Advanced Course in Photocatalytic Reaction Chemistry

understanding chemistry by understanding photocatalysis
understanding photocatalysis by understanding chemistry

Division of Environmental Material Science, Graduate School of Environmental Science
The first semester of Fiscal 2014
08:45—10:15, Thursday at Lecture Room D103

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<< objectives >>
Understanding the mechanism of decomposition of pollutants, methods of photocatalysts preparation, design of practical photocatalytic reaction systems, and strategy for enhancement of photocatalytic activity.

<< goal >>
To understand principle of photocatalytic reaction from the standpoint of chemistry and strategy for practical applications. To obtain scientific method for research on functional solid materials.

<< keywords >>
Photocatalyst, Photoinduced oxidative decomposition, Superhydrophilicity, Excited electron-positive hole, Structure-activity correlation, Higher photocatalytic activity, Visible-light response
<table>
<thead>
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<th></th>
<th>Date</th>
<th>Topic</th>
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<td>introduction of photocatalysis</td>
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<td>2</td>
<td>April 17</td>
<td>interaction between substances and light</td>
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<td>3</td>
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<td>electronic structure and photoabsorption</td>
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<td>4</td>
<td>May 1</td>
<td>thermodynamics: electron and positive hole</td>
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<td>adsorption</td>
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<td>May 15</td>
<td>Kinetic analysis of photocatalysis (Professor Ewa Kowalska)</td>
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<td>May 22</td>
<td>Kinetic analysis of photocatalysis</td>
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<td>11</td>
<td>June 19</td>
<td>Kinetic analysis (Professor Mai Takase)</td>
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<td>12</td>
<td>June 26</td>
<td>action spectrum analysis (1)</td>
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<td>13</td>
<td>July 3</td>
<td>action spectrum analysis (2)</td>
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<td>14</td>
<td>July 10</td>
<td>crystal structure of titania</td>
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<td>15</td>
<td>July 17</td>
<td>design and development of photocatalysts</td>
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<td></td>
<td>July 24</td>
<td>deadline for submission of special report</td>
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</tbody>
</table>
comments on this lecture

Please send email in Japanese or English within 48 hours

to: ohtani@cat.hokudai.ac.jp
subject: pc2014MMDD-XXXXXXXX
body:

(full name)
(nickname)
(comments and/or questions on today's lecture)
principle of photocatalytic reaction

electronic structure of semiconductors and insulators
conduction and valence bands separated by bandgap
photoexcitation beyond the bandgap

1) photoexcitation
   = electron and hole
2) relaxation
3a) reduction & oxidation
3b) recombination
Q: Draw photoabsorption spectrum of chlorophyll.

- electronic absorption spectrum = UV-Vis: extent of photoabsorption is plotted against wavelength
- hint: wavelengths of red and blue lights are 650 nm and 450 nm.
- chlorophyll c
interaction between light and substance

- electronic/vibrational/rotational energies are "quantized", i.e. discrete level of energy
- energy gap: energy difference between the levels
- Only light of energy which is the same as energy gap is absorbed.
- photoabsorption = excited state
- Excited state must release the energy to go back to ground state.
photoabsorption = excitation

excitation from ground state to excited state
excited state: first, second, third ...
difference in energy = energy gap
excitation = supplying energy to excite
Heat (energy) is too small to excite.
Photons have enough energy for various modes of excitation.
Q: What is "Boltzmann distribution"?

Energy distribution: occupied state/unoccupied state
Boltzmann distribution: occupied/unoccupied balance depending on the energy gap between them

\[
\frac{N_{\text{unoccupied}}}{N_{\text{occupied}}} \propto e^{-\frac{\Delta E}{k_B T}}
\]

\(\Delta E\) energy difference between unoccupied and occupied states
\(k_B\) Boltzmann constant = gas constant \((R)\) divided by Avogadro's number \((N_A)\).
\(T\) absolute temperature
Q: What is "Boltzmann distribution"?

Energy distribution: occupied states
Boltzmann distribution: occupied/unoccupied balance depending on the energy gap between them

\[ \frac{N_{\text{unoccupied}}}{N_{\text{occupied}}} \propto \exp(-\frac{\Delta E}{k_B T}) \]

- \( \Delta E \) energy difference between unoccupied and occupied states
- \( k_B \) Boltzmann constant = gas constant \((R)\) divided by Avogadro's number \((N_A)\).
- \( T \) absolute temperature

- Large energy gap = higher distribution in the lower state
- Due to the smaller heat energy at room temperature, all the electronic and vibrational states are of ground state.
distribution of excited state

for state-to-state excitation
  source: ground state (must exist = occupied)
  destination: excited state (must be vacant = unoccupied)

probability of excited state
  • electronic excitation (ultraviolet/visible): ?
  • vibrational excitation (infrared): ?
  • rotational excitation (microwave): ?

\[
\frac{N_{\text{unoccupied}}}{N_{\text{occupied}}} \propto \exp\left(-\frac{\Delta E}{k_B T}\right)
\]

\[k_B T \text{ (at 300 K)} = 4.14 \times 10^{-21}\text{J}\]
energy of a photon

assuming
ultraviolet/visible: $4.14 \times 10^{-19}$
infrared: $4.14 \times 10^{-20}$
microwave: $4.14 \times 10^{-24}$

ca. $10^{-23} \sim 24 \text{ J}$
ca. $10^{-19} \sim 21 \text{ J}$
ca. $10^{-18} \sim 19 \text{ J}$
distribution of excited state

for state-to-state excitation
  source: ground state (must exist = occupied)
  destination: excited state (must be vacant = unoccupied)

probability of excited state
  • electronic excitation (ultraviolet/visible): $e^{-2} [0.13]$
  • vibrational excitation (infrared): $e^{1} [2.7]$
  • rotational excitation (microwave): $e^{3} [20]$

\[
\frac{N_{\text{unoccupied}}}{N_{\text{occupied}}} \propto \exp\left(-\frac{\Delta E}{k_B T}\right)
\]

$k_B T$ (at 300 K) = $4.14 \times 10^{-21}$J
photoabsorption spectrum

electronic excitation: a sharp line should appear

Q Why a broad absorption is observed?

accompanying vibrational and rotational states
Semiconductors and insulators have similar electronic structure. Electronic conductivity of semiconductors lies between those of conductors and insulators, due to impurities and narrow band gaps.
All the electrons in any level of valence band can be excited to any level in conduction band, giving wide range of photoabsorption.
absorption edge wavelength

absorption edge: corresponding to band gap
apparently the edge is not SHARP due to distribution of "density of states"

DOS in the bands are not homogeneously distributed

negligible DOS at the edges = less photoabsorption

DOS
Density Of States
electron-hole and relaxation

- **photoexcitation**: excited electron \((e^-)\) in a conduction band (CB) and positive hole \((h^+)\) in a valence band (VB)
- **relaxation**: \(e^-\) at the bottom of CB and \(h^+\) at the top of VB
- levels of energy of relaxed \(e^-\) and \(h^+\) not depending on the irradiation wavelength
relaxation and recombination

femtosecond pump-probe photoabsorption spectroscopy

relaxation < 1 ps
band position

- photoexcited electron = bottom of conduction band (CB)
- positive hole = top of valence band (VB)

How the positions of CB and VB are controlled?

- band position
- thermodynamics
- water photolysis
electronic structure of anatase and rutile

<table>
<thead>
<tr>
<th></th>
<th>anatase</th>
<th>rutile</th>
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</thead>
<tbody>
<tr>
<td>conduction band</td>
<td>(-0.20 V)</td>
<td>(+0.04 V)</td>
</tr>
<tr>
<td>valence band</td>
<td></td>
<td></td>
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</tbody>
</table>

potential vs. NHE at pH = 0

-0.05 V ($O_2^+/O_2$)
0 V ($H_2/H^+$)
0.79 V (Ag/Ag$^+$)
1.23 V ($H_2O/O_2$)

flat-band potential = conduction band bottom

band gap = distance between CB and VB

correlation between band gap and CB position

Fig. 3. Measured flat band potentials and effective band gaps in semi-conducting oxides. ●, oxides without partly-filled d-levels; ▲, oxides with partly-filled d-levels; ■, oxides formed anodically on metals.

band structure of metal oxides and sulfides

TiO₂
conduction band (mainly orbital of titanium)

WO₃
level of oxygen reduction

valence band (mainly orbital of oxygen)
doped nitrogen/sulfur orbitals

metal oxide

valence band (mainly orbital of sulfur)
conduction band (mainly orbital of metal)

metal sulfide

level of hydrogen production

level of oxygen reduction
band position

- photoexcited electron = bottom of conduction band (CB)
- positive hole = top of valence band (VB)

How the positions of CB and VB are controlled?

- band position
- thermodynamics
- water photolysis
thermodynamics and kinetics

thermodynamics = equilibrium:
considering the (chemical) energies of SOURCE and PRODUCT(S)
without any information on the mechanism

kinetics:
velocity of reaction to reach an equilibrium

Gibbs energy ($\Delta G$)
activation energy ($E_a$)

Show $\Delta G$ and $E_a$ in this illustration
thermodynamics and kinetics

thermodynamics = equilibrium:
considering the (chemical) energies of SOURCE and PRODUCT(S)
without any information on the mechanism

kinetics:
velocity of reaction to reach an equilibrium

Gibbs energy ($\Delta G$)
activation energy ($E_a$)

\[ \Delta G < 0 \]
\[ E_a < E'_a \]
Gibbs energy change

both reaction, reduction by $e^-$ and oxidation by $h^+$, can be spontaneous, considering independently

Photocatalyst can drive reaction of $\Delta G > 0$. 

![Diagram showing the energy bands and electron/hole movement during photoabsorption](image-url)
necessary conditions for photocatalysis

Electrode potential of substrate to be reduced must be more anodic compared with the bottom of conduction band of photocatalysts.

Electrode potential of substrate to be oxidized must be more cathodic compared with the top of valence band of photocatalysts.

charge separation = Reactions by photoexcited electrons and positive holes occur separately.
band position

- photoexcited electron = bottom of conduction band (CB)
- positive hole = top of valence band (VB)

How the positions of CB and VB are controlled?

- band position
- thermodynamics
- water photolysis
photosynthesis

Solar energy is stored as chemicals.
photocatalytic decomposition of water

hydrogen production from water by solar light
low-cost material may be used as a photocatalyst
### History of Photocatalytic Water Splitting

<table>
<thead>
<tr>
<th>Year</th>
<th>Description</th>
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<tbody>
<tr>
<td>1969</td>
<td>TiO$_2$ photoelectrode (Fujishima and Honda)</td>
</tr>
<tr>
<td>1980</td>
<td>TiO$_2$ particles (Sato)</td>
</tr>
<tr>
<td></td>
<td>SrTiO$_3$ particles (Domen et al.)</td>
</tr>
<tr>
<td>1990</td>
<td>Mixed metal oxides</td>
</tr>
<tr>
<td></td>
<td>K$_4$Nb$<em>6$O$</em>{17}$ (Domen et al.)</td>
</tr>
<tr>
<td></td>
<td>Na$_2$Ti$<em>6$O$</em>{13}$ (Inoue et al.)</td>
</tr>
<tr>
<td>1998</td>
<td>NaTaO$_3$ (quantum efficiency 50%/Kudo et al.)</td>
</tr>
<tr>
<td>2001</td>
<td>Two-step visible-light photolysis with iodide mediator (Abe et al.)</td>
</tr>
<tr>
<td>2004</td>
<td>One-step visible-light photolysis by GaN:ZnO solid solution (Domen et al.)</td>
</tr>
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</table>
hydrogen evolution by GaN:ZnO photocatalyst

Domen's group
(The University of Tokyo)
Comments on this lecture

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  nickname
  comments on this lecture
  question(s)

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太谷文章
某教授
きょうははじめて光触媒について詳しく知りました。光触媒ということばは知っていました
が、実際に応用されている例がたくさんあることに驚きました。光触媒の実際の寿命はど	
れくらいですか。
「光触媒のしくみがわかる本」を1冊購入します。

JPY1,200 (77%)  JPY3,500 (79%)