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Control of Photoactivity over Polycrystalline Anatase TiO₂ Thin Films via Surface Potential

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ABSTRACT: The utility of thin-film TiO₂ for photocatalysis would be greatly improved if the spatial variation of the electronic band edges near the surface could be engineered a priori to control the current of photogenerated minority carriers. The present work demonstrates such a concept. In particular, remote oxygen plasma treatment of polycrystalline anatase TiO₂ with specified majority carrier concentration is employed in the test case of methylene blue photodegradation. The photoreaction rate varies by up to 35% in concert with a 0.4 eV change in built-in surface potential measured by photoelectron spectroscopy. The correlation between these changes agrees quantitatively with a photodiode–photocurrent model. The plasma treatment affects concentration of charged native defects within the first few atomic layers of the surface, most likely by lowering the concentration of oxygen vacancies within surface crystallites. In tandem, the position in the deep bulk is controlled via engineering the defect concentration at grain boundaries, thus illustrating the coordinated use of multiple defect engineering practices in polycrystalline material to accomplish quantitative manipulation of band bending and corresponding photocurrent.

INTRODUCTION

Thin-film semiconducting photocatalysts find applications in self-cleaning windows/other weather-exposed surfaces,¹ ² and in antimicrobial,³ ⁴ antifouling coatings.⁵ ⁶ Moreover, the anatase form of TiO₂ is a promising catalyst for water purification and advanced oxidation processes (AOP) because of its low cost, nontoxicity, and capacity for degrading recalcitrant dyes, pesticides, and volatile organic compounds in wastewater. Although suspensions of particles may be used in photocatalytic systems, catalyst separation and recovery impose additional cost. An alternative is to immobilize the catalyst on a support, with the trade-off being a reduction in the active area. This decrease in area could be compensated, however, if minority photocarriers could be driven more efficiently to the surface.⁷ Manipulation of the direction and magnitude of photocurrent is commonplace in conventional optoelectronics, mostly via semiconductor band-engineering techniques that employ heterostructures with background carrier concentrations via manipulation of the concentrations and spatial distributions of substitutional and native point defects. Rarely is a free surface involved, however, which in photocatalysis provides both the locus of chemical activity and an additional pathway to accomplish band engineering. In particular, surface photocurrent may be driven through manipulation⁸ of near-surface electric fields via the magnitude and sign of the surface potential, V₀, which in principle may be manipulated in turn via the controlled placement of charged point defects on or very near the surface. This form of defect engineering, which translates into band engineering for photocurrent control, has been demonstrated in conventional microelectronics applications⁹ –¹² but not in thin-film photocatalysis. The present work demonstrates such a concept through the use of remote oxygen plasma treatment of polycrystalline anatase TiO₂ in the case of methylene blue (MB) photodegradation.

The unambiguous demonstration of this idea stems partly from the complexities of polycrystalline wide band gap semiconductors with electrically active grain boundaries and partly from the difficulty in controlling background carrier concentration reliably. This latter difficulty is especially pronounced because of a dearth of dopants having shallow donor or acceptor levels,¹³ effects of poorly controlled concentrations of native point defects serving as donors or acceptors,¹⁴,¹⁵ and effects of charged defects at grain boundaries.¹⁶ Nevertheless, recent work in this laboratory has demonstrated that suitably prepared polycrystalline anatase effectively acts as a uniform medium with a donor concentration N_D that varies with the engineered concentration of grain boundary defects.¹³,¹⁶,¹⁷ N_D scales inversely with film thickness because of a progressive decrease in grain boundary area that is available for accumulating defects with excess

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This effect felicitously avoids the need for extrinsic dopants, which engender complications that could affect reaction rates such as segregation to the surface. The width of the space charge layer (SCL) near the surface varies with $N_D$, and a wider SCL leads to a larger volume from which generated photocarriers can be swept to the surface to increase the photocurrent.

The present work focuses on a different form of defect engineering, in which the spatial distribution of charged defects is controlled by employing remote oxygen plasma treatment to change the concentration of charged native defects within the first few atomic layers of the surface, most likely by lowering the concentration of oxygen vacancies within surface crystallites. The literature on MB photodegradation by TiO$_2$ is voluminous, making this reaction a useful, well-characterized test case for unambiguously demonstrating phenomena that result from band manipulation.

**METHODS**

**Photocurrent Model.** A key parameter in band engineering is the width of the SCL, the behavior of which is governed by the equation

$$W = \sqrt{\frac{2\varepsilon_0 \varepsilon_s V_s}{\varepsilon_0 N_D}}$$

where $W$ is the SCL width, $\varepsilon$ the dielectric constant of the semiconductor, $\varepsilon_0$ the permittivity of free space, $q$ the electronic charge, $V_s$ the surface potential, and $N_D$ the (spatially uniform) donor carrier concentration. Within the SCL, the built-in electric field can play a crucial role in the transport of charge carriers to and from the surface of the semiconducting material, effectively influencing the type and number of charges that get to participate in surface reactions. We had previously reported the change in photoactivity of a polycrystalline anatase TiO$_2$ photocatalyst based on variations in $N_D$, where we obtained good adherence of actual rate improvement with that predicted by a photocurrent model based on the photodiode and governed by the equation

$$I_{pc} = I_0(1 - e^{-\alpha W}) + I_0 \left( \frac{aL_p}{1 + aL_p e^{-\alpha W}} \right)$$

where $I_{pc}$ is the minority charge photocurrent, $I_0$ the photocurrent if all incident light stimulated electron–hole pairs (EHPs), $\alpha$ the absorption constant, and $L_p$ the minority charge diffusion length. The first term in parentheses represents the drift component of the photocurrent while the second term represents the diffusion component. In contrast to our previous work where $N_D$ was varied to effect changes to the photocurrent, we now vary $V_s$ to test the photocurrent model’s correlation with photocatalytic activity.

The methodology employed in this study makes use of normalized changes with respect to reaction rate measurements made on 300 nm films. There is good reason to believe that photocarriers generated within the SCL are effectively promoted to the surface. There are reports in the literature that the lifetime of electron–hole pairs (EHPs) in TiO$_2$ is in the vicinity of $10^{-9}$ s, whereas the time taken to sweep the EHPs out of an SCL of 50 nm with a surface potential of 0.1 eV can be calculated to be on the order of $10^{-12}$ s. If we assume a typical donor charge concentration of $\sim 10^{17}$ cm$^{-3}$ for TiO$_2$, increasing the surface potential from 0 to 1 eV results in the increase of $I_{pc}$ from 1 to 10 $\mu$A cm$^{-2}$. This represents an increase by a factor of about 10 and translates to an extra $\sim 10^{12}$ cm$^{-3}$ s$^{-1}$ of minority charges migrating to the surface. Although not all charges promoted to the surface this way will get to participate in a surface reaction, we think it reasonable that the catalytic turnover frequency (TOF) will scale by the same factor as the photocurrent.

Wilson and Idriss investigated the reconstructed surfaces of the TiO$_2$(001) – {011} and {114} faceted surfaces and the effect they had on the photoreaction of acetic acid. They argued that changes in reactivity are due to the changes in the electric field in the SCL caused by the last-layer atomic arrangement of the surface. The surface potentials and SCL width for the two facets were estimated from the quantum yield of acetic acid decomposition, with $V_s$ calculated to be 0.18 and 0.023 V for the {011} and {114} facets, respectively, while their SCL widths were estimated at 18.2 and 6.6 nm, respectively. The quantum yield of the {110} facet over that of the {114} facet was about 2.5 times. Using our model with key parameters of donor concentration as $N_D = 1 \times 10^{17}$ cm$^{-3}$ and dielectric constant of $\varepsilon_s = 170$ used by those authors, together with other nonadjustable parameters like $\alpha$ and $L_p$, the predicted improvement is 2.3 times, as shown in **Figure 1**. The increase in apparent quantum yield was measured by the authors to be a factor of 2.5, close to the estimated improvement in photocurrent (or equivalently, quantum yield) by our photocurrent model. This result indicates the applicability of the current model to their system and reinforces the case that surface fields affecting charge-transfer kinetics across the surface could and should play a dominant role.

**Figure 2** shows the trend in drift and diffusion components of the photocurrent within a range of 1 eV for surface potential. We see that improvements to the reaction rates will come mainly from the drift component of the photocurrent. This should come as no surprise as band engineering seeks to control the preferential flow of electrons or holes to the catalyst surface by manipulating the built-in field in the SCL. For flat bands where there is no electric field, we can expect hole promotion to the surface to be diffusion-controlled.

During the development of the photocurrent model, a number of assumptions were made. We assumed that changes in turnover frequency (TOF) are proportional to changes in photocurrent and that the donor concentration (primarily in the form of native defects at grain boundaries) throughout
the bulk is uniform. The polycrystalline films we used were also assumed to act as uniform media. What comes as surprising then is the effectiveness of this formulation in predicting rate changes by considering the flux of minority charge carriers to the surface, demonstrating the importance of the near-surface field in the optimization of surface photocatalytic reactions.

**Experimental Details. Photoreaction Rate Measurements.** The photoreaction of aqueous methylene blue (MB) over TiO$_2$ anatase thin film was measured on a setup comprising a reaction vessel, ultraviolet (UV) light source and a UV–visible (UV–vis) spectrometer (UV-3600 from Shimadzu). The UV light source used was the UVP Blak-Ray B-100 high-intensity UV lamp which houses a 100 W Sylvania H44GS-100 M mercury spot light bulb that strongly emits in the 365 nm UV wavelength.$^2$

A stock solution of 0.8 mM MB was prepared using deionized water. In each photodegradation experiment a solution of 5 $\mu$M MB was obtained by diluting 0.625 mL of 0.8 mM solution in a 100 mL volumetric flask with deionized water.

The photoreaction was carried out batchwise with an initial MB concentration of 5 $\mu$M over 100 min of UV irradiation at pH 6.4. The concentration of the solution after the UV irradiation was determined using a UV–vis instrument from Perkin Elmer, with the standard curve obtained in the UV–vis spectrometer (UV-3600 from Shimadzu) and used to calculate the pseudo-first-order rate equation given by,$^{10-21,34}$

$$ r = k_CMB $$

(3)

where $r$ is the reaction rate, $k_C$ the apparent rate constant, and $C_{MB}$ the concentration of MB.

**Remote Oxygen Plasma Treatment of TiO$_2$.** Remote oxygen plasma treatment was performed in a stainless steel chamber 12 in. in diameter with a sample holder 8 in. in diameter. The plasma was generated by applying an RF (13.56 MHz) between two electrodes and is composed of electrons, charged ions, and neutral molecules. The thin film was placed on a platform in the center of the chamber, which acted as the cathode. Oxygen was fed into the chamber via a mass flow controller set at 20 scfm. The plasma operates on the basis of a simplified ion space-charge-limited model$^{35}$ where the plasma ion energy and the ion flux are related to the sheath voltage as

$$ E_{ion} \propto V^{4/5}P_0^{-1/2} $$

(4)

where $E_{ion}$ is the plasma ion energy, $n_{ion}$ the ion flux, $V$ the sheath voltage, and $P_0$ the oxygen pressure. Throughout the treatment, the RF power used was 50 W and chamber pressure was kept at 100 Pa. Treatment times were varied from 10 to 90 min. A bias of 1.1 kV was set up via a mesh placed above the films to prevent the impingement of energetic positive ions onto the surface that might damage the film.

Other experimental methods have been described previously.$^{5,16}$ A bias of 1.1 kV was set up via a mesh placed above the films to prevent the impingement of energetic positive ions onto the surface that might damage the film.

**Characterization.** X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were performed in a Thermo VG Scientific ESCALAB 250 Photoelectron Spectrometer with an ultrahigh vacuum system (base pressure $\sim$10$^{-10}$ mbar), using a monochromated X-ray source (Al K$_\alpha$ at 1486.6 eV) and helium discharge lamp, respectively. The work function of the instrument and the energy scale were calibrated using a clean Ni reference. Brunauer–Emmett–Teller (BET) surface area was studied in Micromeritics ASAP 2420. X-ray diffraction (XRD) patterns were obtained at room temperature with a high-resolution Bruker D8 diffractometer from Bruker AXS operated at 45 kV and 40 mA with a Cu K$_\alpha$1 primary X-ray beam ($\lambda$ = 1.5406 Å).

**RESULTS**

**Plasma Treatment.** Oxygen plasma treatment is used frequently in industry as well as in research. In cases where the area of interest is the material surface, plasmas may be set up so that the impinging ions do not damage the bulk material. This is commonly seen in surface cleaning$^{36}$ and the ashing of photoresists, as well as in the surface modification of TiO$_2$ to change their performance profile, such as improving the efficiency of dye-sensitized solar cells$^{37,38}$ and changing the responsiveness of photodetectors.$^{39,40}$ There are also cases where ion bombardment of the material is desired, such as in extending the bandwidth of light-response into the visible region for photocatalysis.$^{10}$ Although it can be assumed that surface modification has occurred via plasma treatment, the mechanism behind the reported changes was either unexplored or commonly attributed to the increase in oxide to suboxide ratios after treatment with oxygen. We believe that in the present case the changes could be directly attributed to variations in the surface potential and that it is possible to “re-pin” the Fermi level through the action of oxygen plasma treatment. Microstructural changes to the TiO$_2$ films after plasma treatment were precluded by performing the treatments at room temperature.

To correlate our result to the degree of band bending, we precluded contributions from other sources, allowing us to establish with confidence that changes in MB degradation rates were caused by affecting the near-surface electric field responsible for electron–hole separation and in our case, the promotion of photogenerated holes to the catalyst surface. To
date, we believe no reports have attempted a coherent synthesis of experimental data on surface field changes and photocatalytic rate changes, bolstered by a simple, yet predictive photocurrent model. We think a fuller picture can be obtained when these elements are brought together to offer a richer, deeper insight into the optimization of surface processes.

**Methylene Blue Degradation Rate.** Figure 3 shows the percentage change in initial rate of MB degradation with various surface treatment times. The treatment times range from 10 to 90 min with an obvious decrease in initial rate with increasing length of treatment time. Successive runs on a single piece of film show robustness and repeatability of the treatment protocol, as shown in Figure 4. The film, treated with a positive bias to shield the film from impinging cations, showed a decrease in MB degradation rate and retained this diminished activity even after exposure to water and ambient air. Successive treatment for 20 min with bias served to decrease the rate further in a nearly linear fashion for up to about 40 min of treatment before showing signs of reaching a minimum near 60 min of treatment. Treating the film for as short a time as 30 s without the use of bias caused the MB degradation to revert to the rates before any oxygen plasma treatment, and a subsequent treatment of 60 min with bias indicates a similar drop in photoactivity as three consecutive 20 min treatments. Because the films were exposed to water and ambient air after each 20 min treatment, it is reasonable to believe that any change to the film caused by treatment is irreversible under normal conditions.

![Figure 3](image-url)

**Figure 3.** Percentage change in initial rate versus treatment time. (The line is meant to guide the eye.) The trend is one of decreasing initial rate with plasma treatment time, stabilizing near the 60 min mark. Changes were calculated by comparing the initial rates after treatment with the average of initial rates before treatment. Errors are standard errors of coefficient from regression analysis.

![Figure 4](image-url)

**Figure 4.** Graph showing successive runs on a single piece of film. The graph is divided into various regions. Starting from the left, there is no change in the initial rate when the film was treated for 20 min at 50 W input power and 10 Pa O₂. When the O₂ pressure was increased from 10 to 100 Pa, successive treatment with a positive bias decreased the photoactivity of the film. Treatment of the film without bias caused the photoactivity to revert to that before any treatment, and a subsequent treatment of 60 min with bias indicates a similar drop in photoactivity as three consecutive 20 min treatments. Because the films were exposed to water and ambient air after each 20 min treatment, it is reasonable to believe that any change to the film caused by treatment is irreversible under normal conditions.

**Film Composition and Phase Identification.** Figure 5a shows the X-ray photoelectron spectroscopy survey scan of a 300 nm thin-film sample. The identity of the spectrum is consistent with that of TiO₂, where clear and strong peaks for Ti 2p, O 1s, and C 1s can be observed. The X-ray diffraction spectra for the 300 nm films are shown in Figure 5b. The spectra are matched with the anatase phase of TiO₂ and show a predominance of (101) facet planes.

Scanning electron microscopy (SEM) was used to compare the microstructure of the films before and after plasma treatment, as shown in Figure 6. No noticeable change to the surface was observed after treatment, allowing us to preclude contributions from microstructure to changes in reaction rate.

**Surface Oxidation State and Binding Energy Shift.** Figure 7 shows the C 1s XPS peak. The main peak at 284.6 eV is attributed to graphitic carbon and is used as a reference for the other peak positions. Two other C 1s peaks at higher binding energy can be identified as C−O and O==C−OH species, respectively.

![Image](image-url)

**Figure 7.** XPS O 1s and Ti 2p peaks in Figure 8 were both found to shift toward higher binding energy upon the remote oxygen plasma surface treatment. The XPS O-to-Ti ratio was found to change after the surface treatment, as shown in Figure 9. No obvious trend with treatment time could be perceived, although the change in O 1s/Ti 2p is consistently positive. No clear trend with treatment time could be perceived, although the ratio change is consistently positive. This implies that the O-to-Ti ratio has increased by an average value of 2.5% ± 1, which is consistent with mild surface oxidation of the film surface without a significant change in surface stoichiometry.

XPS O 1s and Ti 2p peaks in Figure 8 were both found to shift toward higher binding energy upon the remote oxygen plasma treatment. Careful analysis revealed that this concomitant O 1s and Ti 2p shift toward higher binding energy increases with duration of treatment time, as shown in Figure 10. This indicates a relaxation of the surface band bending, leading to a decrease in surface field strength, in turn affecting the rate of photohole promotion to the film surface. The Ti 2p peaks consistently shifted more than the O 1s peaks by ~0.1 eV. This could be explained by a relative peak shift of the O 1s...
and Ti 2p peaks occurring together with their shift to higher binding energy. These shifts confirm the more quantitative determination of $V_f$ via ultraviolet photoelectron spectroscopy, which is more accurate.

**Changes in Work Function.** The surface Fermi level was measured via UPS by referencing the valence band edge of TiO$_2$ with the Fermi edge of Ni, where the surface Fermi level was found to be 2.58 eV above the valence band edge. Because the measured band gap of our films is 3.23 eV, this places the surface Fermi level at $E_{FS} = E_C - 0.66$ eV. The Fermi level of the bulk was calculated to be $E_F = E_C - 0.16$ eV, giving us a band bending of 0.5 eV. The work functions of the films were determined through the secondary electron tail of the UPS spectra, also referenced to Ni. The work function determined this way gives a value of 5.4 eV for the untreated films.

Surface work function changes of the thin films with various treatment times are shown in Figure 11. The work function changes were obtained through the secondary electron tail of their UPS spectra. The result shows a decrease in surface work function with increasing treatment times, implying a relaxation of band bending at the film surface.

**Oxygen Plasma Species.** Oxygen plasma was employed to change the surface properties of the TiO$_2$ thin films. Care was taken to set up a bias in order to inhibit the action of energetic positive ions which could damage the film surface. A typical plasma consists of an equal number of positively and negatively charged species such as ions and electrons, together with a number of uncharged species such as neutrals and radicals. In a radio frequency generated capacitively coupled (RFCC) oxygen plasma, the dominant positive species is the O$_2^+$ ion and the dominant negative species is the O$^-$ ion. The O$_2^+$ and O$^-$ ions have a concentration of about $5 \times 10^{15}$ and $4 \times 10^{15}$ m$^{-3}$, respectively, while the electron density is about $1 \times 10^{15}$ m$^{-3}$.

Among the radical species, atomic oxygen and ozone are present in the same amount at low pressures (<120 mTorr) but the O/O$_3$ ratio increases beyond that. In particular, it was found that atomic oxygen can be found in significant concentration ($\sim 10^{18}$ m$^{-3}$) in the cathodic sheath region and plateauing above the sheath.

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**Figure 5.** (a) XPS survey scan of the anatase TiO$_2$ thin film. The binding energy was aligned using the C 1s graphitic carbon peak at 284.6 eV. One can clearly make out the Ti 2p and O 1s peaks identified with TiO$_2$. (b) XRD pattern for the 300 nm films. The dominant surface plane is (101) with its intensity increasing with film thickness. The phase of the TiO$_2$ is matched to anatase, and the particle size is estimated at $\sim 50$ nm using the Scherrer equation.

**Figure 6.** Typical SEM micrographs of the TiO$_2$ anatase surface (a) before plasma treatment and (b) after plasma treatment at 50 W input power and 100 Pa O$_2$ for 60 min. No noticeable changes to the surface microstructure of the film were observed.

**Figure 7.** C 1s XPS peak synthesis. The carbon peaks have been identified as having a main graphitic peak at 284.6 eV and two smaller peaks, namely, that associated with C$=$O and carbonyl, at higher binding energy.

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In a typical RFCC plasma, the frequency used is 13.56 MHz which the electrons respond to but the ions do not because of their masses. The high mobility of the electrons causes a DC self-bias to develop after the first AC cycle. The electrodes experience a high electron current in the first few cycles and become negatively charged with respect to the plasma, resulting in the formation of an ion sheath around each electrode. The potential gradient set up within the sheath contains the negatively charged ions within the bulk plasma while allowing positive ions to diffuse into the sheath and accelerate toward the target placed on the cathode. As such, negative ions play a minimal role in surface treatment. A screen mesh could be set up over the target to tune the acceleration profile of the impinging ions. A positive bias can be used to decelerate and repel the positive ions from bombarding the surface while allowing neutral radicals to diffuse onto the target surface for reactions. In a similar vein, a negative bias can be used to accelerate the positive ions to enhance surface bombardment. In applications where “gentle” surface reactions are desired without damaging the surface through energetic bombardment, the plasma used is obtained at elevated pressures (100–1000 mTorr) where the reactant supply is high and the ion energy low. To this end, we employed our plasma treatment at an RF power of 50 W and O₂ pressure of 100 Pa. The sheath voltage is about 100 V, so a bias of a decade higher was employed to prevent energetic ions from bombarding the film surface.

Figure 8. (a) Ti 2p XPS peaks before and after surface treatment. Peak synthesis of the peaks before and after treatment does not suggest the presence of a significant amount of suboxide material, indicating a low defect density in the original film. (b) O 1s XPS peaks before and after surface treatment. Peak synthesis reveals the presence of OH and Ti–OH species on the surface of the film. Both species fall in magnitude after surface treatment. The decrease of OH species is consistent with the decrease in the density of surface defects, which have been identified as the active sites for water dissociation.

Figure 9. Change in O-to-Ti ratio before and after surface treatment plotted against treatment time. O-to-Ti ratio was obtained from XPS data.

Figure 10. Binding energy shifts of the XPS O 1s and Ti 2p peaks plotted against surface treatment time. Both peaks shifted to higher binding energy level, although the Ti 2p peaks shifted consistently more so than the O 1s peaks. The concomitant peak shift to higher binding energy of the O 1s and Ti 2p peaks points to a relaxation of the band bending near the surface.

Figure 11. Change in work function of the thin-film surface with treatment time. With longer treatment times, the work function of the film surface decreases. This result is consistent with observations of O 1s and Ti 2p XPS peak shifting toward higher binding energy, together with a decreasing surface state density due to surface oxidation from the remote oxygen plasma treatment. The inset shows the secondary electron tail of the UPS spectra.
**DISCUSSION**

**Surface Oxidation and Band Bending.** To assess the effectiveness of the surface treatment, XPS was employed to detect changes before and after the surface modification. The Ti 2p peaks before and after treatment present little difference in terms of their peak shape and suggests that the starting material had a low defect density to begin with. The change in defect density, however, could be evaluated based on the binding energy shift of the XPS peaks.

From XPS data, both the Ti 2p and O 1s peaks presented a shift of up to \( \sim 0.4 \) eV to higher binding energy after surface treatment, as shown in Figure 10. Figure 12 plots the relative energy shift of the XPS peaks.

![Figure 12](image)

**Figure 12.** Relative shift between O 1s and Ti 2p plotted against treatment time with the magnitude calculated from the difference in binding energy shift for the same treatment time. The relative shift attains a value of \( \sim 0.1 \) eV with prolonged treatment time (>30 min), suggesting that the effect of the surface treatment on the surface oxidation state plateaus quickly with longer exposure. The line is drawn to aid the eye.

The magnitude of the relative shift stabilizes at \( \sim 0.1 \) eV after 30 min of treatment, suggesting that the effect of remote oxygen plasma on surface oxidation diminishes markedly with longer exposure. The band-bending relaxation achieved this way is up to 0.4 eV, \( \sim 80\% \) of the original value.

Further evidence of surface oxidation was provided through an analysis of the amount of OH species detected on the film surface through comparing the O 1s spectra before and after surface treatment. The presence of hydrogen at the film surface is most likely derived from the dissociation of adsorbed water. The presence of surface oxygen vacancies plays an important role in the chemisorption of water through the preferential acceptance of the oxygen in the water molecule. Mentry et al. reported that the dissociative adsorption of water is favored by the presence of surface oxygen vacancies, leading to two types of surface OH groups: (1) those belonging to the incorporated oxygen ion and (2) those attached to a nearby bridging oxygen site. Water dissociates readily on the stoichiometric surface of anatase TiO₂, with a coverage approximately 5 times that of molecular water at room temperature on the anatase (101) surface. The adsorption site of water was found to be the 5-fold coordinated Ti sites, Ti(5). Molecular water adsorbs on Ti(5) to form Ti–OH, while the dissociated H⁺ bonds with a bridging O to form a bridging hydroxyl – OH (br). The presence of oxygen vacancies near the surface has been shown to facilitate and promote the dissociation of molecular water to its hydroxyl fragments. These oxygen vacancies, predominantly found at subsurface sites in anatase (101), have been cited as being responsible for promoting many surface reactions such as water splitting, CO adsorption, etc. by acting as active sites for the reactants.

Calculations from the literature using density functional theory indicate that it is unlikely for the oxygen vacancies in the subsurface of anatase to diffuse up to the surface, meaning that a likely explanation for these subsurface defects affecting photocatalysis could be due to their proximity to the surface, acting as a contributor to interfacial charge exchange. The calculations also show that these vacancies tend to stabilize at the first subsurface layer, indicating their ionic radii could very well overlap the surface and affect charge transfer to adsorbates. Figure 13a,b shows a consistent decrease in the OH species across all lengths of surface treatment time. This fall in intensity of the OH species on the film surface after plasma treatment can thus be indicative of a decrease in the density of these surface and near-surface defects post treatment. While the SEM micrographs in Figure 6 suggest that the relative proportion of...
anatase facets does not change after plasma treatment, the decrease in OH species in our result after plasma treatment can suggest a differential change in O vacancy concentration from different facets, such as (101) and (001). Li et al. concluded that the majority anatase (101) surface was hydrophobic, while the minority (001) surface was terminated by dissociated water molecules.\textsuperscript{73} (001) facets have been suggested to be the most active sites theoretically.\textsuperscript{74–76} and some experimental confirmation has accumulated.\textsuperscript{77} The decrease observed here in surface OH species could indicate the preferential oxidation of (001) facets after plasma treatment, resulting in a drop in reactivity observed in our study. It is worth noting that both rate measurements and $V_S$ average spatially over all exposed facets and that even if there were differential changes to O vacancies among the facets, the model would be able to capture it meaningfully through $V_S$.

We postulate that this change in surface defect density affects photocatalytic rate only indirectly through a change in surface potential, and not directly via some atomic scale reaction. In addition, the change in surface potential/photoactivity of the photocatalyst seems to be robust against air and water exposure, retaining the same photocatalytic rates after multiple degradation runs. We believe that this robustness results from the character of oxygen vacancies, where they form preferentially near the surface of anatase TiO$_2$.\textsuperscript{65}

More evidence of mild surface oxidation is given by comparing the O and Ti ratio before and after surface treatment. Figure 9 shows the change in O/Ti ratio after treatment, presenting an increase in the O/Ti ratio, albeit of a modest average value of 2.5% ± 1. This slight increase can be construed as mild surface oxidation of the film surface with no contribution from suboxides (usually requiring changes of >10%), in contrast with a heavily defected surface where suboxide XPS peaks, such as those of Ti$_2$O$_3$ and TiO, could be readily identified.\textsuperscript{37}

It is worth noting that while the plasma removed O vacancies from the material surface, negatively charged ions can exist in the plasma. The electrically biased screen would have actually augmented implantation of such ions into the surface. Although such implantation could have helped to eliminate O vacancies, it could have also induced various kinds of lattice damage whose effects on $V_S$ are unknown. Indeed, observations of band relaxation in response to such implantation have been reported on Si and GaAs.\textsuperscript{79}

Note that surface oxidation can change the number of active sites that mediate photocatalysis. On TiO$_2$ surfaces, oxygen vacancies and/or under-coordinated Ti cations are the active sites for most organic molecules, and changes in the concentration of these sites, rather than the width of the SCL, could conceivably cause some of the change in reactivity. The present paper shows that the model accurately predicts the direction, magnitude, and functional form of the rate change with respect to $V_S$. Assuming that the number of active sites do change after plasma treatment, the effects would act to change the Fermi level of the surface, which directly affects the value of $V_S$. Our previous work\textsuperscript{8} shows that the photocurrent model accurately predicts the direction, magnitude, and functional form of the relationship between rates and $N_p$. The model also predicts and constrains the way rates should vary with an entirely different parameter, $V_S$. Both $N_p$ and $V_S$ act by affecting the width of the space charge layer, although in different and independent ways. The results of the present work accord with both the predictions and constraints imposed by that physical picture in terms of the direction, magnitude, and functional form of the rate versus $V_S$. If the number of active sites does change after plasma treatment, the effects would act in addition to those that necessarily follow from changes in $V_S$. Because we do not observe significant deviation from the prediction based upon $V_S$, the effects from active site concentration are constrained to be rather small.

Surface treatment did not significantly change the adsorption of MB on the film surface, as shown by the absorbance of MB on the films before and after treatment, shown in Figure 14.

The average absorbances before and after surface treatment were both 0.398 ± 0.011. MB in solution is a cationic dye which adsorbs onto the surface of TiO$_2$ through Coulombic interaction with Ti—O through its cationic functional group.\textsuperscript{20} This is evidenced by the influence of solution pH on the amount of MB adsorbed, which affects the surface charge of TiO$_2$. Relative to the point-of-zero-charge of TiO$_2$ (pH ~6.3), a more acidic solution causes the surface to be more positive while a more alkaline solution causes it to be more negative, described by the ionization state of the surface:

\begin{equation}
\text{TiOH} + H^+ \rightleftharpoons \text{TiOH}_2^+ \tag{6}
\end{equation}

\begin{equation}
\text{TiO} + \text{OH}^- \rightleftharpoons \text{TiO}^– \tag{7}
\end{equation}

It is not surprising then that surface treatment of the films did not affect MB adsorption significantly in solution, because solution pH plays the significant role. The insensitivity of MB adsorption to surface treatment implies that at the very least, MB supply at the anatase surface is not responsible for any change in MB degradation rate.

Rate changes caused by the accumulation of surface carbon species are also unlikely because the use of oxygen plasma treatment for surface cleaning is well-documented\textsuperscript{86,82,83} and degradation rates actually decreased after surface treatment. Contributions from carbonaceous species before and after treatment (Figure 15a,b) reveal no significant changes to the carbon content that could explain the fall in rates after treatment. All these suggest that surface carbon played no part in affecting the rate of MB degradation.

**Band Bending Determination via Work Function.**

Work function measurements from UPS showed shifts in work function values consistent with the binding energy shifts of Ti 2p and O 1s from XPS. The work function of a surface is defined as the energy required to remove an electron from the Fermi level in a material, then it put at rest at an infinite

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**Figure 14.** MB absorbance with treatment time, before and after surface treatment. The lack of a trend indicates that adsorption of MB on the films did not vary significantly with treatment time.

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**Figure 15.** Contributions from carbonaceous species before and after surface treatment. The lack of a trend indicates that adsorption of MB on the films did not vary significantly with treatment time.
distance away from the material (usually tens to hundreds of angstroms would suffice). Its value is therefore indicative of the charge-transfer properties near the surface. The work function of oxide semiconductors involves the following components:\textsuperscript{84}

\[ \Phi_S = \mu + \Phi_{BB} + \chi \]  

where \( \Phi_S \) is the surface work function, \( \mu \) the chemical potential, \( \Phi_{BB} \) the degree of band bending, and \( \chi \) the electron affinity. This relationship is presented in Figure 16. For oxidation and reduction of oxide semiconductors within a single phase regime, changes in the work function are determined by the chemical potential and the degree of band bending while the electron affinity remains constant, giving us

\[ \Delta \Phi_S = \mu + \Delta \Phi_{BB} \]  

At room temperature, work function change is due mainly to the band-bending component, while the change in chemical potential is negligibly small.\textsuperscript{85} As such, we can attribute the change in work function for our thin films after surface treatment to a relaxation in band bending:

\[ \Delta \Phi_S = \Delta \Phi_{BB} \]  

The work function change from UPS and the binding energy change in XPS both give a value of \( \sim 0.4 \) eV. This is consistent with a decrease in O vacancies after surface treatment as the density of surface states correlates positively with the degree of band bending,\textsuperscript{86} whereas for charge equilibrium to occur between the surface and the bulk, less charge transfer is required, resulting in a smaller SCL.

**Correspondence of Photocatalytic Rates with Model.**

A comparison between the changes in initial rate of MB degradation with the model prediction as embodied in eq 2 shows good correspondence, as shown in Figure 17. There are no adjustable parameters in the photocurrent model—the parameters were either measured or estimated. With longer surface treatment times, the rate of MB degradation falls accordingly up to about 35% from before the treatment. Because the primary pathway by which MB is degraded is through oxidation,\textsuperscript{19} our results suggest a diminished ability at the surface to oxidize and degrade MB. This direction of change predicted by the photocurrent model implies a relaxation of the surface band bending caused by a decrease in magnitude of the surface potential. In the present system, we calculate our quantum yield, \( QY \), by considering the initial number of MB molecules degraded per unit time versus the number of holes promoted to the surface per unit time, according to the following equation:

\[ QY = \frac{r_0}{I_{PC}} \]  

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**Figure 15.** (a) C=O to graphitic carbon area ratio and (b) O=O–OH to graphitic carbon area ratio across six samples. No significant changes in the ratios could be perceived before and after surface treatment. It seems that remote oxygen plasma treatment does little to alter the presence of such carbon species. As such, we attribute changes in photoactivity to causes other than the relative amount of such species on the catalyst surface.

**Figure 16.** Band model representing the components which make up the work function of an oxide semiconductor.

**Figure 17.** Comparison between change in initial rate of MB degradation and the change in the photocurrent from the model. The surface potential for the untreated surface (the point furthest to the right) was measured to be 0.5 eV. Horizontal and vertical errors are standard errors of coefficient from regression analysis.
where \( r_0 \) is the initial rate. These calculations yield a value of 0.15\% ± 0.02\% for \( Q_N \), in line with those reported in the literature. Houas et al.\(^9\) reported values of 0.12\% and 0.14\% for 290 and 340 nm light, respectively, for his study on MB degradation, and Matthews reported a value close to 0.1%\(^{24}\).

**CONCLUSION**

The importance of defect engineering in TiO\(_2\) photocatalysis has been recognized for several years,\(^6\) although the early focus was on the concentration of point defects within crystallites. Similarly, the importance of band bending for photocatalysis had been recognized,\(^8,8^8\,8^9\) although the interest has gravitated on the concentration of point defects within crystallites. Similarly, the importance of band bending for photocatalysis was on the concentration of point defects within crystallites. These twin effects act largely independently to vary the width of the SCL, which in turn affects the proportion of photocarriers that are swept to the surface to induce photochemistry. Such principles should work well for thin-film photocatalysts operating in gases or liquids of low ionic strength. In liquids of high ionic strength, it may prove more difficult to maintain control of surface potential via near-surface defects, as the effects of redox couples within the solution may prevail. These concepts must also be modified for isolated photocatalysts whose width is sufficiently small to put the particle center within the nominal width of the SCL, in which case the particle has insufficient bulk to screen its opposing sides from each other (affecting \( V_S \)), imposing a hard constraint on the maximum width of the SCL from which particles can be swept. Future work should focus on widening the window of accessible values for \( N_D \) and \( V_S \) as well as determining the extent to which extrinsic dopants augment or inhibit the effects of native defects examined here.

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**Notes**

The authors declare no competing financial interest.

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