

Apparent Semiconductor Type Reversal in Anatase TiO₂ Nanocrystalline Films

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The electronic properties of anatase and rutile TiO₂ polycrystalline particle films have been studied using surface photovoltage (SPV) and infrared (IR) spectroscopies. The films were prepared from aqueous suspensions using a range of particle sizes (8–400 nm) and were examined under different ambient conditions. The results show that all of the examined films exhibited the expected n-type semiconductor characteristics in dry nitrogen ambient. Films created from the 30 and 400 nm anatase particles exhibited the largest surface photovoltage and also a broad mid-IR absorption attributed to shallowly trapped electrons. The latter was absent from films made from rutile particles. When examined under as-prepared “wet” conditions, the SPV was reduced in magnitude and the IR signal was absent. Further, the films formed from 8 and 30 nm particles exhibited an apparent p-type behavior in their SPV spectra. Interestingly, small anatase particles are known to exhibit enhanced photocatalytic activity when compared to larger anatase particles. These correlations indicate that water, adsorbed on TiO₂ particles of nanodimensions, induce surface states and enable redistribution of photogenerated charge carriers, which is conducive to photocatalysis.

Photocatalysis at semiconductor surfaces has been extensively investigated over recent decades.^{1–3} Titanium dioxide has usually been the photocatalyst of choice and Degussa P25, which contains about 80% anatase and 20% rutile, has emerged as the benchmark material.³ Photocatalysis studies have spanned well-characterized, single-crystal (usually rutile) surfaces under ultrahigh vacuum (UHV) conditions^{4–6} to polycrystalline powders under catalysis operational conditions.^{7–9} The latter have generally involved the catalyst in contact with an aqueous solution or water vapor. It is acknowledged that the presence of water is important for photocatalysis,^{10–11} but its exact role in the process is poorly understood.^{12–15} Numerous models^{13,16–19} have been proposed for the influence of adsorbed water on charge carrier trapping but consensus has still to be reached.

Surface photovoltage (SPV) spectroscopy has been used to study both polycrystalline and single crystal (110) rutile TiO₂.^{20–22} For both types of material, it was reported that water modified the surface work function of rutile TiO₂ surfaces. There appear to have been no corresponding studies of anatase TiO₂ surfaces. It has been observed that adsorbed water influences a broad mid-infrared spectral absorption between 4000 and 700 cm⁻¹, which arises when TiO₂ polycrystalline films are irradiated with UV light^{13,17,23,24} and that has been assigned to excitation of shallowly trapped electrons.²⁴ Panyatov and Yates¹⁷ observed that this signal decreases when water is chemisorbed to the surface of a thermally reduced P25 TiO₂ film. They propose that the water depletes conduction band electrons during the formation of Ti–OH groups in the early stages of chemisorption. In this paper, we report the results of surface

photovoltage and of infrared (IR) spectroscopies on anatase and rutile polycrystalline films containing a range of particle sizes under different states of surface hydration. The results are discussed in terms of the influence of adsorbed water on the surface charge carrier redistribution.

The TiO₂ samples studied were reference catalysts from the Catalysis Society of Japan and some of their properties are summarized in Table 1.²⁵ All samples were commercially manufactured by a liquid-phase sulfate process and, although from different sources, may be considered comparable for this work. Suspensions of the TiO₂ (0.004 g mL⁻¹) in water (Millipore, Milli-Q, resistivity 18 MΩ cm) were ultrasonically agitated for 5 min, then applied to stainless steel discs for SPV measurements and to an internal reflection prism for collection of attenuated total reflection infrared (ATR-IR) spectra. Excess water was removed using a water pump vacuum (~5 × 10³ Pa) before SPV and IR measurements. The “as-prepared” films were porous, containing an appreciable amount of residual water, and are thus referred to as “wet” films. Scanning electron microscope (Jeol 6700f field effect SEM) images (not shown) showed them to be 1.5–2.5 μm thick. Subsequent drying with nitrogen (BOC, oxygen free, moisture, <10 ppm) reduced the water content of the films, and these samples are referred to as “dry” films.

The surface photovoltage spectroscopy measurements were carried out using an illuminated Kelvin probe apparatus (Besocke Delta Phi, Germany). The contact potential difference (V_{CPD}) between the sample and a vibrating Au grid reference probe was measured. V_{CPD} and SPV are related by

$$V_{CPD} = \frac{1}{e} (W_S - W_R) = -SPV$$

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TABLE 1: Characteristic Data of TiO₂ Samples Used in the SPV and Ir Studies²⁵

TiO ₂ sample	surface area/ m ² g ⁻¹	primary particle size/nm	Ti ³⁺ concentration/ 10 ⁻⁶ mol g ⁻¹	source
anatase 1 JRC-TIO-7	270	8	119	Sakai Chemical SSP-24
anatase 2 JRC-TIO-13	59	30	72	Tayca AMT-600
anatase 3 JRC-TIO-2	18	400	28	Fuji Titanium
rutile JRC-TIO-3	40	40	48	Ishihara

where W_S and W_R are the surface work functions of the sample and the Au reference probe, respectively.^{26–29} The Kelvin probe measures an average signal in a 2.5 mm diameter area and provides ~ 1 mV sensitivity. A 250 W lamp (Oriel QTH) combined with a monochromator (Oriel CS 130) with resolution of about 3 nm (<0.03 eV in the 2.1–3.2 eV scan range) was used to provide the variable wavelength light source. ATR-IR spectra (4 cm^{-1} resolution, averaged over 64 scans) were obtained using a DuraSampIR 3 mm diameter diamond-faced 3 reflection ZnSe prism (ASI SensIR Technologies) in a DigiLab FTS 4000 spectrometer. Ultraviolet (UV) irradiation was carried out with a 2.5 mW 365 nm light-emitting diode.

Figure 1 shows the CPD spectra obtained from several TiO₂ samples. The spectra are of the as-prepared films under room ambient conditions and show changes in the TiO₂ surface work function, reflecting the conduction band minimum at the surface, as a function of the illuminating photon energy. Both the CPD spectra of the rutile films (Figure 1a) and of the 400 nm anatase films (Figure 1d) show changes to a more negative CPD signal at superband gap illumination. This indicates build-up of SPV opposing the original potential difference across the films or particles. That potential gradient causes separation of photogenerated electrons moving into the bulk of the film and of holes to the surface,^{26,28} that is, these films show typical n-type semiconductor behavior.^{22,27–29} However, the 8 nm (Figure 1c) and 30 nm anatase (Figure 1b) particle films show an unexpected increase in the CPD upon superband gap illumination, behavior typical of a p-type semiconductor surface.^{27,28}

The CPD spectra show major surface work function changes when the same films are dried for 12 h under a dry nitrogen

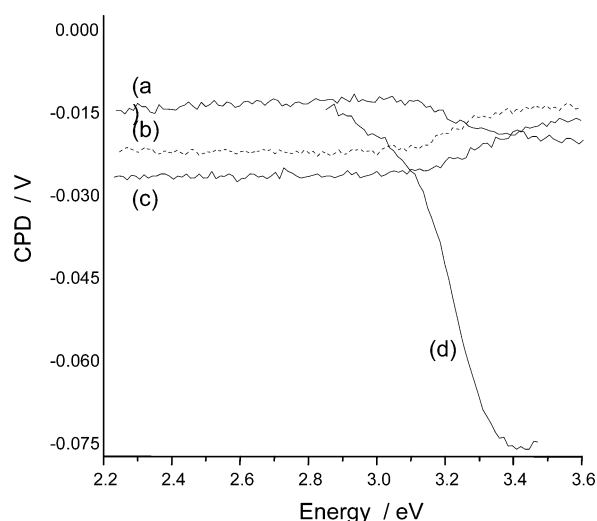


Figure 1. CPD spectra of as-prepared TiO₂ particulate thin films prepared by drying aqueous suspensions. (a) 30–50 nm rutile, (b) 30 nm anatase, (c) 8 nm anatase, and (d) 400 nm anatase. The spectra are offset and spectrum (d) is truncated for clarity.

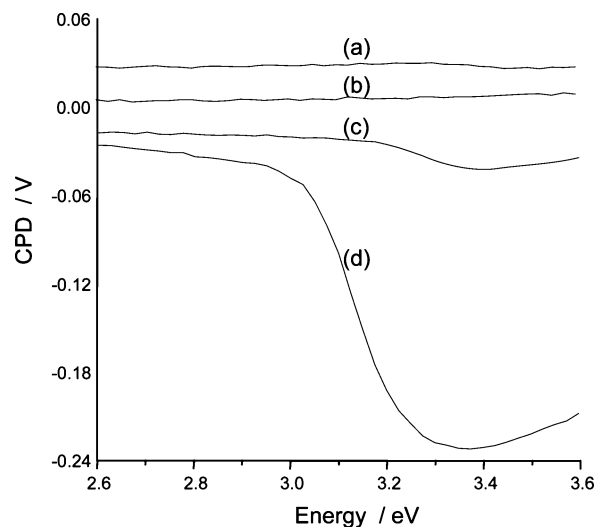


Figure 2. CPD spectra of TiO₂ particulate thin films after 12 h of exposure to dry nitrogen ambient. (a) 30 nm anatase, (b) 8 nm anatase, (c) 400 nm anatase, and (d) 30–50 nm rutile.

flow (Figure 2), with all samples exhibiting n-type behavior under these conditions. The changes in the CPD signal on superband gap illumination of the dried 400 nm anatase and rutile samples (Figure 2c,d) are of greater magnitude than those for the wet films, as previously reported.^{22,29} The most notable change from the data for the wet films (Figure 1) is the apparent switch in behavior of both the 30 and 8 nm anatase from p-type to n-type upon removal of water (Figure 2a,b). Subsequent exposure of all of the films to a wet nitrogen flow decreased the magnitude of the CPD change as shown in Figure 2. However, there was no return of the apparent p-type behavior of the 8 and 30 nm particles, even after several hours of wet nitrogen flow.

Because the CPD spectra in Figures 1 and 2 have been recorded in the presence of some adsorbed water but in the absence of an electrolyte, the charge separation that occurs and the apparent semiconductor type switching must be the result of charge redistribution within the film itself. It is known that the carrier transport mechanism in TiO₂ particle films is influenced by particle size.^{30–34} In large particles, there is a deep space charge (electron depletion) layer and carrier transport is driftlike due to the potential drop at the surface or at grain boundaries. However, in small particles, there is little band bending and the potential gradient experienced by the charge carriers is small. In this case, carrier transport can be considered to be diffusion-like under a concentration gradient from the illuminated surface toward the supporting material (the Dember effect).^{29–32} However, the conventional Dember effect may be modified or opposed when other charge separation processes operate within a film. For example, preferential trapping of one type of carrier at the surface may result in charge separation and produce a potential drop across the film. The latter may then upon illumination lead to a driftlike current opposing the diffusion-controlled current and the production of an electric field. Thus, although band bending in nanoparticles can be negligible, there may be a significant electric field across the film as a whole.^{30–33} Either increased efficiency of hole trapping or decreased efficiency of electron trapping at the surface may produce such an electric field, resulting in upward “band slanting” under illumination and an apparent p-type response in the CPD spectrum. Schiller et al.³⁵ have proposed such a mechanism to explain the observation of p-type behavior in a rutile sample coated with aluminum oxide. It has been reported³⁶

that drying a suspension of 13 nm anatase nanocrystals results in aggregation, the generation of a new electronic state, and extended charge carrier delocalization. The creation of an internal potential would be mitigated by such charge delocalization resulting from aggregation³⁷ and may explain the loss of p-type behavior upon drying, as observed in this work. Duzhko et al.³³ observed a change in the sign of the photovoltage in the subband gap (but not the superband gap) region of both anatase and rutile porous films when they were exposed to a vacuum. They assigned their observations to a diffusion-controlled photovoltage resulting from a change in the charge carrier diffusion coefficients (from $D_h < D_e$ to $D_e < D_h$). These changes were induced by the creation of surface electron traps by the vacuum exposure.

A water-mediated switching between n-type and apparent p-type SPV behavior with superband gap irradiation, similar to that reported here, has been observed for etched CdSe quantum dot (QD) particle films.³⁰ In their nonetched state, the QDs displayed the expected n-type SPV spectra. However, upon etching the QDs exhibited p-typelike behavior under wet nitrogen ambient, but n-typelike spectra were obtained for the same particles under a dry ambient. The effect was more pronounced with smaller crystallites. Features due to band gap states were observed in the SPV spectra, and it was proposed that etch-induced electron and hole surface traps might influence the electric field generated under illumination. In the absence of water, hole trapping predominated and n-typelike behavior was seen. In the presence of water, electron trapping was enabled and the CdSe exhibited apparent p-typelike behavior. Photoelectron spectroscopy revealed the samples remained n-type at all times with respect to the position of the Fermi level, confirming that their sign of the SPV signal was the result of preferential trapping, rather than type conversion. Although the CPD spectra in Figures 1 and 2 show no detectable subband gap features, Yang et al.,²⁹ using SPV spectroscopy, have observed an electron trap induced by water adsorption in Degussa P25 TiO₂ thin films. In that work, TiO₂ thin films had been dried in room ambient for over 24 h and behaved as typical n-type semiconductors. Their CPD signals became increasingly negative as the films dried further. The establishment of a driftlike current may depend on these midgap traps,²⁶ and removal of these midgap states upon drying may be irreversible due to aggregation. Thus, apparent p-typelike behavior may be lost after aggregation and not recovered in wet nitrogen ambient.

It has been established that the effective surface electron affinity (χ^*) of a material may be influenced by dipole contributions from adsorbed molecules.^{22,37} This in turn may affect the work function and the corresponding CPD signal. If these dipole contributions are sufficiently large and of correct orientation, they may be the source of the apparent p-type CPD signal in small particles. For example, Cohen et al.³⁷ showed for n-type CdSe that χ^* increases linearly with the average dipole moment of chemisorbed organic molecules. However, this cannot be true in our case, as discussed below.

Dissociative adsorption occurs on defective TiO₂ surfaces at oxygen vacancies.^{5,38} In the samples used here, the vacancy concentration is low and approximately equal for all samples (see Table 1). Therefore, most of the surface water molecules are physisorbed rather than chemisorbed. The work function at a rutile (110) surface is unaffected by multilayer water adsorption, and the effective dipole moment of water adsorbed on a nearly perfect rutile (110) surface is 0.5 D with little variation upon introduction of O vacancies.^{20,21} Rothschild et al.²² have proposed that a small difference in work function, observed by

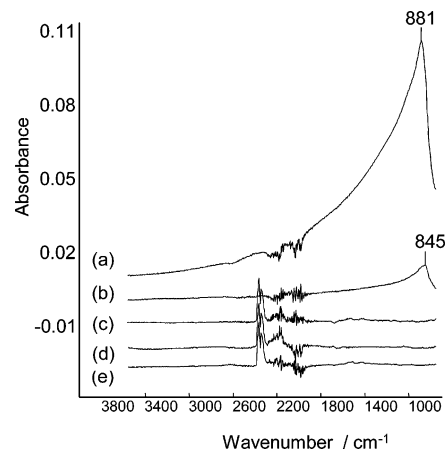


Figure 3. The IR difference spectra induced by UV of some TiO₂ particulate thin films. (a) 400 nm anatase, (b) 30 nm anatase, (c) 8 nm anatase, (d) 400 nm anatase wet, and (e) 30–50 nm rutile. Each spectrum was recorded during exposure to 365 nm UV light after 20 min. All spectra have the same absorbance scale. Background to spectra (a)–(c) is the film after 20 min under a dry nitrogen ambient and before UV exposure. Background to (d) is wet film. Noise in the 2400–2000 cm⁻¹ range is due to atmospheric CO₂ and diamond absorptions.

SPV spectroscopy between oxidized and reduced rutile nanocrystals, is the result of dissociative adsorption at vacancies. A dipole moment of 0.5 D would be expected to produce only a small change in the surface work function. Thus, it seems unlikely that the apparent p-type behavior reported here directly involves surface dipole changes. It has also been shown that the apparent n-type to p-type conversion in CdSe mentioned above³⁰ was the result of changes in the band edge position rather than in the surface dipole.

The data reported here may indicate that water molecules play a special role when adsorbed onto anatase particles. Adsorbed species bound through preferential hole capture may result in the establishment of an intraparticle electric field in the opposite direction to both the normal upward band bending of the larger n-type TiO₂ particles and the conventional Demmer effect that might be expected in smaller particles. Upon illumination, this electric field results in the drift of electrons toward the surface, rather than to the bulk as in the usual n-type depletion layer at n-TiO₂ surfaces. This in turn leads to a reduction of the magnitude of the CPD signal in larger anatase particles and the production of a p-typelike CPD signal in smaller (<30 nm) particles. Photogenerated electrons that reach the surface of smaller particles in this manner may be conducive to photocatalysis at such surfaces and may be the source of their enhanced photoactivity under a particular set of conditions.^{8,39}

Further evidence that adsorbed water is involved in electron trapping may be seen in the IR spectrum of UV irradiated anatase films containing the larger (30 and 400 nm) anatase particles (Figure 3a). These spectra show a broad featureless absorption rising to a maximum at 880–840 cm⁻¹. These spectra match previously reported data from similar experiments on Degussa P25 films, which was explained by excitation of electrons into the conduction band from shallow traps ~0.1 eV below the conduction band minimum.^{23,24} The IR spectra of films prepared from 8 nm anatase shows no evidence of the shallow trap excitation phenomenon (Figure 3b). The absence of the broad IR absorption (and smaller CPD signal) in the wet 400 nm film (Figure 3c) is explained by increased electron-trapping efficiency due to adsorbed water.^{23,24}

Tang et al.⁴⁰ have shown that the smaller effective electron mass in anatase compared to that in rutile thin films results in shallow donor states in anatase that are not present in rutile. Thus, rutile may not be expected to exhibit the shallow trap IR absorption observed here for the anatase samples with large particle sizes (Figure 3d). From this it can be concluded that not only are the shallow traps reported here and elsewhere^{13,17,23,24} associated with anatase but that they are also associated with larger particles (≥ 30 nm).

In conclusion, it has been shown using surface photovoltage spectroscopy that thin films of nanosized anatase particles (≤ 30 nm) exhibit p-type-like behavior when wet. Interfacial water molecules create a potential gradient across the particulate film that results in increased efficiency of electron trapping at the illuminated surface. Thus, charge separation of photogenerated carriers favors drift of electrons to the surface where they are available to facilitate catalytic activity. Removal of water molecules from the same samples results in reversion to n-type behavior, possibly due to aggregation. The IR absorption behavior under UV illumination in the 400 nm particulate thin films shows the existence of shallow electron traps whose filling is also controlled by the water content of the film.

Both SPV and IR spectroscopic results indicate that primary particle size and physisorbed water play important roles in the charge carrier behavior of anatase TiO₂. Although they relate to different electron distribution processes, both sets of results indicate that the presence of physisorbed water enhances electron trapping at the surface.

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