The effect of chemisorbed dyes on the *I–V* tunnel characteristics of nanocrystalline anatase TiO$_2$ observed in scanning tunnelling spectroscopy

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Abstract

We report UHV STM/STS studies on nanocrystalline TiO$_2$ films in the presence and absence of adsorbed dye sensitisers (chlorophyll b and a Ru-bipyridyl dye). Interconnected and aggregated TiO$_2$ nanocrystallites with mean diameters typically of 30–80 nm and different pore sizes are observed in STM images. The results obtained show that the surface apparent bandgap (SABG) depends strongly on tip height above the surface. However, under controlled tunnelling conditions, the SABG of as-prepared thin films is consistent with the bulk bandgap of 3.2 eV, but a quite different, lower SABG is observed when a sensitising dye is adsorbed. Moreover, the characteristic measured in this case is dependent on the choice of dye, showing that the STM *I/V* characteristic is sensitive to the adsorbed dye, rather than merely to the effect of surface adsorbed water. We discuss possible mechanisms for this effect, and the use of this effect in the optimisation of dye-sensitised photovoltaic cells (DSPECs). © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Porous, nanocrystalline semiconducting films of wide bandgap oxides such as anatase TiO$_2$ and ZnO form an important new class of electronic materials. The films exhibit extraordinary optical and electronic properties attributable to their small grain size and large surface area to volume ratio. When contacted with electrolytic or solid state hole conductors they form electronic junctions of very large area. These are important in photovoltaic, photocatalytic and biosensing applications. Of particular interest is their potential use in a number of charge-separating devices such as the dye-sensitised photovoltaic cell (DSPEC) (liquid state) and the dye-sensitised solid state (DSSS) cell which are considered to be possible alternatives to Si-based photovoltaics [1–3]. O'Regan and Grätzel [1] have demonstrated a remarkably efficient solar cell based on dye-sensitised nanoporous TiO$_2$. These cells consist of a porous TiO$_2$ anatase film prepared on a conducting substrate, stained by inorganic dyes that absorb visible illumination, and then

filled with a liquid electrolyte. A photon absorbed by the dye molecule leads to fast (fs–ps) transfer of an electron into the n-type TiO$_2$ and to an opposing increase in the charge state of a molecule in the electrolyte. Electrons diffuse through the TiO$_2$ to the collecting substrate, and ionic counter-charge is collected by a Pt top electrode immersed into the electrolyte. Unfortunately, the liquid electrolyte may degrade over a period of time, and an alternative is to create a DSSS cell by replacing the liquid electrolyte with a transparent p-type material such as CuI [2,3]. For efficient electron–hole pair separation, it is then essential that the first excited state of the dye is located above the conduction band minimum of the TiO$_2$, while the ground state must lie below the upper edge of the valence band of the p-type material. A detailed knowledge of the possible bandgap excitations in these devices is thus essential.

Here, we report UHV STM/STS studies on nanoporous TiO$_2$ films in the presence and absence of dye sensitisers. The work is part of wider studies aimed at investigating the electronic structure of the p–n junction at the heart of the DSSS cell. STM *I/V* curves are employed to measure the variation in 'surface apparent bandgap' (SABG) with adsorbed dye, and thus the extent to which the STM *I/V* characteristic may be used to give information about the states introduced into the bandgap of the TiO$_2$ film by dye

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adsorption. In order to deconvolute the effect of the dye from other influences on the STM *I/V* curves, two different dyes, having very different UV/visible absorption spectra (essentially red and green pigments) are chosen.

2. Experimental

TiO$_2$ films were deposited onto F-doped CTO glass (Solaronix, $1 \times 2\,cm^2$, sheet resistance $\sim 17\,\Omega/cm^2$) using a colloidal suspension of TiO$_2$ (formed from hydrolysis of titanium isopropoxide) as described previously [4]. The films were characterised by XRD and found to be anatase phase TiO$_2$ [5]. No impurity reflections, or reflections due to rutile were detected, to within the 1% noise level. Ruthenium bipyridyl dye (RuL$_2$(NCS)$_2$, where L = 2, 2′-bipyridyl-4, 4′-dicarboxylic acid, Solaronix) was coated on TiO$_2$ by immersing the TiO$_2$ film in a refluxing ethanolic solution of dye (2×10^{-3} M) for 45 min; a process known to yield around a monolayer coverage of dye [6,7], after which the film takes on a reddish tint. Chlorophyll b was extracted from spinach according to the reported method [8], and was coated onto the TiO$_2$ film from a solution of chlorophyll in acetone, following the same method used for the ruthenium bipyridyl dye.

STM measurements were performed using an Omicron UHV STM/AFM system under a base pressure lower than 10^{-10} mbar. Tungsten tips were employed in STM experiments, which were prepared by electrochemical etching and subsequently cleaned in UHV by e-beam heating. STM images were recorded in constant current mode at a positive sample bias, typically of +3.5 or +4.0 V (tunnelling into empty states), using a scan rate of 850–1000 nm/s. For STS measurements, the tip–sample distance was kept constant during repeated measurements by initially setting the scanning conditions using a fixed current and sample bias voltage (typically 0.5 nA and 4.0 V). The tip was positioned above the feature of interest, the feedback loop was switched off, and tunnelling currents were then recorded in the scanning voltage range of −10.0 to +10.0 V. The variation of this characteristic with tip height above the sample was also investigated, by measuring its variation with initial scanning voltage.

3. Results

Fig. 1 shows typical STM images of the TiO$_2$ films obtained. These are consistent with those obtained by other workers from TiO$_2$ nanocrystalline films [9]. They indicate a porous and rough surface morphology of TiO$_2$ nanocrystallites, and a large number of pores between the samples. The particles appear to aggregate to form larger clusters, as indicated by the line profiles shown in the figure. These show a surface roughness of around 30–80 nm in the vertical direction, suggesting that this is the fundamental crystallite size,
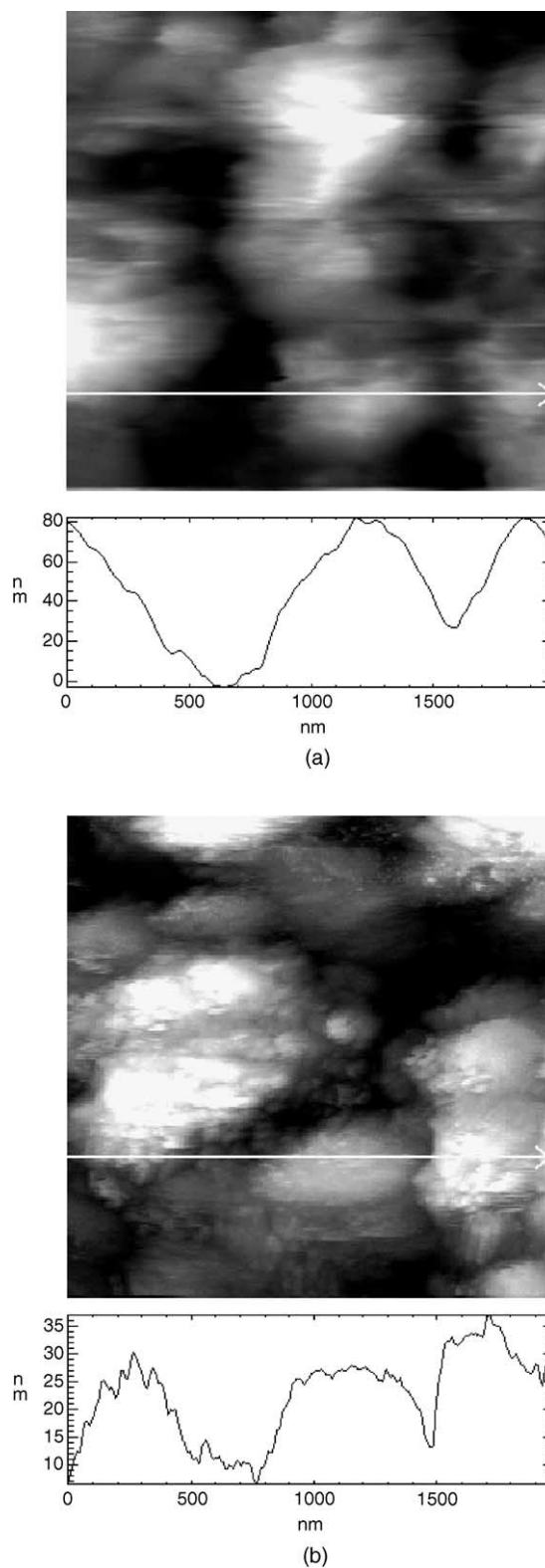

Fig. 1. STM images of a typical nanocrystalline TiO$_2$ thin film: (a) uncoated film; (b) film coated with Ru-bipyridyl dye, each showing a line profile along the direction indicated by the white arrow, at tunnelling conditions of +3.5 V (sample), 0.2 nA.
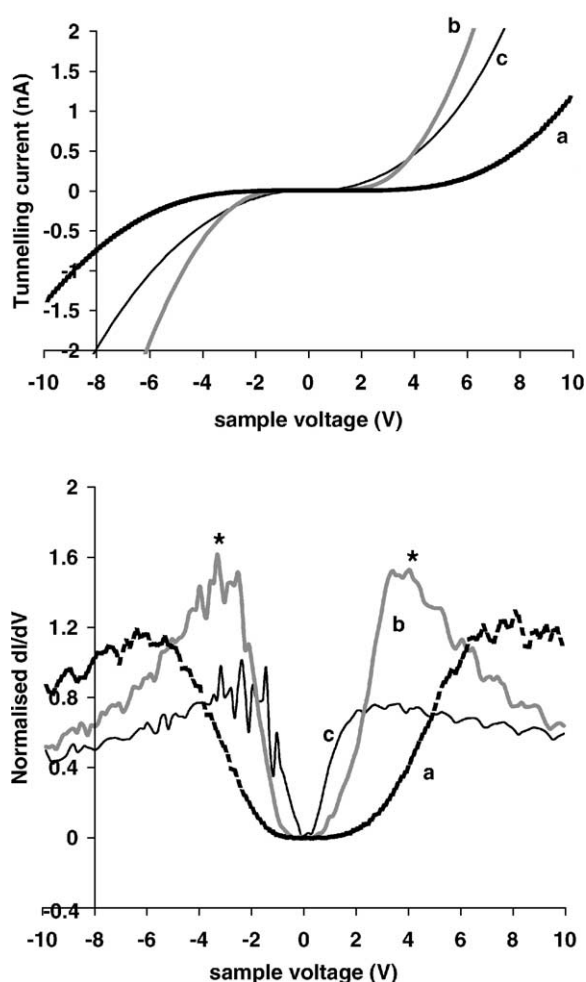
Fig. 2. Representative STM I/V characteristic (upper panel) and normalised dI/dV curves (lower panel) for: (a) nanocrystalline TiO_2 film; (b) Ru-bipyridyl dye-coated nanocrystalline TiO_2 film; (c) chlorophyll-coated nanocrystalline TiO_2 film. Tunnelling conditions were determined as in the text, using initial values of 0.5 nA and +4.0 V (sample) for tip positioning.

but with clustering of these units into approximately 500 nm (or larger) clusters in the horizontal plane. In contrast to single crystal surfaces, the substantial surface roughness precludes the study of the morphology at better resolution. At these low resolutions, there are no obvious changes in gross surface topology on dye adsorption, as is seen in Fig. 1.

The surface electronic properties of the nanoporous TiO_2 films were studied using STS, taken for both dye-sensitised and uncoated films, for a series of positions on each film, and also for a range of initial sample bias settings (which controls the tip height above the surface in each STS scan). Fig. 2 shows typical STS I/V and normalised dI/dV curves obtained from the films. As has been noted previously [9], the I/V characteristic was found to vary with lateral position across the sample, and with tip height above the surface. This is discussed further below. It was thus necessary to take a large number of measurements at a number of fixed tip heights in order to obtain values representative of the

sample. We adopt two measures to characterise the I/V curves. The first we term the SABG, which is the measured voltage difference between the anodic and cathodic onsets in the normalised dI/dV curve. This is widely used as a measure of the surface bandgap of semiconductors in general, and has been applied to nanoporous TiO_2 [9]. However, in some cases (for example in many of the I/V measurements obtained after chlorophyll adsorption) it was not possible to determine a SABG in this way. We have also therefore characterised the I/V measurements by the voltage difference between the intensity maxima in the dI/dV curves on either side of the Fermi energy (the points marked by asterisks in Fig. 2). This we term 'ΔGM' meaning the difference in gradient (dI/dV) maxima. The ΔGM measure is of course substantially larger than the SABG, but in our measurements was found to scale in size with SABG. For the present purposes, this measurement is therefore adopted merely as an indication of the relative size of the SABG. (As the dI/dV measurement reflects the joint density of states (JDOS) function of the sample and tip, the ΔGM measurement is in essence a measurement of the gap between the two JDOS maxima on either side of the tunnel junction.)

At an initial sample bias of +3.5 to +4.0 V, in around 50 STS measurements, it was found that the SABG for uncoated films varied between 2.0 and 4.1 eV, and gave an average value of 3.2 eV, agreeing with the reported value of the bulk bandgap of anatase TiO_2 of 3.26 eV [10], and with previous STM measurements of nanoporous anatase films [9]. These conditions (sample bias +4.0 V tunnelling current 0.5 nA) were therefore applied to TiO_2 films coated with both Ru-bipyridyl dye and chlorophyll, and resulting representative I/V and dI/dV data are also shown in Fig. 2. In both cases, a narrowing of the SABG can be observed in the presence of the dye, and importantly, the characteristic for the Ru-dye differs from that for chlorophyll. In each case the measurement was repeated at around 20 points on the sample at fixed tunnelling conditions, and the typical average characteristic is shown here.

Data obtained for both samples, and for uncoated TiO_2 under fixed tunnelling conditions (initially positioning the tip using 0.5 nA, +4.0 V) are quantified in the histogram shown in Fig. 3. In the case of chlorophyll-sensitised samples, the dI/dV characteristic is quite narrow, making it difficult to define SABG. The histogram therefore shows the values of ΔGM for the samples. The diagram shows the wide spread of values obtained at different points on the samples. The ΔGM histogram peaks at 4–5 eV for chlorophyll-sensitised films, 7–8 eV for Ru-bipyridyl-sensitised films and at 11–12 eV for uncoated TiO_2 films, reflecting the changes in SABG observed in Fig. 2. Thus, we conclude that the adsorption of a dye onto the surface of the TiO_2 film influences the STM I/V characteristic causing a narrowing of the SABG (and reduction in ΔGM), and that the extent of the effect is dependent on the type of dye adsorbed.

The same general effects are seen at other values of the applied sample bias. However, as is typical for a sample
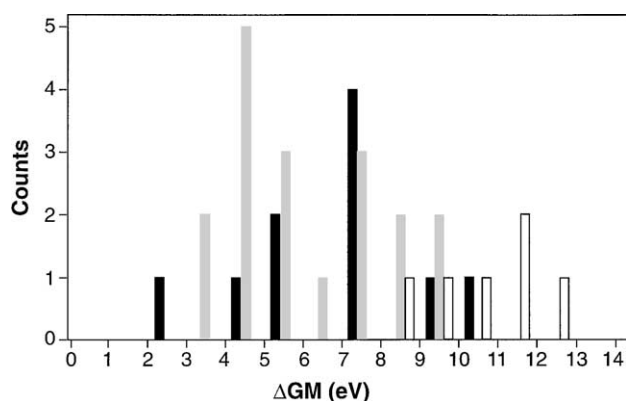
Fig. 3. Combined ΔGM histogram for nanocrystalline TiO_2 film (white), Ru-bipyridyl dye-coated nanocrystalline TiO_2 film (black) and chlorophyll-coated nanocrystalline TiO_2 film (grey), indicating the shift in the measured ΔGM values on adsorbing a dye-sensitiser onto the TiO_2 film. ΔGM is the voltage difference between the dI/dV maxima, defined as discussed in the text. The x-axis scale indicates measurements falling between 1 and 2 eV, and 2 and 3 eV, etc.

which is not metallic, the measured I/V characteristics are strongly dependent on the initial applied sample bias (which affects the tip height above the surface in the subsequent STS measurement) [11]. Fig. 4 shows the variation in I/V and normalised dI/dV for uncoated and dye-sensitised films, as the initial applied sample bias is varied between +4.0 and +1.5 V, and illustrates the necessity of making repeated measurements under fixed tunnelling conditions. In all cases the SABG collapses on reducing the bias, although the effect is much less marked for the chlorophyll-stained sample than for the other samples. However, it is clear that at bias values in the range +4 to +2.5 V, the SABG is larger for uncoated TiO_2 than for the Ru-bipyridyl-sensitised film, and this again shows a 'wider' characteristic than the chlorophyll-sensitised film. The factors affecting the I/V characteristics of these films are discussed further below.

4. Discussion

In the case of semiconducting samples, such as these TiO_2 films, the STM I/V curve may be affected by adsorption through a variety of mechanisms. Only in the case of tunnelling into a metal will the full sample bias be dropped across the tunnelling gap; in the case of semiconducting samples, a large part of the bias may be dropped across the sample itself in a space charge region directly below the tip. This leads to an I/V characteristic which is affected by a multiplicity of factors, including the carrier concentration, tip height above the surface, surface band bending effects, surface charge [11] and (in the case of granular samples) by intergrain space charge effects. In addition, the adsorption of a dye molecule on the surface should create new states in the bandgap, which will influence the SABG. A further potential influence is the adsorption of water, creating sur-

face OH^-. Narrowing of the SABG on aged nanocrystalline TiO_2 films, resulting in a reduction of SABG from 3.1 to 1.8 eV has been noted by Lin et al. [9], and attributed to surface bandgap states created by adsorbed OH^-. However, our observation that different dyes have a different effect on the I/V characteristic shows that the phenomenon we observe is not solely attributable factors such as this.

In considering the possible effects of dye adsorption, we begin by considering the new energy levels which may be created in the bandgap by adsorption of a dye at the surface of the film. Electron–hole pair separation in dye-sensitised photovoltaic devices is effective because the singlet ground state of the molecule, S_0, lies below the conduction band level of the TiO_2, (and in the case of a DSSS cell, below the valence band edge of the overlying p-type layer), while the excited state, S^* lies above it [12]. Absorption of a photon by the dye thus leads to creation of an electron–hole pair, where the electron migrates into the conduction band of the TiO_2, while the hole enters the adjoining p-type layer (DSSS), or solution (DSPEC). This is illustrated schematically in Fig. 5, which neglects any possible band bending effects, or the presence of any defect states in the TiO_2 bandgap.

In the absence of a dye, and of any surface or electronic defects (such as donor levels in n-type TiO_2), the STS experiment probes tunnelling into the conduction band of TiO_2 (at positive sample bias), and tunnelling from the filled valence band (at negative sample bias). Notwithstanding the various factors affecting the STS referred to above (space charge effects, etc.), the SABG to some extent reflects the bulk bandgap. However, we might expect that in the presence of a dye, the STS experiment becomes sensitive to the difference in tunnelling onset between the filled singlet ground state of the dye, S_0 (at negative sample bias) and the empty conduction band (or donor levels) of the TiO_2 film (at positive sample bias). This is illustrated schematically in Fig. 6. This leads to a clear mechanism for narrowing of the SABG measured in STS. Moreover, as the band edge positions of anatase TiO_2 relative to the redox potentials of both Ru-bipyridyl dye and chlorophyll b are known [12,13], we may combine this information with the optical absorption spectra of the Ru-bipyridyl dye [14] and chlorophyll b [15] to give a prediction of the positions of the new energy levels created in the TiO_2 bandgap by adsorption of both dyes, as shown in Fig. 6. This indicates that we expect to see a larger effect (smaller SABG) for chlorophyll than for the Ru-bipyridyl dye, as we observe experimentally.

This very qualitative description is helpful as a start to understanding the STS measurements, in particular the narrowing of SABG on adsorption of a dye, but it does not explain the narrowing observed on both the anodic and cathodic sides of the I/V characteristics. As we have noted, in the case of nanoporous TiO_2, a large number of other factors have an influence on the STS characteristic, as part of the applied bias is dropped in the sample in the space charge layer directly below the tip. This leads to an STS characteristic which may be affected by sample carrier concentration, tip
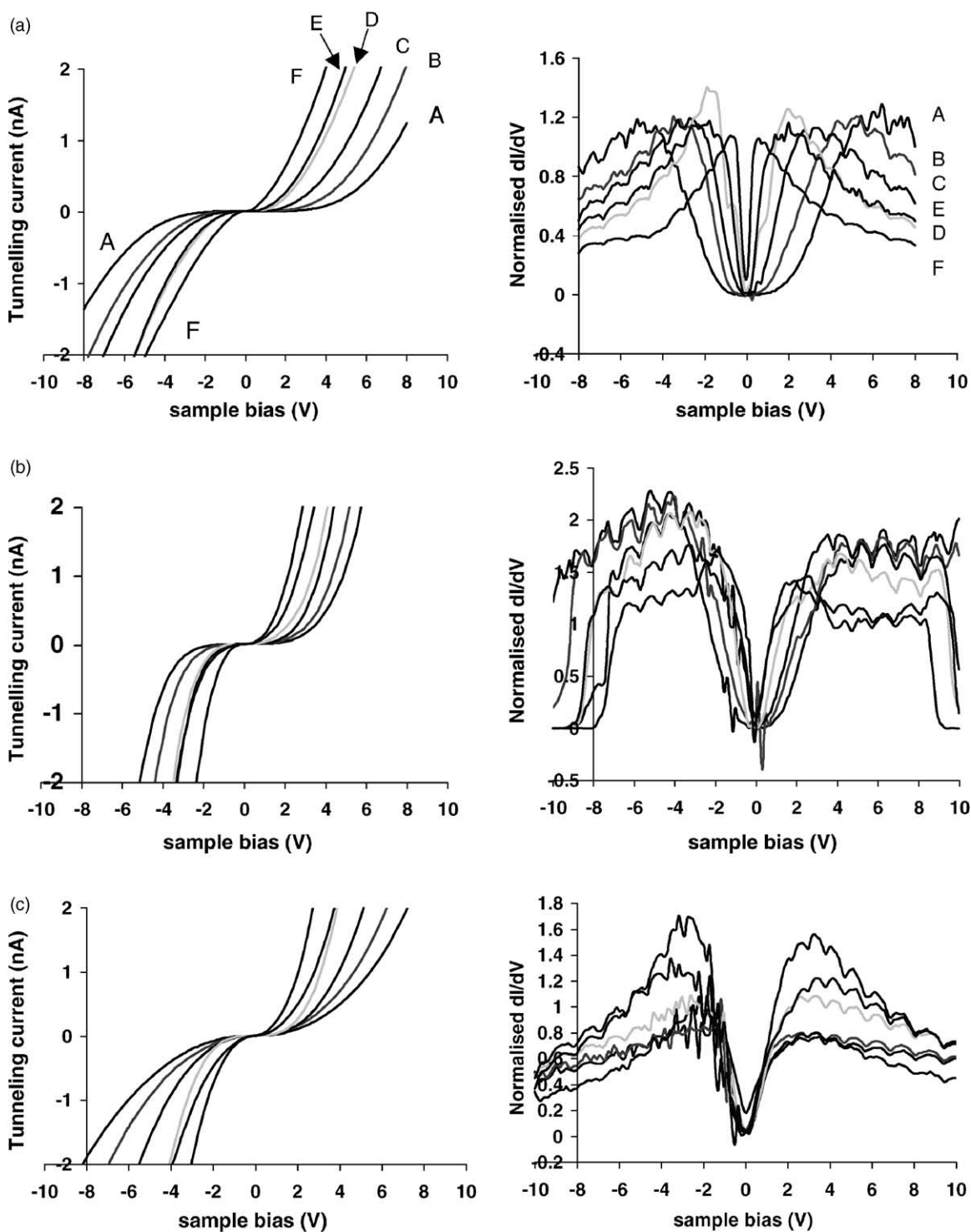
Fig. 4. Variation of tunnelling current (and corresponding normalised dI/dV measurement) with initial applied sample bias for: (a) nanocrystalline TiO_2 film; (b) Ru-bipyridyl dye-coated nanocrystalline TiO_2 film; (c) chlorophyll-coated nanocrystalline TiO_2 film. Initial tunnelling conditions are 0.5 nA (in all cases) and applied sample bias of +4.0 V (A), +3.5 V (B), +3.0 V (C), +2.5 V(D), +2.0 V(E), and +1.5 V(F).
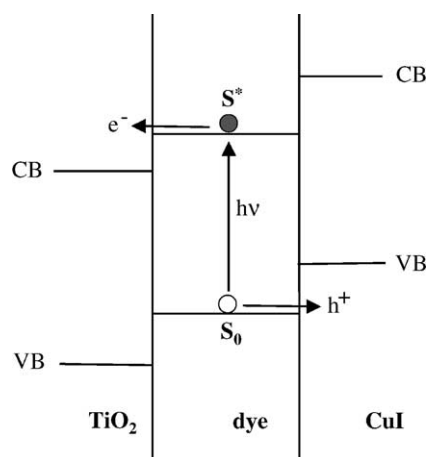
Fig. 5. A schematic diagram, neglecting band bending effects, showing the relative band positions of the n-type (TiO_2) and p-type (CuI) layers of a typical DSSS, and the ground (S_0) and excited (S^*) states of the sensitising dye (adapted from Ref. [2]).

height above the surface (as shown in Fig. 4), surface band bending, intergrain space charge effects and changes in surface charge induced by adsorption. A full analysis of these differing effects awaits a future modelling study, but we consider here the most important effects on the STS. By using a constant morphology and fixed tunnelling conditions, we have attempted to maintain a constant bulk carrier concentration and tip height above the surface. Band bending effects in nanocrystalline TiO_2 photovoltaics used in DSPEC cells
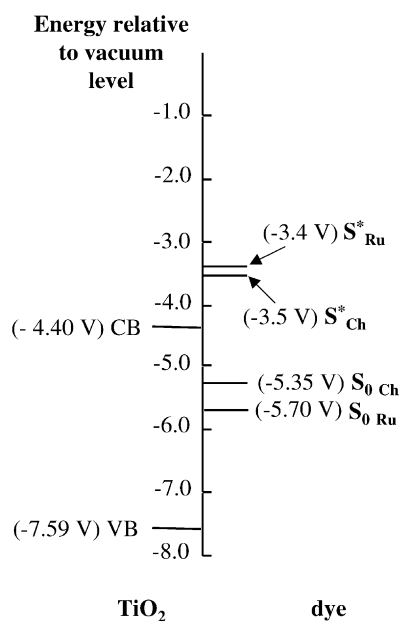
have commonly been regarded as unimportant, because the nanocrystallites themselves are typically too small to maintain a surface space charge layer, and they are surrounded, in normal operation, by a conducting electrolyte [12]. However, our experiment uses UHV, so this assumption may not be valid in our case. However, any changes in surface band bending on adsorption of the dye should produce asymmetric effects on the STS dI/dV curve, with a much stronger effect at positive sample bias (tunnelling into the sample) than at negative bias [11]. A similar effect is predicted for changes in surface charge on adsorption [11]. Although we do observe a slightly larger effect at positive bias than at negative bias (Fig. 3), significant effects are also observed at negative bias. This leads us to suppose that a full description of the observed phenomenon must also include changes in intergrain charging effects which may occur on surface adsorption.

5. Conclusions

The STM I/V characteristics of nanocrystalline TiO_2 electrodes of the type used in DSPEC cells are influenced by a number of factors including lateral position on the grains and tip height above the surface. However, multiple experiments designed to control or average these variables indicate that the SABG is also strongly dependent on the adsorption of sensitising dyes, in a way which may be qualitatively explained by the creation of new surface states in the bandgap by the adsorbing dye. This suggests that the effect may be of use in the design of the p–n junction at the heart of DSPEC and DSSS cells, in allowing the optimisation of the choice of dye. Further modelling studies designed to provide a more quantitative explanation of this phenomenon are underway.

Acknowledgements

Fig. 6. Schematic diagram, neglecting band bending effects showing energy alignment of the dye ground (S_0) and excited (S^*) states with the anatase surface [12–15]. In the case of dye-coated samples, tunnelling between S_0, and the TiO_2 conduction band is measured, leading to a marked narrowing of SABG. This should be most marked in the case of chlorophyll.

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