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Visible light-induced long-lived charge separation across a sensitised nanostructured TiO_2–polyviologen membrane

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The preparation of a transparent nanostructured TiO_2 membrane and its sensitisation to visible light by chemisorption of a tris-bipyridyl ruthenium complex is described. Also described, is the subsequent deposition of a polyviologen film on one face of the sensitised membrane. Absorption of a visible photon by a sensitiser molecule is followed by injection of an electron into the conduction band of the nanostructured TiO_2 membrane and by conduction band state mediated electron transfer to a viologen oligomer. By these means, the energy of a visible photon is converted into chemical potential stored in the form of an oxidised electron donor and a reduced electron acceptor on opposite sides of a membrane.

Introduction

Substantial effort is being directed toward the development of stable and efficient regenerative photosynthetic cells for the conversion of solar energy in to a fuel.[1] A possible approach to the design and construction of such cells is the following:[2] to adopt the energy conversion strategy of the higher plants but to utilise modern materials, not necessarily found in natural systems, to construct the cell.

At the heart of a natural photosynthetic system are organised molecular assemblies capable of harvesting light and of transporting charge across a membrane.[3] Together these assemblies convert the energy of a solar photon into chemical potential stored in the form of an oxidised electron donor and a reduced electron acceptor on opposite sides of a membrane impermeable to the high energy products of the coupled oxidative and reductive cycles.

Preparation of a nanostructured TiO_2 membrane (40 μm thick) sensitised by chemisorption of **1** (Scheme 1) has been described.[2] The large surface roughness (about 5000) of the nanostructured membrane ensures the adsorbed sensitiser molecules are effectively stacked and that the probability of absorption of an incident visible photon is close to unity.[2b,4] It was suggested, therefore, that this assembly might be employed as the light harvesting component in an artificial photosynthetic cell.[2]

Modification of a sensitised nanostructured TiO_2 membrane by co-adsorption of the salicylate–viologen complex **2** (Scheme 1) has also been described.[2b] Absorption of a visible photon by the sensitiser **1** is followed, in the presence of a suitable sacrificial donor, by electron injection into the nanostructured TiO_2 membrane and by conduction band mediated electron transfer to the co-adsorbed viologen **2**. Although the overall quantum efficiency for charge separation is only 0.1%, the fact that the rectifying properties of the semiconductor membrane inhibit back electron transfer and that, as a consequence, the reduced viologen formed persists for up to 5 min in a carefully degassed electrolyte is of significance. It was suggested, this assembly might be employed to both harvest light and separate charge in an artificial photosynthetic cell.[2]

Two limitations of the above assembly are the following: first, that the oxidised electron donor **1** and reduced electron acceptor **2** are not on opposite sides of a membrane, and secondly, that the membrane is not impermeable to the high energy products of coupled oxidative and reductive cycles. Reported here are the findings of a study directed toward addressing the first of these limitations.

Experimental

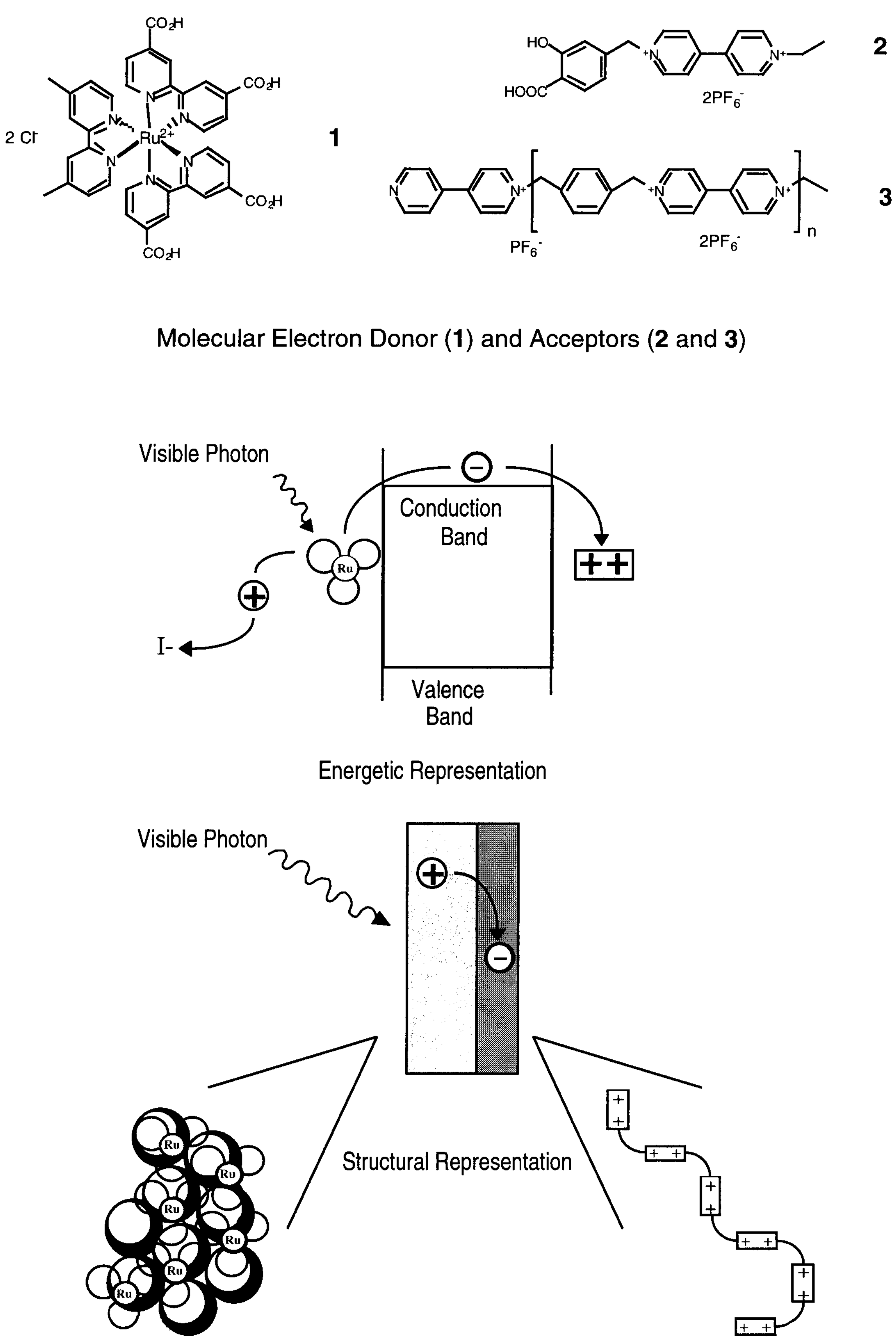
The approach adopted has been to utilise a nanostructured TiO_2 membrane sensitised by adsorbed **1** and coated on one face by a polyviologen film **3** (Scheme 1). Adopting this approach, the electron donors (ruthenium complex) are stacked within the membrane, while the electron acceptors (viologen oligomers) are adsorbed at one face of the membrane.

A 40 μm thick transparent nanostructured TiO_2 (anatase) membrane, possessing a surface roughness of about 5000, was prepared as described in detail elsewhere.[2b] The sensitiser **1**[5] and viologen **2**[6] were synthesised also as described elsewhere. The polyviologen **3** was synthesised following the method outlined by Factor and Heinsohn[7] and is composed of oligomers possessing eight viologen units.[8] The nanostructured membrane was placed in an acidified (1×10^{-2} mol dm^{-3} $HClO_4$) ethanolic solution of **1** (2×10^{-5} mol dm^{-3}) for 12 h and a transparent film of **3** cast on one face of the sensitised membrane from a 0.1% wt. acetonitrile–acetone (1 : 1, v/v) solution. As may be seen from the scanning electron micrograph (SEM) in Fig. 1, the polyviologen film formed does not interpenetrate the nanostructured TiO_2 membrane. Further, by examining a region in which the polyviologen film is partially detached, the thickness of this film is estimated to be about 1 μm.

Both unsensitised and sensitised nanostructured TiO_2–polyviologen membranes were mounted on a platinum support using Agar Scientific silver paint and incorporated as the working electrode of a closed three-electrode single compartment cell.[9] The counter electrode was a platinum and the reference electrode saturated calomel (SCE). An aqueous electrolyte solution (0.2 mol dm^{-3} $LiClO_4$, pH 3.0 by added perchloric acid) was employed and degassed by bubbling with argon for 30 min. The electrochemical cell was placed in the sample compartment of a Hewlett–Packard 8452A diode array spectrometer and potential control provided by a Solartron SI 1287 potentiostat. The spectrometer beam was transmitted though a 5 mm circular aperture in the platinum support on which the membrane was mounted. All spectra were recorded with respect to a background measured at 0.00 V. *in situ* Bandgap and visible excitation employed the 355 nm and 532 nm outputs respectively of a Nd : YAG laser for 60 s (0.2 cm^2, 10 Hz, 2 mJ uncorrected).

Results and Discussion

Previous studies have established that the potential of the conduction band edge (V_{cb}) of the nanostructured TiO_2 mem-



Molecular Electron Donor (**1**) and Acceptors (**2** and **3**)

Energetic Representation

Structural Representation

Scheme 1

brane at the semiconductor–liquid electrolyte interface exhibits Nernstian behaviour in aqueous electrolyte and that V_{cb} is -0.51 V at pH 3.0.[2b,10] Therefore, at an applied potential of -0.70 V electrons occupy the available trap and conduction band states of the nanostructured TiO_2 membrane and reduce the polyviologen film. Accordingly, the spectrum in Fig. 2(a) is assigned principally to the radical cations of the viologen oligomers in the polyviologen film.[10,11] It is noted that the absorption maximum at about 600 nm suggests formation of spin-paired diamagnetic dimers by a fraction of the radical

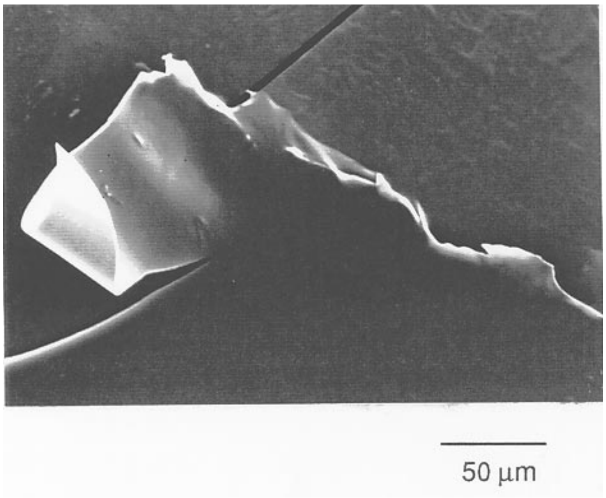


Fig. 1 SEM of nanostructured TiO_2 membrane modified by a polyviologen film **3** adsorbed at one face

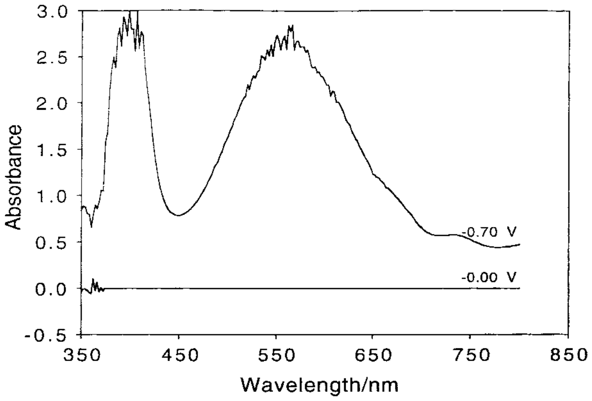


Fig. 2 Optical absorption spectra of an unsensitised TiO_2 nanostructured membrane modified by a polyviologen film **3** adsorbed at one face and measured at the indicated applied potentials *versus* SCE

cations present in the polyviologen film. Assuming all viologen monomers in the polyviologen film are reduced, the extinction coefficient of the radical cation of a viologen monomer is 13 700 $mol^{-1} cm^{-1}$ and the volume of a viologen monomer is 410 Å^3, we estimate the following: first, that there are 650 randomly oriented viologen monomers stacked normal to the surface of the nanostructured TiO_2 membrane, and secondly, that the deposited polyviologen film is at least 0.5 μm thick. In practice, and as confirmed by the SEM in Fig. 1, the polyviologen film will be substantially thicker due to disordered packing of the viologen monomers.

Bandgap excitation under open circuit conditions of an unsensitised TiO_2–polyviologen membrane in the presence of ethanol (10% by volume) as a hole scavenger leads to reduction of the polyviologen film, see Fig. 3(a).[12] It is noted, that the extent of reduction of the polyviologen film yields a lower limit for the quantum efficiency for charge separation of 0.7%.[13] It is noted also, that there is no change in the absorbance at about 600 nm assigned principally to the radical cations of the viologen oligomers during 40 min, [Fig. 3(b)]. On the basis of these observations it is concluded, that electrons are transferred from the constituent nanocrystals of the nanostructured TiO_2 membrane to the constituent oligomers of the polyviologen film and that this results in long-lived charge separation. It is also concluded, that the ethanol radicals formed upon hole scavenging, or their products, are not reduced by the radical cations of the viologen oligomers.

Visible excitation of a sensitised nanostructured TiO_2–polyviologen membrane in the presence of KI (0.05 mol dm^{-3}), leads to reduction of the polyviologen film and oxidation of the iodide ion (I^-).[2,12] It is noted, that the extent of reduction of the polyviologen film yields a lower limit for the quantum efficiency for charge separation of 0.1%,[14] see Fig. 4(a). It is noted also, that the absorbance at 600 nm assigned principally to the radical cations of the viologen oligomers decays during 15 min, see Fig. 4(b). On the basis of these observations it is concluded that electrons are transferred, *via* conduction band states, from the sensitiser molecules adsorbed at the constituent nanocrystals of the nanostructured TiO_2 membrane to the constituent oligomers of the polyviologen film and that this results in long-lived charge separation. It is also concluded that the iodine radicals (I•) formed by electron transfer to the oxidised sensitiser, or their disproportionation products, are reduced by the radical cations of the viologen oligomers. A detailed kinetic study, to be reported in the near future, supports this view and shows that the rate of decay of the viologen radical cation formed depends on the concentration of the iodine radical present in solution.[15]

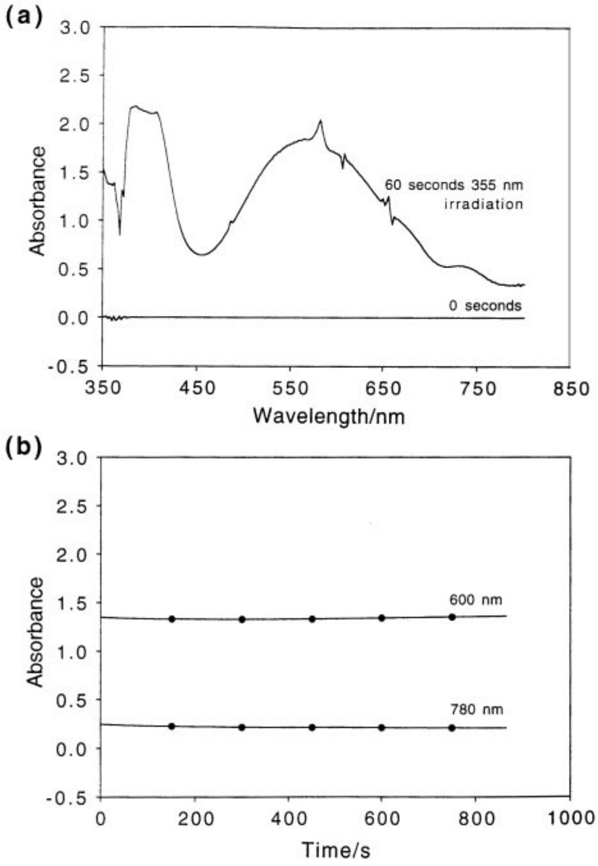


Fig. 3 (a) Optical absorption spectra of an unsensitised TiO_2 nanostructured membrane modified by a polyviologen film **3** adsorbed at one face measured prior to and following pulsed irradiation under open circuit conditions for 60 s at 355 nm in a deaerated aqueous electrolyte containing added ethanol. (b) Decay of absorbance at indicated wavelengths. (Although not plotted, no change in the measured absorbance at 600 or 780 nm was observed even after 40 min).

Conclusions

It has been possible to use visible light to achieve long-lived charge separation by electron transfer from the sensitiser molecules adsorbed at the surface of the constituent nanocrystals of a TiO_2 membrane to the constituent viologen oligomers of a polyviologen film adsorbed on one face of the same membrane. This has been possible, not because the molecular or condensed phase components utilised possess novel or

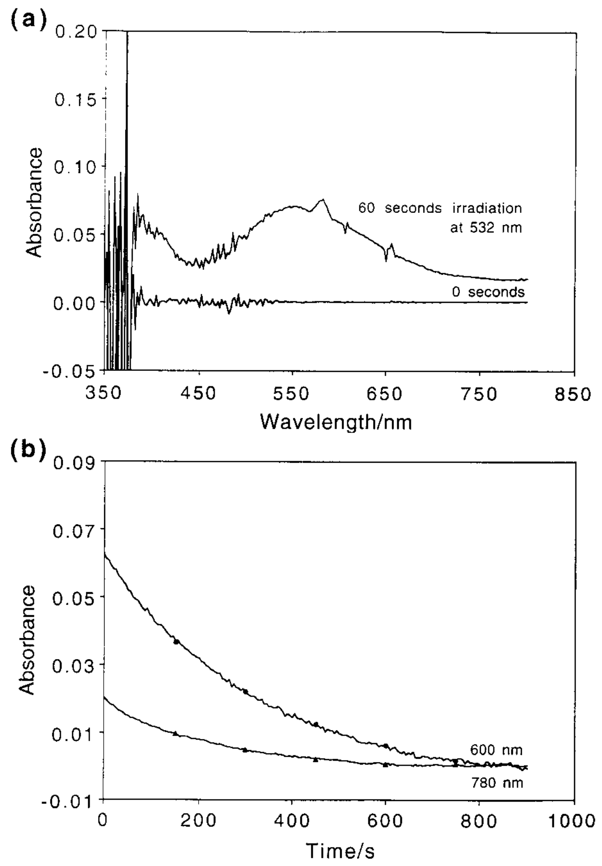


Fig. 4 (a) Optical absorption spectra of a sensitised TiO_2 nanostructured membrane **1** modified by a polyviologen film **3** adsorbed at one face measured prior to and following pulsed irradiation under open circuit conditions for 60 s at 532 nm in a deaerated aqueous electrolyte containing added KI. (b) Decay of absorbance at indicated wavelengths.

unique properties, but because their spatial organisation has been carefully controlled.

Future studies will be directed toward increasing the efficiency of charge separation, toward modifying the nanostructured semiconductor membrane to ensure it is impermeable to the products of coupled oxidative and reductive cycles, and toward replacing the ruthenium sensitiser and viologen molecules with molecular species more suitable to practical applications, for example, photosynthesis.

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8 The terminal monocation : non-terminal dication ratio has been determined by ^1H NMR spectroscopy and by elemental analysis. The results of these analyses indicate the polyviologen is composed of oligomers containing nine and seven viologen monomers respectively. An average of these two values was taken.

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12 In the absence of ethanol no reduction of the polyviologen film is observed following bandgap excitation. Similarly, in the absence of potassium iodide no reduction of the polyviologen film is observed following visible excitation.

13 The value for the overall quantum efficiency, defined as the total number of photons absorbed by the membrane in 60 s divided by the number of viologen monomers reduced, is a lower limit for the following reasons: no account has been taken for reflection or transmission losses, while the yield of reduced viologen was measured only after 60 s irradiation.

14 Similar assumption to those above have been made. In addition, the absorbance by the sensitised membrane at 532 nm is 0.3, see ref. 2.

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