited semiconductor to the electron acceptor retained in the CD cavity. Motivated by the above findings, we attempted to sensitize TiO_2 nanocrystalline films coated with β -CD by ruthenium polypyridyl dyes. The observed enhancement of the photocurrent was marginal, possibly because of poor retention of the Ru complex within the β -CD cavity (inclusion of a molecule in a CD cavity depends on the molecular size and hydrophobic interactions [10]). After examining a number of dyes, we found that methyl violet (MV) readily forms inclusion compounds with β -CD. However MV is not adsorbed on TiO_2 (or TiO_2 coated with β -CD). We found that MV iodide is well adsorbed on CuI (p-type semiconductor of band gap about 3.1 eV) as well as on β -CD coated CuI. In β -CD-coated and MV-adsorbed photocathodes, a marked increase in the photocurrent was noticed.

2. Experimental details

CuI was deposited on conducting fluorine-doped tin oxide glass plates by the following method. CuI (0.2 g) and KI (0.5 g) were dissolved in 30 ml of acetone. The solution was electrolysed with the conducting glass plate as the anode and a platinum mesh as the counterelectrode. The current was potentiostatically controlled at 12 mA cm^{-2} for 15 s. Growth at high current density in a short duration of time deposited colloidal size crystallites. MV iodide was prepared from the chloride (Aldrich) by boiling the solid dye in a saturated solution of KI. Upon cooling, less soluble MV iodide separated out and was purified by recrystallization.

β -CD (Aldrich) was coated on the CuI surface by keeping the plate immersed in an aqueous solution of β -CD (0.5 g ml^{-1}) for 30 min and drying in an air current. The glass plate was then immersed in a solution of MV iodide (0.1 g ml^{-1}) containing β -CD (0.25 g ml^{-1}) to prevent leaching of β -CD coated on CuI. To carry out photoelectrochemical measurements, CuI-coated plate was placed in $\text{KI} + \text{I}_2$ (I^- , 0.1 M; I_2 , $7.5 \times 10^{-6} \text{ M}$) solution in a fibre glass rectangular vessel. The three-electrode configuration was adopted and a platinum mesh ($2 \text{ cm} \times 2 \text{ cm}$) was used as the counterelectrode.

3. Results and discussion

Fig. 1 shows the absorption spectrum of an aqueous solution of MV in the absence and presence of β -CD. A slight red shift in the latter spectrum originates from the MV monomer anchored inside the β -CD cavity. Figs. 2(a) and 2(b) compare the time development of the short-circuit photocurrent in the two cases for different intensities of illumination. In both cases there is a rapid decay of the current (especially at higher intensities of illumination). This is because of pho-

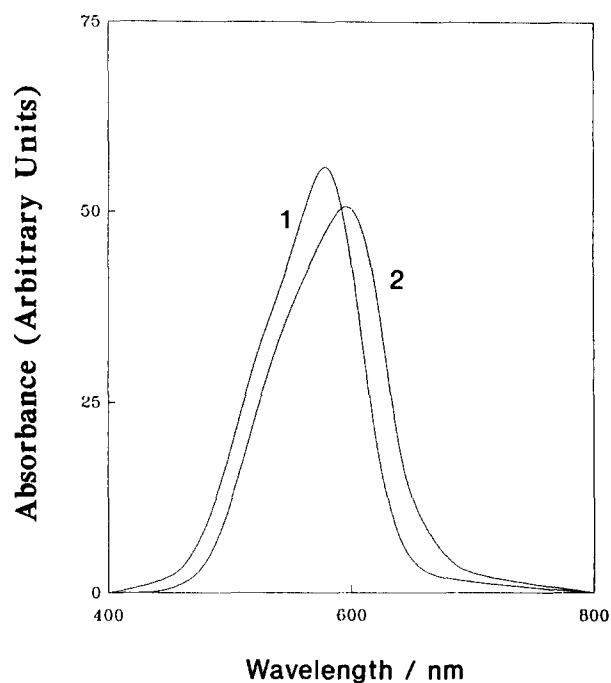
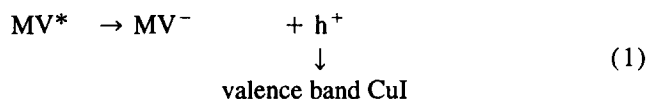


Fig. 1. Absorption spectrum of an aqueous solution of MV (curve 1) and MV + β -CD (curve 2) ($[\text{MV}] = 1.2 \times 10^{-5} \text{ M}$; $[\beta\text{-CD}] = 1.1 \times 10^{-3} \text{ M}$).

to-degradation of the dye; MV is unstable and rapidly reduced when the dye cation reacts with hydroxyl ions:

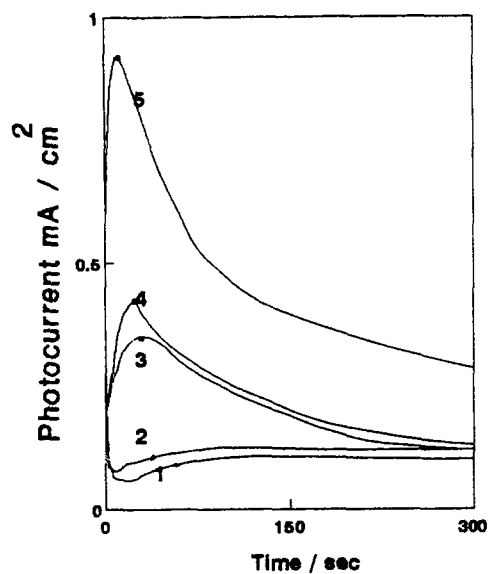


where MV^* is the photoexcited MV molecule and MVH is the MV leuco-compound.

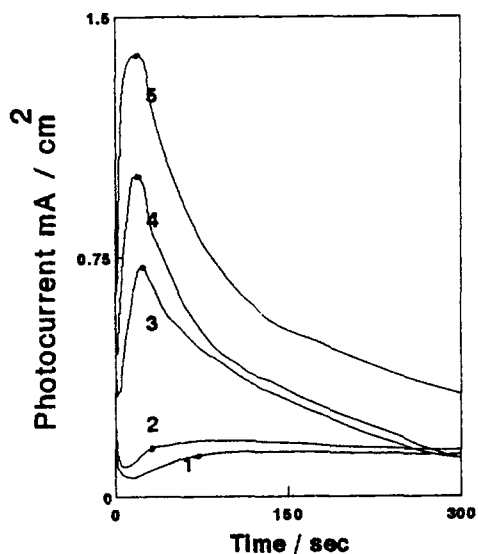
However, reaction (2) is in competition with dye regeneration via



When Figs. 2(a) and 2(b) are compared, it is seen that the maximum photocurrent in electrodes coated in β -CD is higher and the effect of β -CD becomes more apparent at higher intensities. When the light is switched on, there is an initial transient photocurrent that decays almost instantaneously; this is more significantly visible at low intensities of illumination. This behaviour is noticeable in most photocathodes in the presence of oxygen. It is likely that the transient originates from rapid acceptance of photogenerated electrons by oxygen adsorbed on the surface of the semiconductor. In deoxygenated solution this effect is not seen. A plot of maximum photocurrent vs. light intensity is shown in Fig. 3. It is very likely that the effect of β -CD is suppressing intermolecular quenching by preventing the formation of dye molecular aggregates during adsorption on the CuI surface. Although the resolution is poor, the diffuse reflectance spectra of dye-coated CuI in the presence of β -cyclodextrin gives a less broad absorption peak, suggesting that formation of aggregates is suppressed. Quenching via

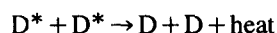


(a)



(b)

Fig. 2. Time development of the photocurrent of (a) the CuI/MV photocathode and (b) the CuI/ β -CD/MV photocathode at light intensities of 40 W (curve 1), 60 W (curve 2), 100 W (curve 3), 200 W (curve 4) and 950 W (curve 5).



(4)

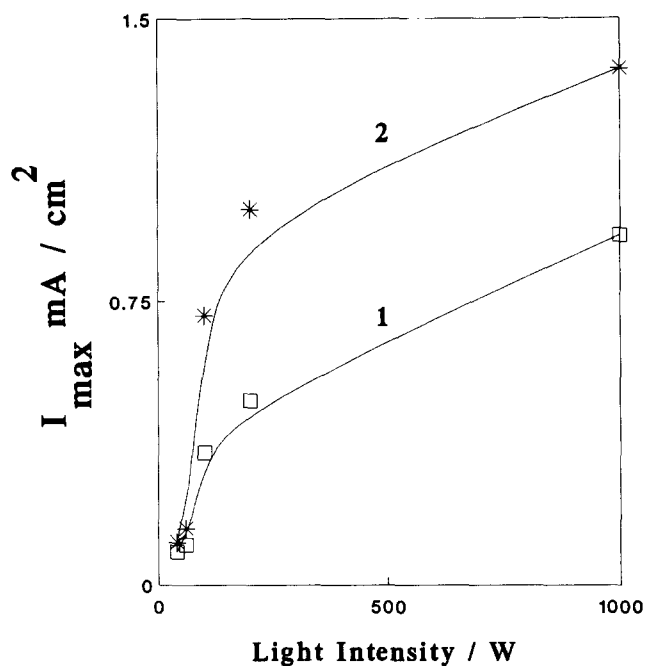


Fig. 3. The variation in the maximum photocurrent with the intensity of illumination in the absence of β -CD (curve 1) and in the presence of β -CD (curve 2).

to the first approximation is proportional to the square of the light intensity and rapidly increases with increase in the intensity of illumination. The effect of β -CD becomes readily noticeable at higher intensities of illumination, when the quenching by aggregate formation is suppressed. β -CD facilitating charge transfer to redox species could also play some role in enhancing the photocurrent.

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