

A transparent nanostructured semiconductor membrane modified by an adsorbed electron donor and electron acceptor

João Sotomayor,^a Robert W. Hoyle,^b Geoffrey Will^b and Donald Fitzmaurice^{*b}

^aDepartment of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

^bDepartment of Chemistry of Physical and Inorganic Chemistry, New University of Lisbon, 2825 Monte de Caparica, Portugal

Unsupported transparent nanoporous-nanocrystalline TiO₂ membranes are prepared which are 20 μm thick anatase structures and have an associated surface roughness of *ca.* 1100. Visible-light induced charge injection by the adsorbed ruthenium complex, [bis(4,4'-dicarboxy-2,2'-bipyridine)(4,4'-dimethyl-2,2'-bipyridine)ruthenium(II)] dichloride **1**, has been demonstrated for these membranes. Also demonstrated has been blue-light induced reduction of the adsorbed viologen, 1-ethyl-1'-[4-carboxy-3-hydroxyphenyl)methyl]-4,4'-bipyridinium perchlorate **2**.

The recent past has seen significant activity directed toward the development of practical devices based on transparent nanocrystalline-nanoporous semiconductor electrodes. Such devices include regenerative photoelectrochemical solar cells, lithium-insertion batteries, photochromic and electrochromic windows and chemical sensors.^{1,2} Nanostructured semiconductor films are also being used as anti-bacterial coatings on ceramic surfaces in hospitals and in food preparation areas, and as photoactive substrates to degrade organic contaminants in water.^{3,4} Generally, the nanostructured semiconductor electrodes and films referred to above consist of nanoporous-nanocrystalline TiO₂ (anatase) films supported on conducting glass or ceramic substrates respectively.

Applications for unsupported transparent nanoporous-nanocrystalline semiconductor electrodes and films, hereafter referred to as nanostructured membranes, are also foreseen. Firstly, in the absence of a substrate a wider range of techniques may be used to study the fundamental properties of nanostructured semiconductor materials. Secondly, such membranes are likely to facilitate the development of continuous production methods for those devices currently based on nanostructured electrodes and films, and permit the retro-fitting of such films to substrates in existing structures. Finally, such membranes are also likely to facilitate the development of new devices and applications. For example, the rectifying properties of such membranes are being exploited in the development of artificial water splitting systems.⁵

The findings presented here describe our efforts to prepare transparent unsupported nanostructured TiO₂ membranes⁶ and to investigate their properties using spectroelectrochemical techniques.⁷⁻⁹ Specifically, we describe the preparation, characterisation and the potential dependent optical emission and absorption spectroscopy of nanostructured TiO₂ membranes (20 μm thick) prior to and following their modification by adsorption of [bis(4,4'-dicarboxy-2,2'-bipyridine)(4,4'-dimethyl-2,2'-bipyridine)ruthenium(II)] dichloride or 1-ethyl-1'-[4-carboxy-3-hydroxyphenyl)methyl]-4,4'-bipyridinium perchlorate. The resulting insights into the properties of nanostructured semiconductor materials in general, and semiconductor membranes in particular, are considered. Also considered are possible applications for such membranes.

Experimental

Preparation of unsupported transparent nanostructured TiO₂ membranes

The nanostructured membranes studied are formed using 10 nm TiO₂ nanocrystals in a sol-gel preparation. The precursor

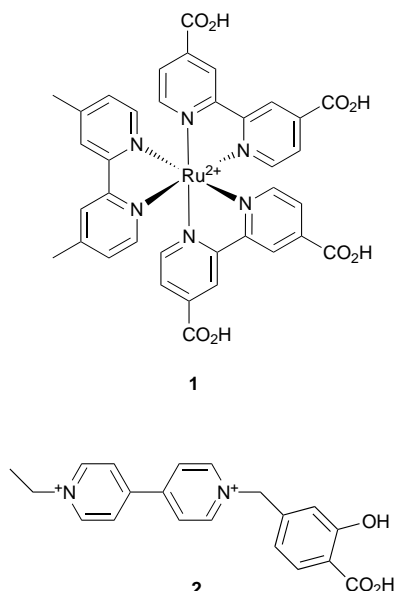
TiO₂ sol is prepared following the method developed by Grätzel and co-workers.^{10,11} Briefly, a colloidal TiO₂ dispersion was prepared by hydrolysis of titanium isopropoxide which yields crystallites with an average diameter of 7 nm. The above dispersion was autoclaved at 200 °C for 12 h to increase the average crystallite diameter to 10 nm. The resultant dispersion was then concentrated to 160 g l⁻¹ and Carbowax 20 000 (40 mass% equiv. of TiO₂) added to yield a white viscous sol. This sol was used to deposit a film on a glass substrate that had previously been treated with a solution of Triton X-100 (5% in propan-2-ol) and dried in air for 15 min. After allowing the sol-film to dry in air for 30 min, the resulting gel-film was lifted from the glass substrate using a sharp blade. Finally, the unsupported gel-film was fired in air at 450 °C for either 12 or 24 h to yield an unsupported transparent nanostructured TiO₂ membrane.

Modification of nanostructured membranes

An unmodified nanostructured TiO₂ membrane was placed directly into a saturated ethanolic solution of either [bis(4,4'-dicarboxy-2,2'-bipyridine)(4,4'-dimethyl-2,2'-bipyridine)ruthenium(II)] dichloride **1** (2×10^{-5} mol dm⁻³, pH 2.0) or 1-ethyl-1'-[4-carboxy-3-hydroxyphenyl)methyl]-4,4'-bipyridinium perchlorate **2** (2×10^{-3} mol dm⁻³) for 24 h, see Scheme 1. Preparation of these compounds has been described in detail elsewhere.^{12,13} Modified membranes were washed thoroughly with ethanol and stored in a darkened vacuum desiccator prior to use.

Potential dependent optical absorption and emission spectroscopy of nanostructured membranes

An unmodified or modified nanostructured membrane formed the working electrode of a closed three electrode single compartment cell, the counter electrode being a platinum electrode and the reference a saturated calomel electrode (SCE). An ohmic contact was formed by mounting a membrane on a platinum support using Agar Scientific silver paint.¹⁴ A circular aperture (5 mm diameter) in the platinum support allowed the spectrometer beam to be passed. The aqueous electrolyte solution, degassed by bubbling with Ar for 30 min, contained LiClO₄ (0.2 mol dm⁻³) at the stated pH (added perchloric acid or potassium hydroxide). Potential control was provided by a Thompson Electrochem Ministat and a Hewlett-Packard 3310B Function Generator. The cell was incorporated into the sample compartment of a Hewlett-Packard 8452A diode array absorption spectrometer or a Perkin-Elmer 3000 fluorescence



Scheme 1

spectrometer. For emission studies the excitation source from the fluorescence spectrometer was blocked and the all lines output (200 mW cm^{-2}) of a Coherent Ar-ion laser (Innova 70-5) used to irradiate the sample. All spectra were recorded with respect to a background measured at 0.00 V vs. SCE .

Bandgap irradiation of nanostructured membranes

An unmodified or modified transparent nanostructured TiO_2 membrane formed the working electrode of the electrochemical cell described above. The aqueous electrolyte solution employed contained LiClO_4 (0.2 mol dm^{-3}) with 10% by volume ethanol added to scavenge photogenerated holes.¹⁵ The solution was acidified by addition of perchloric acid solution and degassed by bubbling with argon for 30 min prior to use. The cell was placed in the sample compartment of a Hewlett-Packard 8452A diode array spectrometer and the nanostructured membrane irradiated *in situ* for 60 s using the pulsed output of a Continuum-Surlite Nd:YAG laser at 355 nm (10 Hz, 2 mJ). The reported pulse energies are not corrected for reflection losses. When the applied potential is not reported, open-circuit conditions applied.

Structural characterisation

Transmission electron microscopy (TEM) was performed on a JEOL 2000FX TEMSCAN whilst a JEOL JSM-5410LV was used for scanning electron microscopy. X-Ray diffraction (XRD) patterns were obtained using a Phillips PW 1730 system.

Results and Discussion

Structural characterisation of a nanostructured membrane

Fig. 1 is a low resolution SEM showing the membrane to be $20 \mu\text{m}$ thick with a suggested nanoporous structure. Further, from the corresponding XRD spectrograph [d -spacing = 3.48 \AA (100), 2.35 \AA (35), 1.89 \AA (38), 1.67 \AA (34), 1.47 \AA (29); the relative intensity is in parentheses] it is clear that the constituent nanocrystallites are TiO_2 anatase.¹⁶

From the optical absorption spectrum of a nanostructured membrane, shown in Fig. 2(a), it is possible to calculate the bandgap energy, E_g . For many semiconductors it has been shown that, the relationship between the photon energy, $h\nu$, and the absorption coefficient, α , near the absorption edge for an indirect transition is given by eqn. (1),¹⁷ where β_i is the

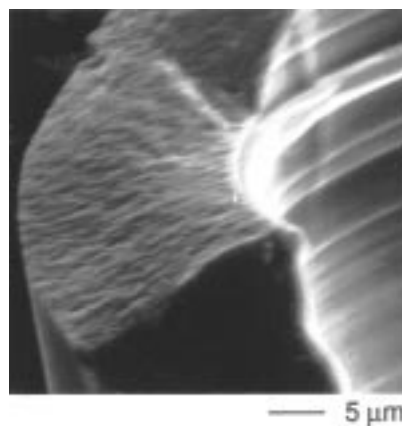


Fig. 1 SEM image of nanostructured membrane

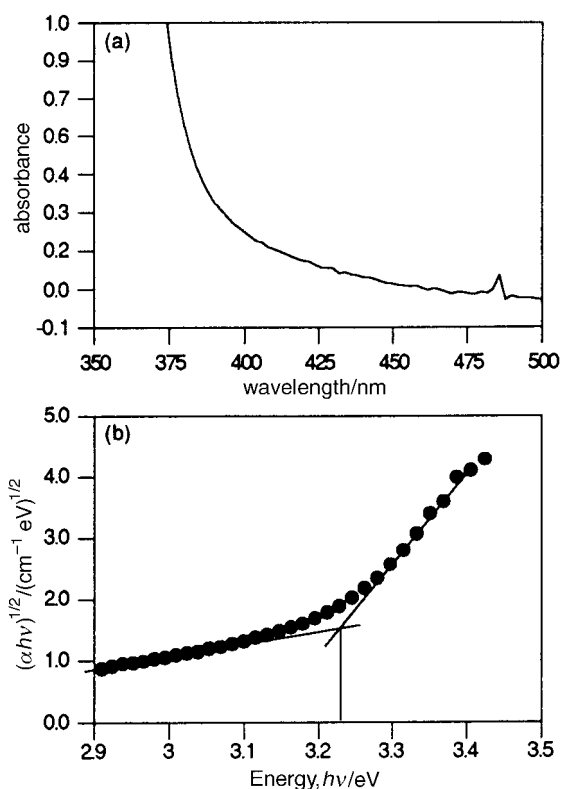


Fig. 2 (a) Optical absorption spectrum of nanostructured membrane. (b) Graphical determination of bandgap energy of membrane in (a).

absorption constant.

$$\alpha = \frac{\beta_i (h\nu - E_g)^2}{h\nu} \quad (1)$$

The absorption coefficient, α , is calculated using eqn. (2),¹⁸

$$\alpha = \frac{2.303 \times 10^{-3} A \rho}{lc} \quad (2)$$

where A is the measured absorbance, ρ is the density of the semiconductor (3.89 g cm^{-3} for anatase),¹⁵ l the optical pathlength (0.002 cm) and c is the concentration of TiO_2 (1.945 g dm^{-3} assuming a void fraction of 0.5).¹⁰ Therefore, for indirect transitions in TiO_2 , plotting $(\alpha h\nu)^{1/2}$ vs. $h\nu$, gives two straight lines [shown in Fig. 2(b)]. The intercept of these lines gives the bandgap absorption edge to be $3.22 \pm 0.05 \text{ eV}$.¹⁹ This value is in good agreement with previously reported values for TiO_2 anatase.¹⁵

Potential dependent optical absorption spectroscopy of an unmodified nanostructured membrane

The potential dependent optical absorption spectra of an unmodified transparent nanostructured TiO_2 membrane have been measured. It is noted, that in the absence of a quantitative model that would allow the potential distribution within the membrane to be simulated, it is assumed that the potential of the membrane is equal to the potential applied to the Pt support.

The spectra measured at applied potentials -0.70 , -0.80 and -0.90 V for a membrane fired for 12 h are shown in Fig. 3(a). These spectra, measured at applied potentials close to or more negative than the potential of the conduction band edge at the semiconductor/liquid electrolyte interface V_{cb} (-0.68 V at pH 2.5, see below), are assigned to electrons present in trap and conduction band states.^{9,20} Interestingly, the absorbance loss at wavelengths shorter than the bandgap absorption edge (380 nm), previously assigned to the Burstein shift that accompanies the filling of the available states of the conduction band by electrons, is not apparent.^{21,22} In this respect, these spectra differ from those previously reported for nanostructured TiO_2 films supported on fluorine doped tin oxide glass where a Burstein shift reduced the absorbance above the bandgap energy at applied potentials close to or more negative than V_{cb} .^{8,20} It is concluded therefore, that the measured absorbance changes in Fig. 3(a) are principally due to the filling in of trap states by electrons.

In order to reduce the density of trap sites in the nanostructured membrane, the firing time was increased to 24 h. It was expected that the density of trap states would be significantly lower than in a membrane fired for 12 h and therefore, that the measured absorbance changes at applied potentials close to or more negative than V_{cb} (-0.40 V at pH 2.5, see below) would be due principally to the filling of the available states of the conduction band by electrons.^{8,20} These expectations

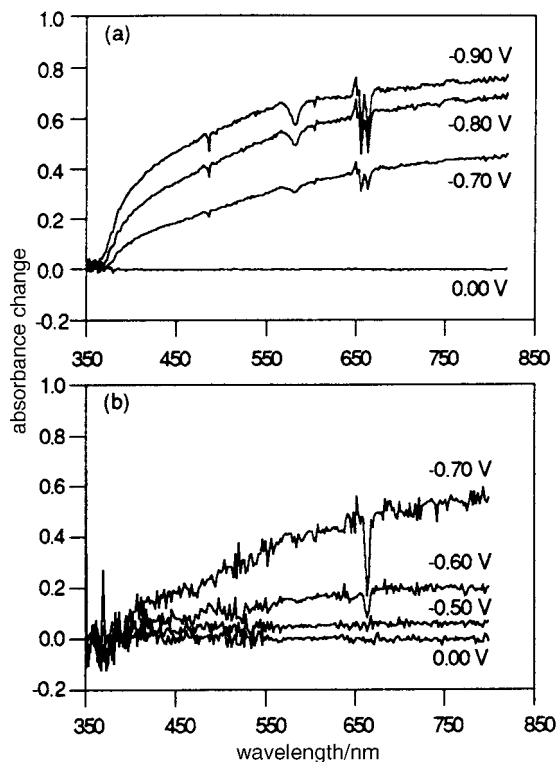


Fig. 3 Potential dependent optical absorption spectra of an unmodified nanostructured membrane fired for (a) 12 h and (b) 24 h measured at the indicated applied potentials (*versus* SCE) in an aqueous electrolyte solution at pH 2.5. All spectral changes were measured against a background recorded at 0.00 V.

are supported by the optical absorption spectra shown in Fig. 3(b). The spectra were recorded at applied potentials of -0.50 , -0.60 and -0.70 V. Specifically, the measured spectra agree well with those previously reported for nanostructured TiO_2 films (on fluorine doped tin oxide glass) where a Burstein shift is observed at applied potentials more negative than V_{cb} .^{18,22} Further, the magnitude of the measured absorbance change is smaller than in Fig. 3(a) although, the applied potentials are more negative than V_{cb} by a similar amount.

To determine V_{cb} the absorbance change for a membrane at 780 nm was plotted against the applied potential, see Fig. 4(a).^{9,20} The onset potential for light absorption by a membrane, determined from Fig. 4(a), is plotted in Fig. 4(b) as a function of pH of the electrolyte.²³ It is shown that the membranes fired for 12 and 24 h exhibit a shift in V_{cb} to more negative potentials by 61 and 68 mV per pH unit, respectively. These values agree well with the value of 59 mV per pH unit as previously reported for metal oxide electrodes in aqueous electrolyte solution.¹⁵ However, the values at pH 0.0 depend strongly on firing time; membranes fired for 12 and 24 h have values of V_{cb} equal to -0.53 and -0.23 V, respectively. In fact, this is not unexpected if we assume there are more amphoteric states at the surface of a membrane fired for 12 h than at the surface of a membrane fired for 24 h; V_{cb} would be expected to be more negative at a given pH for the former.⁸ It should be noted that if the absorbance change measured for membranes fired for 12 h is assigned principally to the accumulation of trap electrons then, as stated above, the value of V_{cb} may be at more negative potentials.

Finally, it is useful to directly compare the spectrum of a membrane fired at 24 h and measured at an applied potential of -0.60 V, with that of a membrane fired for 12 h and measured at an applied potential of -0.90 V. In each case, the

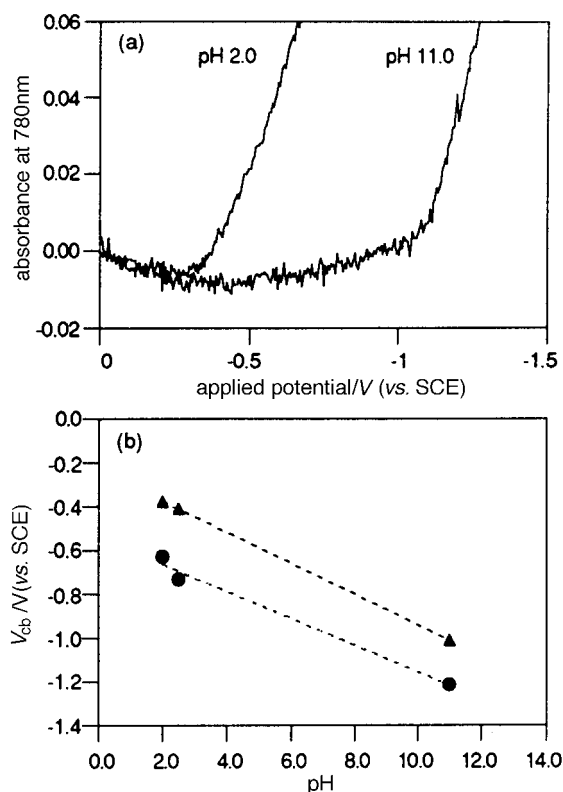


Fig. 4 (a) Optical absorption at 780 nm of a nanostructured membrane fired for 24 h measured at the indicated applied potentials (*versus* SCE) and pHs. All spectral changes were measured against a background recorded at 0.00 V. (b) Onset of absorbance at 780 nm, as determined in (a), plotted against pH of the aqueous electrolyte solution for nanostructured membranes fired for (●) 12 h and (▲) 24 h.

applied potential is *ca.* 0.21 V more negative than V_{cb} (at pH 2.5) although it is apparent that the observed absorbance change for a membrane fired for 24 h is less than the change observed for a membrane fired for 12 h. The above further supports the assertion that there is a smaller contribution to the measured absorbance by trapped electrons in the case of a membrane fired for 24 h.

All subsequent studies were performed using nanostructured membranes fired for 24 h.

Potential dependent optical emission and absorption spectroscopy of a modified nanostructured membrane

A nanostructured membrane was modified with the ruthenium sensitizer **1**; the absorption spectra prior to and following modification are shown in Fig. 5(a). From the increase in absorbance measured at 480 nm and using an absorption coefficient for the ruthenium complex of $13\,300\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$,¹² the concentration of adsorbed **1** was calculated to be 2.4×10^{16} molecules per cm^2 . Assuming that there are 2×10^{13} Ti^{4+} sites per cm^2 at which the sensitizer may be adsorbed,²⁴ we estimate a surface roughness of approximately 1200. This value agrees reasonably well with those reported for a $10\ \mu\text{m}$ thick nanostructured film on conducting glass (1000) and for a $2\ \mu\text{m}$ thick nanostructured membrane (300).^{6,10}

When the applied potential is changed from 0.00 to -0.65 V (0.2 mol dm^{-3} LiClO_4 , pH 3.5) for a membrane modified with **1**, an increase in the intensity of the optical emission spectra at 600 nm is clearly seen [see Fig. 5(b)]. At -0.65 V the applied voltage is 0.18 V more negative than V_{cb} (-0.47 V , pH 3.5) and electrons are accumulated in the available states of the conduction band. As previously reported by O'Regan *et al.*,²⁵ electron injection from an adsorbed sensitizer becomes

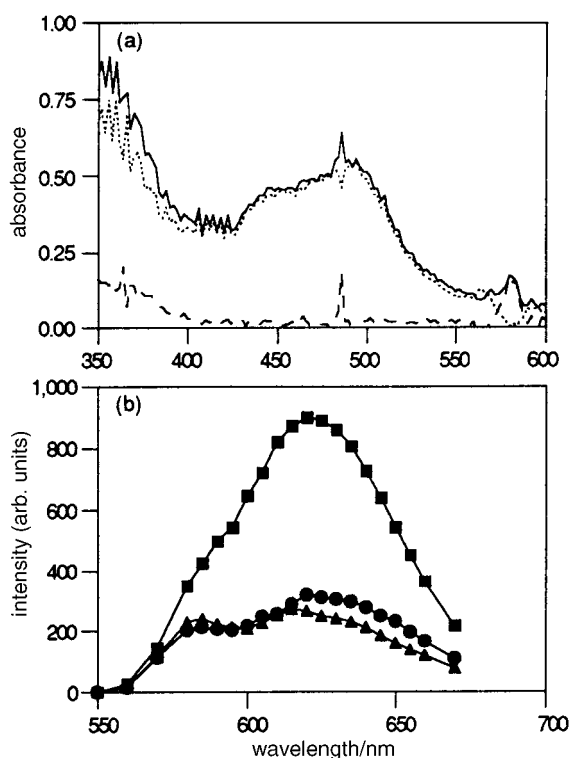
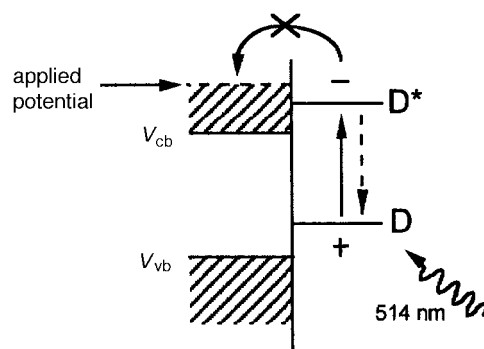


Fig. 5 (a) Optical absorption spectrum of a nanostructured membrane fired for 24 h prior to (---) and following (—) its modification by adsorption of **1**. The difference of these two spectra (.....) is the absorption that can be assigned to adsorbed **1**. All spectra were measured in air. (b) Optical emission spectra of nanostructured membrane in (a), measured initially at 0.00 V (▲), -0.65 V (■) and again at 0.00 V (●) (*versus* SCE) in an aqueous electrolyte solution at pH 3.5.



Scheme 2 At negative applied potentials the electronically excited state of the adsorbed electron donor (D^*) cannot photoinject an electron into the occupied states of the conduction band. Decay to the ground state is accompanied by emission of a red photon.

inhibited and accordingly there is an increase in luminescence from the electronically excited state of **1**, see Scheme 2.

On returning to an applied potential of 0.00 V the luminescence spectrum agrees well with that measured initially. The reversibility of the spectra confirms that the luminescence observed at negative potentials does not result from the desorption of **1**.

The incomplete quenching of the luminescence, observed at 0.00 V, is believed to be a result of adsorbed sensitizer molecules which have weak electronic coupling between the electronically excited state of **1** and the TiO_2 conduction band.

In this context, we note it is not possible to exclude, on the basis of the data presented, the possibility that the luminescence observed at negative applied potentials is due, not to filling of the available conduction band states, but to a weakening of the electronic coupling of the sensitizer and the conduction band states.

Potential dependent optical absorption spectra for a membrane modified by the electron acceptor **2** are shown in Fig. 6(a). At applied potentials more negative than V_{cb} (-0.43 V at pH 3.0) the characteristic spectrum of the radical cation of viologen is observed,^{26,27} a result of conduction band mediated reduction of **2**, see Scheme 3.¹³

An applied potential of -0.6 V is sufficiently negative that all adsorbed **2** will be reduced. The contribution of conduction band electrons to the spectrum can be assessed by comparison with an unmodified membrane recorded under similar conditions. Therefore, from the difference in absorbance at 600 nm the concentration of adsorbed **2** can be calculated to be *ca.* 2.0×10^{16} molecules per cm^2 .²⁷ Assuming that there are 2×10^{13} Ti^{4+} sites per cm^2 at which a sensitizer may be adsorbed,²⁴ a surface roughness of *ca.* 1000 is estimated. This value agrees well with that determined for membranes modified by adsorbed **2**.

In summary, a sufficiently negative potential applied to a transparent nanostructured membrane inhibits electron transfer from the ruthenium based donor **1**, and induces electron transfer to the viologen based acceptor **2**.

Light-induced optical absorption spectroscopy of a nanostructured membrane

The light-induced optical absorption spectrum of an unmodified transparent nanostructured TiO_2 membrane was measured in an aqueous electrolyte solution (10% ethanol v/v) at pH 3.0 ($V_{cb} -0.43\text{ V}$) under open circuit conditions, see Fig. 7. Also shown are the absorption spectra, recorded under similar conditions, for an unmodified membrane at applied potentials of -0.50 and -0.60 V .

It is clear from the above findings, that the extent of filling of the available states of the conduction band by electrons under bandgap illumination is equivalent to the extent of their

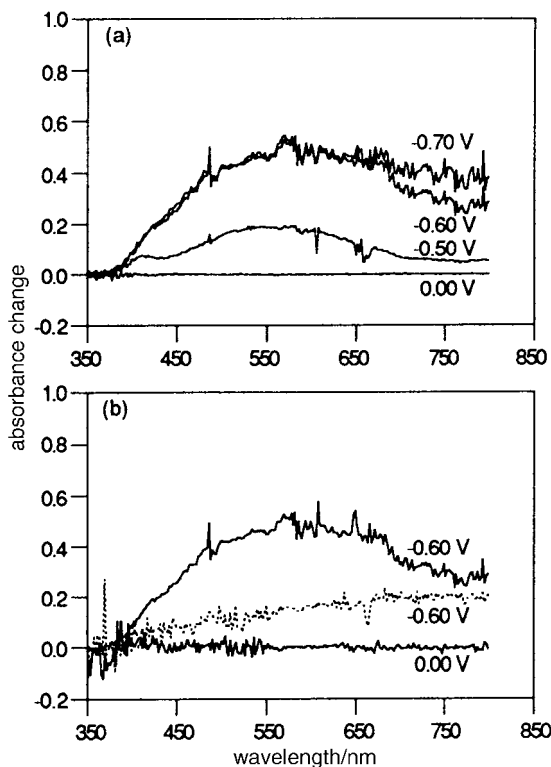
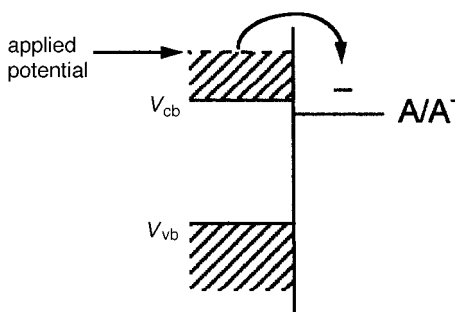


Fig. 6 (a) Potential dependent optical absorption spectra of a nanostructured membrane fired for 24 h, following modification by adsorption of **2**. Spectra were measured at the indicated applied potentials (*versus* SCE) in an aqueous electrolyte solution at pH 3.0. All spectral changes were measured against a background recorded at 0.00 V. (b) Comparison of spectrum measured at -0.60 V in (a) and at -0.60 V in Fig. 3(b).



Scheme 3 At negative applied potentials the adsorbed electron acceptor (A) is reduced by electrons present in the conduction band states

filling at an applied potential of between -0.50 and -0.60 V. It should be noted, that for a carefully degassed sample the spectrum assigned to conduction band electrons persists for some minutes following irradiation.

Fig. 8 shows spectral changes induced by bandgap excitation of a nanostructured membrane modified by adsorbed **2**. The spectra shown were, as above, recorded in an aqueous electrolyte solution (10% ethanol v/v) at pH 3.0 ($V_{cb} -0.43$ V) under open circuit conditions.

Based on the findings in Fig. 7, we would expect that due to the occupation of the available trap and conduction band states by electrons, the effective applied potential is between -0.50 and -0.60 V. It was also seen in Fig. 6 that at applied potentials more negative than V_{cb} electron transfer can be initiated to the adsorbed viologen **2**. Consistent with these expectations the characteristic spectrum of reduced viologen is obtained following bandgap excitation of the nanostructured TiO_2 membrane. It should be noted that in a carefully

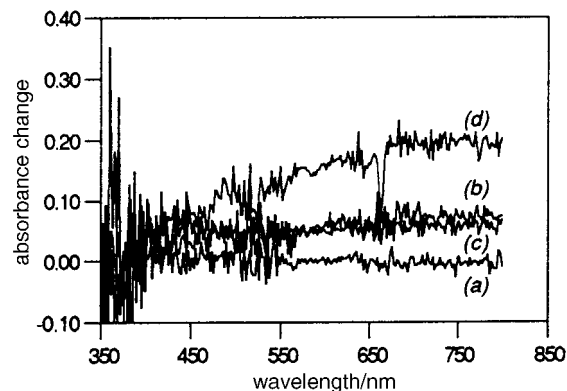


Fig. 7 Optical absorption spectra of a nanostructured membrane fired for 24 h prior to (a) and following (b) bandgap excitation under open circuit conditions using the pulsed output of a Nd:YAG laser (2 mJ pulse $^{-1}$, 10 Hz) at 355 nm. The sample was irradiated for 60 seconds in an aqueous electrolyte solution (10% EtOH v/v) at pH 3.0. Spectra measured under similar conditions at (c) -0.50 V and (d) -0.60 V (*versus* SCE) are shown for comparison.

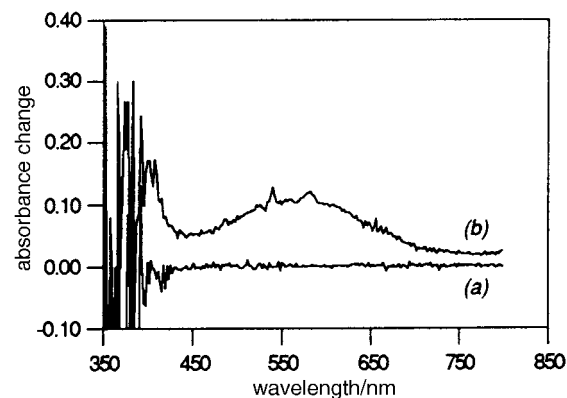
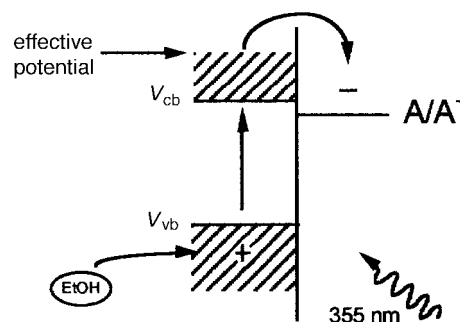


Fig. 8 Optical absorption spectra of a nanostructured membrane fired for 24 h and modified by adsorption of **2**, prior to (a) and following (b) bandgap excitation using the pulsed output of a Nd:YAG laser (2 mJ pulse $^{-1}$, 10 Hz) at 355 nm. The sample was irradiated for 60 s under open circuit conditions in an aqueous electrolyte solution (10% EtOH v/v) at pH 3.0.



Scheme 4 Following bandgap excitation in the presence of ethanol as a hole scavenger the adsorbed electron acceptor (A) is reduced by the electrons present in the conduction band states

de-aerated system the reduced viologen spectra persists for several minutes. Also, in the absence of ethanol as a hole scavenger, no absorption by reduced viologen was detected as electron-hole recombination dominates. In short, due to filling by electrons of the available trap and conduction band states a fraction of the adsorbed **2** are reduced, see Scheme 4.

Conclusions

In conclusion, transparent nanostructured membranes have been prepared. It has been demonstrated that potentiostatic control of the Fermi level within the colloidal-like particles of the membrane is possible.

For a membrane modified with an adsorbed electron donor, such as **1**, electron injection can be inhibited at applied potentials more negative than V_{cb} . Correspondingly, for a membrane modified by an adsorbed electron acceptor, such as **2**, electron transfer can be initiated at applied voltages more negative than V_{cb} .

It has also been demonstrated that a sufficiently negative effective applied potential can be achieved by bandgap irradiation of the TiO_2 membrane to initiate electron transfer to the electron acceptor **2** adsorbed at the membrane surface.

Future work is directed toward the development of stable and efficient regenerative photosynthetic cells for the conversion of solar energy into a fuel. Our approach will be to utilise the rectifying and architectural properties of the wide bandgap nanostructured semiconductor membranes described here.⁵

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