Photochemistry on TiO$_2$ Semiconductor Surfaces

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Electrochemical Photolysis of Water at a Semiconductor Electrode

Although the possibility of water photolysis has been investigated by many workers, a useful method has only now been developed. Because water is transparent to visible light it cannot be decomposed directly, but only by radiation with wavelengths shorter than 190 nm (ref. 1).

For electrochemical decomposition of water, a potential difference of more than 1.23 V is necessary between one electrode, at which the anodic processes occur, and the other, where cathodic reactions take place. This potential difference is equivalent to the energy of radiation with a wavelength of approximately 1,000 nm. Therefore, if the energy of light is used effectively in an electrochemical system, it should be possible to decompose water with visible light. Here we describe a novel type of photo-electrochemical cell which decomposes water in this way.

Electrolysis of water can occur even without applying electric power if one of the following three conditions is fulfilled. First, oxygen evolution occurs at a potential more negative than that at which hydrogen evolution occurs in normal conditions; second, hydrogen evolution occurs at a potential more positive than that at which oxygen evolution occurs in normal conditions; third, the potential for oxygen evolution is made more negative and that for hydrogen evolution is made more positive, until the former is more negative than the latter.

Current–voltage curves of a semiconductor n-type TiO₂

Upon UV excitation, both electrons and holes are photochemically active towards adsorbates on the TiO$_2$ surface.
SCHEMATIC PHOTO-EXCITATION IN A SOLID FOLLOWED BY DE-EXCITATION EVENTS

Surface Recombination

Volume Recombination

A
B
C
D

A-
D+

hν

CB
VB

++
-
Motivation? TiO$_2$ Based Photocatalytic Technology Works!

TiO$_2$ Based Systems are Efficient Photocatalysts

Taken from: Fujishima, Hashimoto, Watanabe, “TiO$_2$-Photocatalysis, Fundamentals and Applications”, BKC Inc. Tokyo, 1999
**TiO$_2$ as a Photochemical Substrate**

**STRUCTURE OF RUTILE AND ANATASE TiO$_2$**

- **Rutile**
  - $d_{\text{eq}}^{\text{Ti-O}} = 1.949$ Å
  - $d_{\text{AP}}^{\text{Ti-O}} = 1.980$ Å
  - $a = 4.593$ Å
  - $c = 2.959$ Å
  - $E_g = 3.1$ eV
  - $\rho = 4.250$ g/cm$^3$
  - $\Delta G_f^0 = -212.6$ kcal/mole

- **Anatase**
  - $d_{\text{eq}}^{\text{Ti-O}} = 1.934$ Å
  - $d_{\text{AP}}^{\text{Ti-O}} = 1.980$ Å
  - $a = 3.784$ Å
  - $c = 9.515$ Å
  - $E_g = 3.3$ eV
  - $\rho = 3.894$ g/cm$^3$
  - $\Delta G_f^0 = -211.4$ kcal/mole

**TiO$_2$ (110) - DEFECT SITES**

- Single Bridging Vacancy
- Double Bridging Vacancy
- Lattice Vacancy
Atomic Structure of TiO$_2$(110) Surface

The surface density of oxygen vacancy sites is regulated by annealing conditions (time, presence of O$_2$)

TiO$_2$(110)-(1x1) surface without oxygen vacancies is stochiometric (TiO$_2$)

Heating TiO$_2$ above $\sim$ 700 – 800 K $\rightarrow$ O-vacancy defects (reduced TiO$_2$)
He Ion Scattering Spectroscopy – Detects $^{18}\text{O}_2$ on Vacancy Defect Sites

$^{18}\text{O}_2$ on Vacancy Defect Sites

$\sim 8\%$ defects in surface adsorb $^{18}\text{O}_2$

• TiO$_2$ Photochemistry – Useful for Removal of Organics by Sequence of Reaction Events

\[ \text{CH}_3\text{OH} \xrightarrow{h\nu} \text{H}_2\text{C}=\text{O} \xrightarrow{O_2 + h} \text{H-COOH} \xrightarrow{O_2 + h} \text{CO}_2 + \text{H}_2\text{O} \]

• Sequence of complex organic oxidation reactions makes the study of photophysics difficult

• \[ h\nu + \text{TiO}_2 \xrightarrow{h + e} \]

\[ \text{O}_2^{-}(\text{a}) + h \xrightarrow{\text{TiO}_2} \text{O}_2(\text{g}) \]
Detailed Studies of $\text{O}_2$ Photodesorption from TiO$_2$(110)

- Providing insight into the mechanisms of photon-induced electron-hole pair production and the activation of adsorbed molecules by these charge carriers.
Mechanism for Oxygen Photodesorption from TiO$_2$(110)

\[
O_{\text{VAC}} + O_2 \rightarrow O_2^-
\]


\[
h^+ + O_2^- \rightarrow O_2
\]

O$_2$ Photodesorption from TiO$_2$(110)

O₂ Photodesorption from TiO₂(110):

\[ k_1 F_{hv} \]

\[ hν + TiO_2 \rightarrow e + h \]

\[ k_2 \]

\[ h + T \rightarrow T^+ \] (hole capture by a hole trap)

\[ k_3 \]

\[ e + h \rightarrow \text{heat} \] (on recombination sites)

\[ k_4 \]

\[ h + O_2^-(a) \rightarrow O_2(g) \]

Rate of photodesorbing oxygen scales proportionally with the square root of the incident light intensity:

\[
\frac{d[\theta_{O_2}]}{dt} = -k_4 \left( \frac{k_1}{k_2 + k_3} \right)^{1/2} F_{hv}^{1/2} \theta_{O_2}
\]
$h\nu = 3.4 \pm 0.05 \text{ eV}$

$T = 110 \text{ K}$

$F_{hv} = 4.08 \times 10^{14} \text{ cm}^2 \text{ s}^{-1}$

$Y_{(O2)}^0$ (Amps x $10^{-9}$)

$Y_{(O2)}^0$ vs Flux$_{hv}^{1/2}$ (photons$^{1/2}$ cm$^{-1}$ sec$^{-1/2}$)

$\nu = 3.4 \pm 0.05 \text{ eV}$

$T = 110 \text{ K}$
Bulk Hole Trapping Sites Within TiO$_2$

After hole trap filling, $k_2$ ceases to contribute to the charge exchange process.

Hole trap centers (T) and average range of photogenerated holes which will be trapped.
Careful studies of hole trapping enhancement by added CH$_3$OH have been made.

FEATUER ARTICLE

Monitoring Hole Trapping in Photoexcited TiO$_2$(110) Using a Surface Photoreaction

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The hole-induced photodesorption of chemisorbed O$_2$ from a TiO$_2$(110) single crystal has been employed to monitor the kinetics of electron—hole pair ($e^-$—$h^+$) formation and hole trapping. Excitation is produced by 3.4 ± 0.05 eV photons at 110 K. Two separate O$_2$ desorption processes have been found which are characteristic of low photon fluxes and high photon fluxes. At a critical photon flux, $F_{\text{in}}$(crit), the slow O$_2$ photodesorption process suddenly converts to a fast process, signaling the saturation of hole traps in the TiO$_2$ crystal. Consequently, this allows photogenerated holes to more efficiently reach the surface, causing more rapid O$_2$ photodesorption. The estimated bulk concentration of hole traps is approximately $2.5 \times 10^{18}$ cm$^{-3}$, involving a fraction of about $3 \times 10^{-5}$ of the atomic sites in the bulk. Both the slow and fast O$_2$ photodesorption processes are described by a rate law that is proportional to $F_{\text{in}}^{1/2}$, indicating that the steady-state concentration of holes, [h], is governed by second-order $e^-$—$h^+$ pair recombination kinetics. Effective use is made of a hole scavenger molecule, adsorbed methanol (CH$_3$OH), to probe the role of added hole traps on the rate of the photodesorption of adsorbed O$_2$ molecules and on the magnitude of $F_{\text{in}}$(crit).
Summary

• Charge carrier dynamics monitored by quantitatively studying a simple model photoreaction – O$_2$ photodesorption.

• F$_{hv}$ rate law found – caused by second-order e-h recombination kinetics.

• Artificial enhancement of hole trapping by adding CH$_3$OH – a hole trap molecule.
$^{18}\text{O}_2$ Photodesorption from TiO$_2$(110)

$F_{hv} = 4.08 \times 10^{14}$ photons cm$^{-2}$s$^{-1}$

$E_{hv} = 3.4 \pm 0.05$ eV

$T = 110$ K
Kinetics of Hole Trapping-As Studied by O$_2$ Photodesorption

- Holes are either partially filled or completely filled by the time the first point is measured [in $\Delta t$ (sampling)].
- $\Delta t$ (sampling) = 0.10 seconds
- Therefore, at $F_{hv}(\text{crit.})$:
  - $0.10 \text{ s} \times F_{hv}(\text{critical}) = \# \text{ photons needed to saturate holes in photon penetration depth.}$
  - Photon penetration depth = $\approx 100\text{Å} \times 10^{-8}\text{cm} \text{ Å}^{-1} = 10^{-6}\text{ cm}$
  - Therefore, density of traps = $\approx F_{hv}(\text{crit}) \times \Delta t \ / 10^{-6}\text{ cm} = \approx 3 \times 10^{18}\text{ cm}^{-3}$
Conclusion- O$_2$ Photodesorption Detector of Hole Trapping Phenomenon

- First highly-controlled study of charge carrier trapping effect on TiO$_2$ single crystal.

- Hole trapping strongly inhibits surface photoreaction.

- Hole trap density estimated to be $\sim$3x10$^{18}$cm$^{-3}$.

- This hole trap density corresponds to $\sim$3x10$^{-5}$ fraction of atomic sites in the crystal bulk.
A Recent Development - Explanation of UV-Induced TiO$_2$ Hydrophilicity
“Light-Induced Amphiphilic Surfaces”

Rong Wang, Kazuhito Hashimoto, Akira Fujishima, Makota Chikuni, Eiichi Kojima, Atsushi Kitamura, Mitsuhide Shimohigoshi, Toshiya Watanabe


**TiO₂ - UV-induced Hydrophilicity - Applications**

**Anti-fogging**

60% of Toyota automobiles already use this technology today.

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Taken from: Fujishima, Hashimoto, Watanabe, “TiO₂-Photocatalysis, Fundamentals and Applications”, BKC Inc. Tokyo, 1999

Taken from: Hata, Kai, Yamanaka, Oosaki, Hirota, Yamazaki, JSAE Review 21, 97-102, 2000
SUNCLEAN SELF-CLEANING GLASS BY PPG IS DESIGNED TO...
MAKE YOUR LIFE EASIER.
Liquid-Solid Contact Angle Measurements

As $\gamma_{SL}$ increases, $\theta$ decreases
Apparatus for H$_2$O Contact Angle Measurements on TiO$_2$(110)

a. High Pressure Wetting Chamber
   - UV-Lamp
   - Syringe
   - Contact Angle Camera
   - Window
   - Sample with H$_2$O-droplet
   - Admission of H$_2$O vapor, O$_2$ or Ar
   - Vacuum Pumps
   - Differentially Pumped Triple Seal
   - LEED Optics
   - Auger Spectrometer
   - Ion Gun

b. TiO$_2$(110) Crystal Mount
   - Stainless steel tube
   - Copper block
   - Thermocouple wires
   - TiO$_2$ crystal
   - Cryo reservoir
   - Tungsten rod
   - Tungsten wire
   - Tantalum clip
   - Tantalum plate
This technology allows study of contact angle for pure H₂O under conditions of:

- well controlled initial surface cleanliness
- well controlled atmosphere
- well controlled photon flux
Typical H$_2$O Contact Angle Showing Sudden Onset of Wetting of TiO$_2$(110)

$P_{O_2} = 1$ atm; hexane = 120 ppm

0 s

154 s

155 s
Hexane Vapor Effect on the UV-Induced Wetting of TiO$_2$(110)

T = 297-302 K
P$_{O_2}$ = 1 atm

$P_{hv} = 1.1 \times 10^{17}$ photons cm$^{-2}$s$^{-1}$ (2.1-4.4 eV)

$P_{hv} = 0.049$ W cm$^{-2}$

$	heta_C$, Contact Angle (degrees)

0 ppm hexane
120 ppm hexane
360 ppm hexane

Region of uncertainty
Schematic Origin of Wetting Delay Period

Hexane Coverage

Induction Periods

100 ppm C\textsubscript{6}H\textsubscript{14}

200 ppm C\textsubscript{6}H\textsubscript{14}

300 ppm C\textsubscript{6}H\textsubscript{14}

O\textsubscript{2} and C\textsubscript{6}H\textsubscript{14}

TiO\textsubscript{2}
Hexane Effect on the Wetting Delay of UV-Induced Wetting of TiO$_2$(110)

$P_O = 1$ atm
$T = 297-302$ K
$F_{hv} = 1.1 \times 10^{17}$ photons cm$^{-2}$ s$^{-1}$ (2.1-4.4 eV)
$P_{hv} = 0.049$ W cm$^{-2}$
Sudden Hydrophilic Effect due to Hydrocarbon Photooxidation on TiO$_2$

$O_2 + C_6H_{14}$ → $H_2O$

Initial non-wetting $C_6H_{14}(a)$

$ hv = 2.1 - 4.4 \text{ eV} $

Critical point just before wetting

Sudden droplet wetting
Conclusions

- Hydrophilicity model involving hydrocarbon photooxidation to produce clean wettable TiO$_2$ is likely to be true.

  - Induction period scales with ppm concentration of hexane in O$_2$.


Photochemistry on semiconductors occurs by e-h pair production in the substrate, accompanied by charge transfer to adsorbed species.

Defect sites are important,
- On surface for adsorption of molecules.
- In bulk-promoting charge-carrier recombination.

Second-order e-h recombination can give $F^{1/2}_{h\nu}$ dependence of photochemical kinetics.

Hole traps reduce photochemical efficiency.

Hydrophilicity induced by UV on TiO$_2$ - caused by photooxidation of organic layers in equilibrium with hydrocarbons in atmosphere, causing cleanup of TiO$_2$ surfaces.
## Acknowledgements

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