TiO$_2$ Surface Active Sites for Water Splitting

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The mechanism of photoreactivity between the TiO$_2$ surface and H$_2$O, and the related charge transfer, is considered in terms of both collective and local properties. It is shown that the effective charge transfer between TiO$_2$ and water requires the presence of surface active sites that are able to provide electron holes to adsorbed water molecules. Titanium vacancies located at or near the surface are identified as the active sites for water adsorption leading to the formation of an active complex and resulting, in consequence, in water splitting. A model of the photoreactivity between the TiO$_2$ surface and water is proposed. This model indicates that the photoreactivity of the TiO$_2$-based photoelectrode may be enhanced through imposition of the surface active sites (Ti vacancies) in a controlled manner by surface engineering.

1. Introduction

Hydrogen generated from water splitting with solar energy (solar-hydrogen) represents a sustainable fuel that is 100% environmentally safe in the cycles of its generation and utilization.[1] Consequently, solar-hydrogen has the capacity to provide global energy security at potentially (massive production) very low cost.

The most critical issue in solar-hydrogen generation is the development of a high-performance photoelectrode that exhibits the following: high efficiency in the conversion of solar energy into chemical energy (hydrogen) [this may be achieved when the photoelectrode exhibits high photoreactivity with water], resistance to corrosion and photocorrosion is aqueous environment, and low processing costs. There is a growing awareness that titania (TiO$_2$), and TiO$_2$-based oxide systems, best meet the above requirements and, therefore, are the most promising candidates for the development of a photoelectrode for solar-hydrogen generation.[2−5]

The studies on solar-hydrogen are concentrated on the development of photoelectrochemical cells (PECs), which are able to split water by using solar energy.[6] The basic reactions steps involved in photoelectrochemical solar-hydrogen generation, using PECs equipped with a single photoelectrode, are as follows:

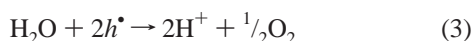1. Photoionization over the band gap

$$h\nu \rightarrow e' + h^\bullet \tag{1}$$

where h is the Planck constant and ν is the light frequency.

2. Charge separation:

$$e' + h^\bullet \rightarrow e'_{bulk} + h^\bullet_{surf} \tag{2}$$

3. Reaction between water and electron holes at the surface of the photoanode:

$$H_2O + 2h^\bullet \rightarrow 2H^+ + {}^1/_2 O_2 \tag{3}$$

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4. Transport of hydrogen ions from the photoanode to the cathode through the liquid electrolyte.

5. Transport of electrons to the cathode through the external circuit.

6. Reaction between electrons and hydrogen ions at the cathode:

$$2e' + 2H^+ \rightarrow H_2 \tag{4}$$

The reaction at the photoanode, expressed by eq 3, is the key reaction of the PEC. Its progress requires efficient charge transfer between the surface of the photoanode and water.

So far, photoreactivity between TiO$_2$ and water, and the related charge transfer, has been considered in terms of collective electrical properties, such as electronic structure and flat band potential, as the driving force for the charge transfer.[6−9] It has also been assumed that the charge transport kinetics within PEC is determined by these collective properties. The present work shows that efficient water decomposition must also be considered in terms of active surface sites available on the surface of the photoelectrode, which enables the formation of an active complex between TiO$_2$ and water leading, subsequently, to effective water splitting into oxygen and hydrogen.

The objective of the present work is to consider the role of both collective and local factors in the photoelectrochemistry of TiO$_2$. The local factor is considered in terms of a photoreactivity model describing the role of Ti vacancies in the formation of the active complex with water.

2. Defect Disorder

TiO$_2$ is a nonstoichiometric compound. Reduced TiO$_2$ exhibits an apparent deficit of oxygen.[10] Therefore, the formula TiO$_{2-x}$ is comonly used. Its defect disorder has been considered in terms of oxygen vacancies and titanium interstitials.[10] These defects lead to the formation of donor levels located in the upper part of the energy band gap as shown in Figure 1.

The principle of lattice charge neutrality requires that the positive charge, resulting from the presence of donor-type defects, is compensated by a negative charge. It has been initially considered that the positive charge related to donors is com-

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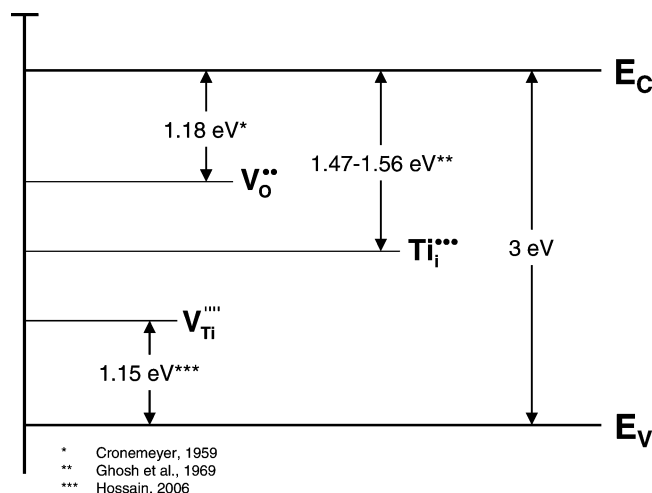*J. Phys. Chem. B, Vol. 110, No. 37, 2006* **18493**

Figure 1. The band model of TiO$_2$ showing the energy levels of point defects.[13−15]

TABLE 1: Ionization Energies of Point Defects and Band Gap for TiO$_2$

species/band gap	ionization energy [eV]	refs
titanium interstitials	1.23−1.56	14, 15
oxygen vacancies		
singly ionized	0.75−0.76	13, 14
doubly ionized	1.17−1.18	14, 15
titanium vacancies	1.15	15
band gap	3.0−3.3	16−21

pensated by acceptor-type impurities.[11] The recent discovery of the formation and transport of titanium vacancies[12] indicates that these defects play a major role in charge compensation. It has been shown that titanium vacancies are the only negative ionic defects in undoped TiO$_2$.[12] Therefore, these defects may be considered in terms of the reactivity between TiO$_2$ and water, which requires acceptor-type active sites.

As seen in Figure 1, both oxygen vacancies and Ti interstitials form donor levels,[13,14] while titanium vacancies form acceptor levels at 1.15 eV above the valence band.[15] The related ionization energies of defects in TiO$_2$ are collected in Table 1.

3. Collective Factor

The driving force for the charge transfer within PECs for solar-hydrogen generation has been generally considered in terms of collective properties of the photoelectrode. These are properties of the entire solid forming the photoelectrode, including the electronic structure and the flat band potential.[6−9] The former determines the amount of the absorbed solar energy that is available for conversion. The latter is required for effective charge separation. In certain cases there is a need to apply an external bias voltage, which is also a collective property. The latter is required for adjusting the energy levels for H$^+$/H$_2$ and O$_2$/H$_2$O with respect to the energy levels of the semiconducting photoelectrodes.

The collective factor in photoelectrochemical generation of solar-hydrogen is schematically represented in Figure 2, showing the charge transfer within a PEC that consists of a TiO$_2$ photoanode and a Pt cathode. Details of its performance were discussed elsewhere.[6]

The collective factor model considers the energy conversion efficiency in terms of collective properties. This model assumes that electron holes, which are formed as a result of photoinduced ionization of TiO$_2$ over the band gap, are available for the reaction with water at any point on the surface. In other words,
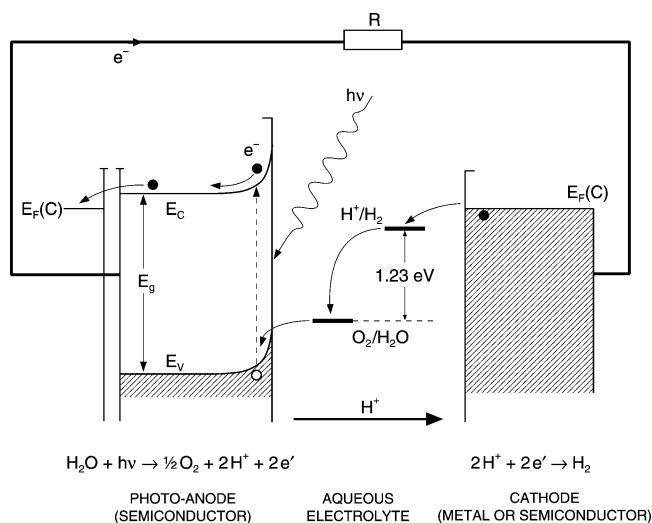

Figure 2. Schematic representation of charge transfer within a photoelectrochemical cell involving a semiconducting photoanode and metal cathode.

the collective property approach does not take into account the local electrostatic interactions at the atomic scale. Consequently, this model ignores the specific surface properties related to the presence of local surface sites formed, for example, by structural surface defects, such as point defects, their local electroactivity, and their effect on the charge transfer.

4. Surface Science Perspective

There has been an accumulation of data on the reactivity between the surface of TiO$_2$ and H$_2$O and O$_2$ molecules that were reported by surface scientists.[22−32] It has been shown that the ideal defect-free surface is not reactive at room temperature.[22−24] Therefore, most of the data reported in the literature consider the reactivity of the defected surface.

Menetrey et al.[25,26] observed that dissociative adsorption of water is the preferred reaction in the presence of oxygen vacancies. The proposed adsorption model considered H$_2$O to dissociate into one OH$^-$ ion that is adsorbed via its O end filling oxygen vacancies, with the remaining H$^+$ ion bonding to a lattice O ion and forming a second type of OH$^-$ species.

Lo et al.[23] claimed that the presence of Ti^{3+} sites on defective surfaces is of particular importance for strong, dissociative adsorption of water. They observed that O$_2$ and H$_2$O adsorption results in reduction of the surface population of Ti^{3+} ions. Lo et al.[23] also indicated that UV illumination results in charge separation leading to the transfer of electrons (in the form of Ti^{+3} species) to the outermost surface layer, while electron holes are located beneath this layer. Consequently, the illumination leads to an increase of surface electronegativity. Such surface exhibits an increased ability to donate electrons, rather that to donate electron holes. This situation, therefore, is not consistent with the present state of understanding that water splitting requires the transfer of electron holes from the TiO$_2$ surface (photoanode) to the adsorbed water species.

Extensive experimental study on the effect of light on the reactivity of TiO$_2$ with oxygen and hydrocarbons has been reported by Bourasseau.[28−32] This study has shown that UV light (in oxygen) leads to a shift of the following reaction to the right:

$$2O^- + h^\bullet \rightleftarrows O_2^- \qquad (5)$$

This shift results in the initial drop of the work function that was monitored in situ during the light-on and light-off regimes.
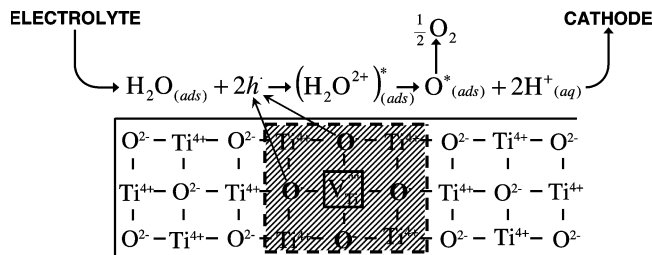
Figure 3. Schematic representation of a model depicting the mechanism of photoreactivity between water molecule and a defect complex at the TiO_2 surface, involving a titanium vacancy and the associated singly ionized oxygen ions, and the related charge transfer.

Therefore, the UV light leads to a decrease in surface population of strongly chemisorbed atomic species O^-, which are converted into weakly adsorbed molecular species.

In summary, the reported data on surface properties of TiO_2 allow the following points to be made: the presence of defects at the TiO_2 surface is essential for its reactivity with H_2O; the oxygen vacancies have been considered as the predominant surface defects; the dark reactivity between defected TiO_2 and H_2O results in the formation of two OH^- species; and the photoreactivity between TiO_2 and H_2O must be considered together along with the photoreactivity between TiO_2 and O_2.

5. Local Factor

The key reaction of photoelectrochemical water splitting, taking place at the photoanode, is represented by eq 3. This reaction requires that an electron hole is effectively transferred to the adsorbed water molecule leading to its splitting. It is clear, however, that efficient charge transfer requires the presence of a strong acceptor site. One should also expect that the mechanism of the reaction represented by eq 3 takes place within several steps and involves the formation of intermediate species. The reaction represented by eq 3 may lead first to the formation of an active complex and, subsequently, result in the restoration of the surface site, which is once again available for adsorption. Identification of such a reaction site is essential for processing photoelectrodes with enhanced photoreactivity.

It has been recently shown that oxidation of TiO_2 leads to the formation of titanium vacancies at the surface and their subsequent transport to the bulk.[12] These defects have not been considered in photoreactivity, so far, because their presence was not evident and not reported. It becomes clear, however, that these defects are the only acceptor-type intrinsic defects in undoped TiO_2, which must be considered as responsible for photoreactivity between TiO_2 and H_2O and the related charge transfer.

The defect disorder model of the TiO_2 surface, involving the titanium vacancies, is shown in Figure 3. This model represents a defect complex involving a titanium vacancy associated with four electron holes that may be either localized or delocalized. This defect complex is the most feasible surface active site that can provide electron holes to water molecules, when they are adsorbed on these sites. The formation of the active complex is, therefore, determined by the charge transfer between the single-valent oxygen ion, associated with the Ti vacancy, and the adsorbed water molecule.

The mechanism of the photoreactivity between the surface of TiO_2 and H_2O may be considered in terms of the following steps:

(1) Adsorption of a water molecule on specific surface active sites comprised of a titanium vacancy (V_{Ti}) and four associated electron holes localized on neighboring oxygen ions, which
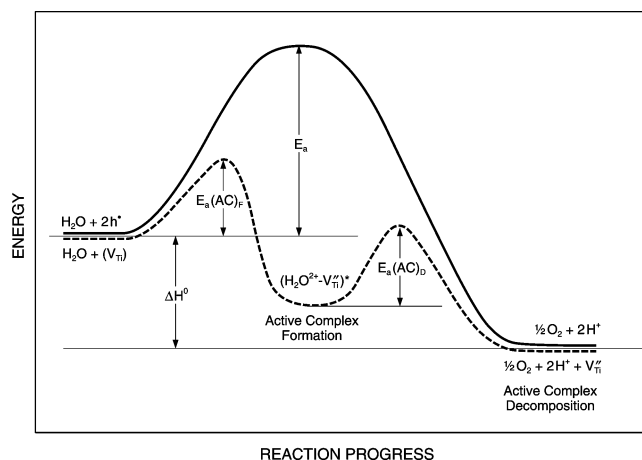

Figure 4. Energy path for photocatalytic water splitting in the presence and absence of surface active sites represented schematically by dashed lines and solid lines, respectively (E_a denotes the activation energy at the absence of the active sites, and $E_a(AC)_F$ and $E_a(AC)_D$ denote the activation energies of the formation of the active complex and its decomposition, respectively).

exhibit strong electron affinity (the ability to donate electron holes):
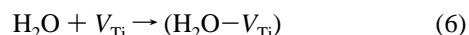
$$H_2O + V_{Ti} \rightarrow (H_2O - V_{Ti}) \qquad (6)$$

where $(H_2O - V_{Ti})$ is a defect complex consisting of a water molecule and a Ti vacancy.

(2) The transfer of electron holes to the adsorbed water species resulting in the formation of a surface-active complex:

$$(H_2O - V_{Ti}) \rightarrow (H_2O^{2+} - V''_{Ti})* \qquad (7)$$
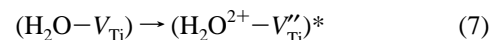
(3) Decomposition of the activated complex into gaseous oxygen and hydrogen ions:

$$(H_2O^{2+} - V''_{Ti})* \rightarrow {}^1/_2 O_2 + 2H^+ + V''_{Ti} \qquad (8)$$
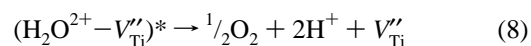
where $(H_2O^{2+} - V''_{Ti})*$ is a metastable surface active complex formed of a water molecule and the Ti vacancy. The transfer of an electron hole, localized on the lattice O^- ions, to the adsorbed water species is represented in Figure 3.

(4) Light-induced ionization over the band gap, leading to the formation of electron−hole pairs, which may be represented by the following reaction:

$$O_O + Ti_{Ti} + h\nu \rightarrow O_O^\bullet + Ti'_{Ti} \qquad (9)$$
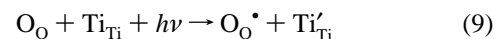
where $O_O^\bullet$ and Ti'_{Ti} are the oxygen O^- and titanium Ti^{3+} ions, respectively, at their correct lattice positions (Kroger−Vink notation).

(5) Reactivation of the surface sites:

$$2O_O^\bullet + V''_{Ti} \rightarrow 2O_O + V_{Ti} \qquad (10)$$
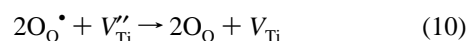
A schematic representation of the mechanism of water splitting (i) according to reactions represented by eqs 6−10 and (ii) defect-free surface is shown in Figure 4 by dashed and solid lines, respectively. The outstanding electron affinity of titanium vacancies has been confirmed by preliminary studies of the interaction energy of a water molecule with different surface sites of rutile, using the ab initio density functional theory. These calculations indicate that the adsorption energy of water on

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oxygen vacancies, Ti interstitials, and Ti vacancies is 105, 320, and 509 kJ/mol, respectively.[33]

It should be noted that none of the preceding studies have considered Ti vacancies as candidates for surface-active sites able to form active complexes with water. The reason for this is that, until now, there has been no evidence for their formation. The recent work shows that these vacancies form at the O_2/ TiO_2 interface almost instantly.[12] However, their transport toward the bulk is extremely slow, leading, in consequence, to the formation of a concentration gradient and a related electrical potential gradient.[34] One should expect that this gradient has an effect on the flat band potential.[1,6] Consequently, the flat band potential is not a specific property of TiO_2 but should be considered as a variable property that depends on the experimental procedure.

6. Conclusions

The mechanism of the photoreactivity of TiO_2 with H_2O should be considered in terms of both the local and collective factors.

Collective Factor. This factor considers the collective properties, such as electronic structure, flat band potential, and bias voltage, as the driving force for charge transfer. The consideration of the collective properties explains the direction of the charge transport within the PEC. This factor, however, is not sufficient to explain the local mechanism of the charge transfer at the electrode/electrolyte interface and its effect on the kinetics of the photoelectrode processes.

Local Factor. This factor considers the local surface active sites that are required for efficient charge transfer within a PEC. It is postulated that the preferred surface active sites, able to provide electron holes to water molecules, leading to their effective splitting, are the defect complexes consisting of titanium vacancies and associated electron holes. The proposed reactivity model indicates the critical role of Ti vacancies in the decomposition of H_2O on the TiO_2 surface. The population of the surface active sites formed by Ti vacancies depends on the TiO_2 processing procedure and, especially, on the oxygen activity in the gas phase during processing or subsequent annealing.

References and Notes

(1) Nowotny, J.; Sorrell, C. C.; Sheppard, L. R.; Bak, T. *Int. J. Hydrogen Energy* **2005**, *30*, 521.
(2) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
(3) Fujishima, A.; Kohayakawa, K.; Honda, K. *J. Electrochem. Soc.* **1975**, *122*, 1487.
(4) Nozik, A. J. *Nature* **1075**, *257*, 383.
(5) Khan, S. U. M.; Al-Shahry, M.; Ingler, W. B. *Science* **2002**, *297*, 2243.
(6) Bak, T.; Nowotny, J.; Rekas, M.; Sorrell, C. C. *Int. J. Hydrogen Energy* **2002**, *27*, 991.
(7) Maruska, H. P.; Gosh, A. K. *Solar Energy* **1978**, *20*, 443.
(8) Gerischer, H. In *Solar Energy Conversion*; Seraphin, B. O., Ed.; Elsevier: Amsterdam, The Netherlands, 1979; pp 115−172.
(9) Chandra, S. In *Photo-Electrochemical Solar Cells*; Gordon and Breach: New York, 1985; pp 98−102 and 163−169.
(10) Kofstad, P. *Nonstoichiometry, Electrical Conductivity and Diffusion in Binary Metal Oxides*; Wiley: New York, 1972.
(11) Balachndran, U.; Eror, N. G. *J. Mater. Sci.* **1988**, *23*, 2676.
(12) Nowotny, M. K.; Bak, T.; Nowotny, J.; Sorrell, C. C. *Phys. Stat. Solidi B* **2005**, *242*, R88.
(13) Cronemeyer, D. C. *Phys. Rev.* **1959**, *113*, 1222.
(14) Ghosh, A. K.; Wakim, F. G.; Addiss, R. R., Jr. *Phys. Rev.* **1969**, *184*, 979.
(15) Hossain, F. M.; Murch, G. E. Sheppard, L. R.; Nowotny, J. Defect Diffusion Data. Submitted for publication.
(16) Cronemeyer, D. C. *Phys. Rev.* **1952**, *87*, 876.
(17) Rudolph, J. *Z. Naturforsch.* **1959**, *14a*, 727.
(18) Frova, A.; Boddy, P. J.; Chen, Y. S. *Phys. Rev. Lett.* **1967**, *157*, 700.
(19) Vos, K.; Krusemeyer, H. J. *Solid State Commun.* **1974**, *15*, 949.
(20) Baumard, J. F.; Tani, E. *J. Chem. Phys.* **1977**, *67*, 857.
(21) Bak, T.; Burg, T.; Kang, S.-J. L.; Nowotny, J.; Rekas, M.; Sorrell, C. C.; Vance, E. R.; Yamawaki, M.; Yoshida, Y. *J. Phys. Chem. Solids* **2003**, *64*, 1089.
(22) Henrich, V.; Cox, P. A. *The Surface Science of Metal Oxides*; University Press: Cambridge, UK, 1994; pp 321−326.
(23) Lo, W. J.; Chung, Y. W.; Samorjai, G. A. *Surf. Sci.* **1978**, *71*, 199.
(24) Henderson, M. A. *Surf. Sci.* **1996**, *355*, 151.
(25) Menterey, M.; Markovits, A.; Minot, C. *Surf. Sci.* **2003**, *524*, 49.
(26) Calatayud, M.; Markovits, A.; Menterey, M.; Mguig, M.; Minot, C. *Catal. Today* **2003**, *85*, 125.
(27) Bourasseau, S. Ph.D. Thesis, Variation du Travail d'Extraction Thermoelectrique du Dioxyde de Titane Pulveruent, Soumis a un Rayonnement Ultraviolet. L'Universite Claude Bernard-Lyon, 1973.
(28) Bourasseau, S. *J. Chim. Phys.* **1973**, *70*, 1467.
(29) Bourasseau, S. *J. Chim. Phys.* **1973**, *70*, 1472.
(30) Bourasseau, S. *J. Chim. Phys.* **1974**, *71*, 122.
(31) Bourasseau, S. *J. Chim. Phys.* **1974**, *71*, 1018.
(32) Bourasseau, S. *J. Chim. Phys.* **1974**, *71*, 1025.
(33) Hossain, F. M. Unpublished data.
(34) Adamczyk, A.; Nowotny, J. *J. Phys. Chem. Solids* **1986**, *47*, 11.