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**Title:** Models for the Photoelectrolytic Decomposition of Water at Semiconducting Oxide Anodes.

**Authors:** J. H. Kowalski, K. H. Johnson, and H. L. Fuller

**Performing Organization:** Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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MODELS FOR THE PHOTOELECTROLYTIC DECOMPOSITION OF WATER
AT SEMICONDUCTING OXIDE ANODES

J. M. Kowalski, K. H. Johnson, and H. L. Tuller
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

ABSTRACT

Surface states at semiconducting TiO₂/electrolyte interfaces are believed to play an important role in charge transfer and thereby the efficiency of photoelectrochemical processes at such interfaces. Theoretical calculations were therefore performed using the SCF-Xα-SW method to determine the position and character of surface states at various characteristic interfaces. At the TiO₂/water interface, antibonding surface states were found which when occupied would explain the experimentally observed dissociation of water into hydroxyl groups at n-type semiconducting TiO₂ surfaces. Similarly, antibonding surface states were found at the TiO₂/OH⁻ interface which when occupied would tend to destabilize the OH bond. A likely mechanism for the dissociation of water and decomposition of certain photoanodes in photoelectrochemical cells based on the above results is presented. The effects of surface reconstruction at heavily reduced TiO₂ surfaces on the validity of our calculations are also discussed.

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INTRODUCTION

The present fuel shortage has stimulated much research concerning the production of hydrogen gas by the photoelectrolysis of water on semiconductor electrode surfaces. To date, only a few semiconducting oxides, including titanium dioxide and some perovskites, have been shown to remain inert in cell operation and decompose water. In all cases surface states at the electrode-electrolyte interface are believed to play an important role in the charge transfer process and thereby the overall efficiency of such cells. (1,2) Little is known, however, concerning the source of these surface states and the manner in which they assist the photoelectrolytic process. In the following, SCF-Xα-SW calculations are presented which serve to clarify some of these issues.

The catalytic behavior of a surface often depends on its ability to interact electronically with the adsorbate. The determination of the electronic structure of the surface perturbed by the chemisorbed species may, therefore, provide a basis for understanding charge transfer catalysis. In order to understand the electronic interaction between water and a TiO₂ surface, cluster molecular-orbital calculations were performed using the Self-Consistent-Field-Xα-Scattered Wave (SCF-Xα-SW) method (3). The SCF-Xα-SW method was chosen over the conventional Hartree-Fock Self-Consistent-Field Linear-Combination-of-Atomic-Orbitals (HF-SCF-LCAO) method since the former is less laborious and costly in computer time and leads to a more reliable description of electronic structure. (3) Molecular orbital methods were chosen over band theory since it offers a more appropriate description of local interactions and chemical bonding. (4) Previous SCF-Xα-SW studies (4) have shown that the local electronic struc-

Key words: Photoelectrolysis, catalysis, titanium dioxide, perovskite titanates
ture of bulk TiO₂ (rutile) can be realistically modelled in terms of a (TiO₆)₈⁻ cluster, yielding results in good agreement with measured photoemission and optical absorption spectra. In the same manner, the chemisorption of H₂O on a titanium dioxide surface can be modelled by the combination of a TiO₂ surface cluster and an adsorbed H₂O molecule. In the remainder of this paper, results for the clean, water-chemisorbed, and OH⁻-chemisorbed surfaces are presented and compared with recently measured photoemission spectra. With these results, a possible mechanism is suggested for the dissociation of water in the photoelectrochemical cell.

RESULTS OF CALCULATIONS

Figure 1a shows the schematic energy level diagram for "bulk" TiO₂ as calculated by the SCF-Xα-SW method along with those for the free oxygen and titanium atoms. Only the Ti3d and O2p levels are shown since they are the only ones involved in bonding on this energy scale. One observes that the titanium 3d level splits into the antibonding ε₉ and ε₂₉ levels which represent the conduction band of bulk TiO₂. The valence band is composed mainly of oxygen bonding and nonbonding 2p character and lies approximately 3eV below the conduction band.

CLEAN SURFACES

The simplest model for the clean (110) titanium dioxide surface is the (TiO₅)₆⁻ cluster which consists of a slightly distorted and truncated octahedron in which a titanium atom is surrounded by five nearest-neighbor oxygen atoms. These slight distortions are ignored in our analysis to simplify calculations. Furthermore, since this is nearly the same local environment of a titanium
atom in the perovskite structure, this cluster also represents the (100) active surface site of SrTiO$_3$. The charge on the cluster is chosen such that the valencies of the atoms sum to zero. This simulates charge transfer with neighboring titanium atoms in the solid.

The calculated energy levels for the (TiO$_5$)$^{6-}$ surface cluster are shown in Figure 1b. Here the 3d levels split further due to the lower symmetry near the surface. Since the cluster method does not correctly treat the Madelung constant, the resultant energy levels are only on a relative scale and must be aligned with the absolute scale. This is usually done by choosing a nonbonding level and aligning it with that of the free atom, since nonbonding levels are not expected to shift much upon bonding. The diagrams are aligned using the O2p nonbonding level, which lies at the top of the valence band.

The splitting of the $t^g_{2g}$ and $e^g$ levels in the surface cluster results in the $d^x_{yz}$ and $d^x_{xz}$ states extending into the energy gap. These band gap surface states are simply due to the truncation of the lattice. In the intrinsic material, only levels to the top of the valence band are filled while these bandgap surface states are empty. If the material is made n-type, however, these surface states become occupied.

Similar calculations were performed for the (TiO$_4$)$^{4-}$ cluster, which represents the oxygen deficient (110) surface. The resultant energy level diagram shown in Figure 1c reveals that the d levels are further split by the reduced symmetry of this surface. A new characteristic surface state, designated by $d^z_{2g}$, is generated at this surface.

SURFACE CLUSTERS WITH CHEMISORBED WATER

To study the interaction of water with a TiO$_2$ surface, calculations for both surface clusters were extended to include a chemisorbed water molecule.
The resultant energy diagrams for both surfaces are largely a superposition of those for the separated clean surfaces and H$_2$O molecule.

The electronic structure of the (TiO$_5$)$^{6-}$H$_2$O cluster is shown in Figure 2, along with that for the clean surface and that for the H$_2$O molecule. The figures are aligned such that the oxygen 2p nonbonding levels coincide, which is the top of the valence band for the surface clusters and the $b_1$ level for the water molecule. The antibonding $a_1^*$ and $b_2^*$ water levels are normally empty and lie about 5eV above the filled $b_1$ level. In the (TiO$_5$)$^{6-}$H$_2$O cluster, the water valence levels are still identifiable (mixing very little with the TiO$_2$ valence band) and are pulled down almost uniformly in energy. The $a_1$ level does, however, shift more to tighter binding energy and bonds more with titanium than the $b_1$ and $b_2$ levels. This suggests that water is chemisorbed onto the surface as an intact molecule and bonds to the surface through the $a_1$ orbital. The antibonding $a_1^*$ and $b_2^*$ water levels are also pulled down in energy but mix more strongly with the TiO$_2$ 3d levels. These states, normally unoccupied in the intrinsic material could however become filled if the material were made n-type by reduction or doping.

Photoemission data of Henrich ($^5$) for water chemisorbed on annealed (110) TiO$_2$ and (100) SrTiO$_3$ surfaces show the H$_2$O levels displaced uniformly about 2eV below the top of the valence band with the $a_1$ orbital shifting more to tighter binding energies, in agreement with our calculations. This suggests non-dissociative water chemisorption on the annealed surface. Our calculations however predict a larger shift for the water levels of about 4eV. This discrepancy may be due to the short bonding distance between the surface and the H$_2$O molecule chosen for the calculation. The bonding distance between the surface titanium atom and the water oxygen atom may very well be greater than
the bulk Ti-O bond length of 1.94 Å chosen. A larger value would have the effect of lowering the attraction between the surface and the water molecule, thereby lessening the perturbation on the H₂O molecule.

Lo, Chung, and Somorjai (2) likewise conclude on the basis of their photoemission studies that water molecules chemisorbed on stoichiometric TiO₂ surfaces remain undissociated. On the other hand, for surfaces reduced by heating to above 800°C or by argon bombardment, they obtained evidence for the existence of dissociated water in the form of hydroxyl groups. We later show that dissociation of water molecules on reduced surfaces of TiO₂ can be explained by considering the destabilizing effects that occupation of the dₜ²₋ₑ₂ antibonding states have on the stability of the H₂O molecule.

SURFACE CLUSTERS WITH ADSORBED OH RADICALS

As a simple model for the TiO₂-electrolyte interface in a photo-electrochemical cell, the (TiO₅)⁶⁻OH⁻ and (TiO₄)⁴⁻OH⁻ clusters were chosen to represent the local electronic interaction between the titanium dioxide surface and basic electrolyte. The resultant energy levels are a superposition of those for the clean surfaces and the OH⁻ ion, with some mixing. The results for the (TiO₅)⁶⁻OH⁻ cluster are shown in Figure (3) along with the energy levels of the OH radical and clean surface cluster. Again the diagrams are aligned at the nonbonding oxygen 2p level, which is the filled π level for the OH⁻ ion. The π and σ OH⁻ levels appear to remain relatively unperturbed upon chemisorption, but the antibonding σ* and π* levels are pulled far down in energy to interact with the TiO₂ d levels resulting in additional surface states within the band gap. In the next section these states will be shown to play a potentially important role in the photoelectrolytic decomposition of water.
DISCUSSION

As a result of our calculations we have been able to predict the relative positions of surface states generated at TiO$_2$-vacuum, -H$_2$O and -OH$^-$ interfaces as well as the character of these states. It should be noted that the absorbate itself has a strong influence on the position, character and number of surface states that exist at a given interface. In the following we consider the consequences that occupation of these surface states have on water dissociation and photoelectrolysis and compare these predictions with experimental evidence.

CLEAN SURFACES

A number of investigators have recently studied the surface electron structure of TiO$_2$ by ultraviolet photoemission spectroscopy (UPS), low-energy-electron diffraction (LEED) and Auger electron spectroscopy (AES). Henrich, et al.\(^6\) observed a UPS peak at about 2.5eV above the bottom of the valence band for annealed TiO$_2$ surfaces which they attributed to surface defect states. This peak increased by more than a factor of 10 under argon-ion bombardment which was shown to result in the formation of Ti$^{3+}$ ions at the surface.\(^6\) Lo, et al.\(^2\) observed similar absorption peaks which were sensitive to annealing and Ar bombardment treatments. Both studies are consistent with our calculations which indicate the existence of normally empty surface states which become occupied upon reduction of the surface resulting in the formation of Ti$^{3+}$ ions. Subsequent exposure of the surface to oxygen results in a sharp decrease in the emission peak indicating a reversible depopulation of the Ti-like surface states.
In investigating the chemisorption of water on variously treated TiO$_2$ surfaces by photoemission (UPS), Lo, et al. (2) discovered that whereas water is adsorbed as an intact molecule on oxidized TiO$_2$ surfaces, it appears to dissociate on reduced surfaces leaving behind (OH) molecules adsorbed on the surface. Henrich, et al. (5) observed similar results for argon bombarded (110) TiO$_2$ surfaces upon exposure of up to 10$^4$ H$_2$O.

Since existence of Ti$^3+$ ions at the surface appears to be critical in determining the manner in which water molecules adsorb on the surface we examine the consequences of surface state occupation on bonding between TiO$_2$ and adsorbed water molecules.

Reduction of the TiO$_2$ surface by argon bombardment or annealing in hydrogen should result in occupation of the d$^*_x$yz-b$^*_z$ levels of the TiO$_2$-OH interface (see Fig. 2). The contour diagrams for these orbitals are shown in Figure 4.

When the d$^*_x$yz and b$^*_z$ orbitals mix, the titanium d lobes and the oxygen 2p lobe (2p$_{yz}$) overlap in a bonding fashion as do the oxygen 2p lobes (2p$_{yz}$) of the lattice and the hydrogen lobe. When the d$^*_x$yz orbital is occupied, as it is in the hydrogenated TiO$_2$ surface with chemisorbed water bonding between the titanium d and oxygen 2p (O$_2$) overlap in a bonding fashion as do the oxygen 2p lobes (O$_2$) of the lattice.

The d$^*_x$yz orbital is antibonding between the titanium d$^*$ and oxygen 2p levels; this is revealed by opposite signs in the overlapping lobes between the titanium and oxygen. In the diagrams, the lobes are shrunk in size and are not shown as overlapping for clarity. The sign inside the lobes represents the phase of the wave-function; overlapping lobes of the same sign signify bonding while overlapping lobes of opposite sign signify antibonding.

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exists for the break-up of chemisorbed water into OH radials on the surface if and only if the surface states with antibonding character are occupied as they are in reduced TiO$_2$. Similar results are also obtained for the (TiO$_4$)$_{4-}$H$_2$O cluster.

**PHOTOELECTROLYTIC DECOMPOSITION OF WATER**

When n-type photoanodes such as TiO$_2$ or SrTiO$_3$ are immersed in liquid electrolytes and are illuminated with band-gap light, oxygen gas (O$_2$) is known to be released. This process of oxygen evolution has been modeled assuming that a Schottky barrier is formed at the solid liquid interface at which electron-hole pairs are formed during illumination. The built-in space-charge field is then believed to cause the photo-generated holes to be swept towards the interface while the electrons are swept away from the interface towards the platinum counter-electrode. The OH$^-$ ions adsorbed at the interface are now believed to lose their electrons to the semiconductor valence band via surface states producing oxygen by the reaction

\[ \text{OH}^- + 2\text{h}^+ \rightarrow \frac{1}{2} \text{O}_2^+ + \text{H}^+ \]

Because the energy of the electrons associated with the OH$^-$ ions (commonly referred to as the OH$^-$/O$_2$ redox level) lie considerably above the semiconductor valence band in energy, direct charge transfer is highly unlikely. The existence of surface states nearly degenerate with the OH$^-$/O$_2$ level would, however, exhibit the high tunneling probabilities necessary for efficient charge transfer across the interface. Although such surface states are believed to play an important role in photoelectrolysis, little is now known concerning their identity.
Examining again the energy levels for the \((\text{TiO}_5)^6-\text{OH}^-\) cluster we find that the states labeled \(d_{xy}^*, d_{yz}^*-\pi^*\) and \(d_{z^2}^*-\sigma^*\) lie within the band-gap. Since the TiO\(_2\) anodes used for photoelectrolysis are n-type with a Fermi level near the bottom of the conduction band, these levels have a high probability of being occupied. Recent surface photocurrent spectroscopy data of Mavroides, et al.\(^1\) for reduced SrTiO\(_3\) operating in an electrolytic cell with basic electrolytic support the occupation of these bandgap surface states.

To explain the observed \(\text{O}_2\) gas released from the semiconductor surface according to the proposed equation above, one must first show a mechanism for splitting the \(\text{O}-\text{H}\) bond in the \(\text{OH}\) radical. In general, bonds are broken by occupying antibonding orbitals or by depopulating bonding orbitals. The \((\text{TiO}_5)^6-\text{OH}^-\) results show the top valence level to be mainly of \(\text{OH}^-\pi\) character. Under illumination in the electrochemical cell, this state would most probably be depopulated. However, since it is a nonbonding \(\text{O}_2\pi\) level, it does not bond with hydrogen so its depopulation would not be expected to destabilize the \(\text{OH}\) bond. On the other hand, the occupation of antibonding orbitals may lead to destabilization of the \(\text{O}-\text{H}\) bond.

If we consider the lowest antibonding orbital, \(d_{xy}^*\), we observe that it does not mix with the \(\text{OH}^-\) orbital due to symmetry conservation and thus contains no \(\text{OH}^-\) character. Similarly, examination of the contour map of the \(d_{yz}^*-\pi^*\) orbital in Figure 5A shows that no \(\text{OH}\) breakup is expected since the \(\pi^*\) orbital contains no \(\text{H}\) bonding.

Occupation of the \(d_{z^2}^*-\sigma^*\) orbital would, however, tend to destabilize the \(\text{O}-\text{H}\) bond since the \(\sigma^*\) orbital is antibonding between the oxygen and hydrogen. Occupation of the \(d_{z^2}^*-\sigma^*\) orbital would also tend to promote bonding between the Ti atom and the oxygen atom of the \(\text{OH}^-\) ion since their wavefunctions are in-phase.
Thus, occupation of the $d_{z^2} - \sigma^*$ orbital would provide a mechanism for breaking the O-H bond, while leaving the O of OH bonded to the surface.

Other antibonding states higher in energy on the $(\text{TiO}_2)_6 - \text{OH}^-$ energy diagram also contain some $\sigma^*$ character, though not as much as the $d_{z^2}^+ - \sigma^*$ level (i.e., less mixing between the $d^*$ and $\sigma^*$ orbitals). For this reason, occupation of the $d_{z^2}^+ - \sigma^*$ orbital is expected to be, in large part, responsible for splitting the O-H bond, although higher states may contribute to some extent.

The contour diagram of the $d_{z^2}^+ - \sigma^*$ orbital (Figure 5B) shows the oxygen atom of the OH radical to be more strongly bonded to the Ti atom than the oxygen atoms of the lattice (which are antibonding with respect to the Ti atom). This suggests that the observed $O_2$ gas released from the oxide surface during photo-electrolysis may originate from the lattice. Oxygen atoms leaving the surface layer would thereby create vacancies which might then be occupied in turn by oxygen ions originating with the adsorbed OH$^-$ ions.

The possibility suggested above that surface oxygen ions may be released preferentially from TiO$_2$ surfaces during illumination, might explain their relative stability to photodecomposition. For non-oxide electrodes, regeneration of the lost surface anions from the adsorbed OH$^-$ ions would not be possible and might therefore explain their propensity to decompose under illumination.

**Extension of Calculations**

The above calculations have been performed using the simplest models possible to represent the ideal clean TiO$_2$ surface interacting with adsorbed species. A major simplification made in our calculations was to assume that the n-type TiO$_2$ and SrTiO$_3$ surfaces differed from the stoichiometric (annealed) surfaces by only the occupation of the bandgap states. Both Henrich, et al. (6) and Lo, et
al.\(^{(2)}\) report, however, that Argon bombarded surfaces and highly reduced (oxygen deficient) surfaces become disordered and show a succession of different surface-defect phases depending on the degree of reduction. In fact, extensive bombardment on the TiO\(_2\) surface results in the formation of a different compound, Ti\(_2\)O\(_3\), on the surface. Similar phenomena are known to occur in bulk TiO\(_2\) upon reduction. A whole range of closely spaced intermediate compounds are formed related to the parent rutile structure by a series of "shear" transformations in which planes of oxygen ions are removed from the lattice resulting in modified Ti-Ti bond lengths and reduced symmetry.\(^{(8)}\)

Such structural transformations are not believed to occur in TiO\(_2\) or the Perovskite titanates made "n-type" by virtue of doping rather than by creation of oxygen deficiency. Consequently, our calculations should be more directly applicable to such surfaces. On the other hand, since similar photoelectrolytic response has been observed for both reduced and doped samples, the implication exists that models presented above are at least qualitatively correct in either case.

Recent studies by Subbarao, et al.\(^{(9)}\) on TiO\(_{2-x}\) and Ti\(_{2-x}\)F\(_{x}\) showed that the fluorine doped TiO\(_2\) exhibited a different spectral response than reduced TiO\(_2\). This difference was characterized by a greater sensitivity to longer wavelengths and generation of higher photocurrent with the fluorine doped material. Similar studies by Kowalski and Tuller\(^{(10)}\) on reduced and Nb doped BaTiO\(_3\) showed the doped material to exhibit much enhanced photocurrents under similar conditions.

The above results are consistent with the expectation that the reduced surfaces will possess surface states with different character and at different energies than the surface states calculated here which are more characteristic of the doped materials. Further work is underway to determine whether surfaces with Ti\(_2\)O\(_3\) character can explain the differences in photoresponse observed for the two types of surfaces.
ACKNOWLEDGEMENT

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REFERENCES


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FIGURE CAPTIONS

1. a) Energy level diagrams of bulk TiO$_2$ and the free titanium and oxygen atoms
   b) Energy levels for the clean (110) TiO$_2$ and (100) SrTiO$_3$ surface modeled by the (TiO$_5$)$_6^-$ cluster or
   c) the (TiO$_4$)$_4^-$ cluster.

2. Calculated energy levels for the (TiO$_5$)$_6^-$, H$_2$O, and (TiO$_5$)$_6^-\text{H}_2\text{O}$ clusters representing the clean TiO$_2$ surface, the water molecule, and the water chemisorbed surface.

3. Calculated energy levels for the clean TiO$_2$ surface, the OH$^-$ ion, and the OH$^-$ chemisorbed surface.

4. Contour diagrams of the $d^\ast_{yz}$ and $b^\ast_2$ antibonding orbitals before mixing in the (TiO$_5$)$_6^-\text{H}_2\text{O}$ cluster.

5. a) Contour diagram of the antibonding $d^\ast_{yz}$ and $\pi^\ast$ orbitals for the (TiO$_5$)$_6^-\text{OH}^-$ cluster.
   b) Contour diagram of the antibonding $d^\ast_{z2}$ and $\sigma^\ast$ orbitals for the (TiO$_5$)$_6^-\text{OH}^-$ cluster.
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\begin{align*}
(TiO_5)^{6-} & \quad OH^- & \quad (TiO_5)^{6-}OH^- \\
"Surface" & \quad \pi^* & \quad \sigma^* \\
& \quad d_{x^2-y^2}^* & \\
& \quad d_{z^2}^* & \\
& \quad d_{xy}^* & \\
& \quad d_{yz}, d_{xz}^* & \\
& \quad \pi & \\
& \quad \sigma & \\
& \quad \sigma(OH^-) & \\
\end{align*}
\]
$d_{yz}^*$

$(\text{TiO}_5)^{6-}$

$b_{2}^*(\pi^*)$

$H_2O$
\( d_{yz}^* \quad \pi^* \quad (\text{TiO}_5)^{6-} \quad \text{OH}^- \)
\[(d_{z^2}^* - \sigma^*)\]

\[(TiO_5)^{6-} OH^-\]