SEMICONDUCTORS AS CATALYSTS FOR WATER SPLITTING

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OUTLINE

• Introduction and history of the discovery of semiconductor photocatalysts
• Photocatalytic water splitting
• Semiconductors as photocatalysts and their properties
• Electrochemistry of semiconductors
• Photo electrochemical system
• Photocatalytic particles in suspension
• Enhancement of photocatalytic activity of semiconductors
• Summary
INTRODUCTION

• Hydrogen is the cleanest, sustainable and renewable energy carrier as well as an essential raw material in many chemical industries.

• Mainly produced by steam reforming the hydrocarbons.

• If one consider the energy and the environmental issues, it must be produced from water using renewable energy sources such as solar light.

• Photocatalytic water splitting is one of the candidates for solar hydrogen production.
History of the discovery of Photocatalytic materials

Dr. Akira Fujishima

Dr. Kenichi Honda

1971
Photocatalysis

A conventional redox reaction
The redox couple: both oxidation and reduction simultaneously

Application to the improvement of living environment such as anti-stain, self cleaning, super hydrophyllicity properties

Light energy conversion as represented by water splitting

- TiO₂ based photocatalysts are widely used
- Perfect catalyst is still challenging
WATER SPLITTING

• Using standard conditions water can reversibly electrolyze at a potential of 1.23 eV, a value derived from the relationship

\[ \Delta G^0 = -nF \Delta E^0 \]

• The overall reaction

\[ H_2O + h\nu = H_2 + \frac{1}{2}O_2 \]

Endothermic reaction

A two electron process with a Gibbs free energy change of 2.46eV - So electrochemical decomposition of water is possible when the cell emf is greater than or equal to 1.23eV
Concepts - why semiconductors are chosen as photocatalysts?

- For conventional redox reaction one is interested in either reduction or oxidation.
- But for water splitting, both the reactions should be carried out simultaneously.

Reduction of hydrogen ions: \[ 2H^+ + 2e^- \rightarrow H_2 \]

Oxygen evolution from hydroxyl ions: \[ 2OH^- + 2h^+ \rightarrow H_2O + \frac{1}{2}O_2 \]

- Band gap is important.
Metals: No band gap, Only reduction or oxidation, Depends on the band position
Insulators: High band gap
So high energy is required to create the appropriate excitons for promoting both of the reactions.

Semiconductor is the best selection
OVERALL WATER SPLITTING

\[ \text{H}_2\text{O} \xrightarrow{\text{hv}} \text{H}_2 + \frac{1}{2}\text{O}_2 \]

\[ \text{O}_2/\text{H}_2\text{O} \xrightarrow{1.23 \text{ V}} \text{H}^+/\text{H}_2 \]

- CB
- VB
- band gap
- h^+
- e^-
- Active sites

V/NHE

0
+1.0
+2.0
+3.0
General properties of semiconductors

Chemical properties -

Semiconductors with high ionicity are stable against corrosion and passivation

Optical properties-

Threshold behavior is extremely important in photo electrochemistry

✓ Materials with band gap 1.1-1.7 eV are the best absorbers for solar energy conversion devices

✓ Visible light absorption is the most desirable property

Depth of light absorption in semiconductors

- Absorbance and transmittance of a material is given by Beer’s law

\[ A = \ln \frac{I}{I_0} = \alpha l \quad T = \frac{I}{I_0} = \exp(-\alpha l) \]

Optical path length \( l \), \( I, I_0 \) – transmitted and incident light intensity. \( \alpha \)- absorption coefficient

- Direct band gap semiconductors have large absorption coefficient \( (10^4 - 10^5 \text{ cm}^{-1}) \)

\[ \alpha = \frac{A(h\nu - E_g)^m}{h\nu} \]

Here \( m \) is a constant which depends on the optical transition, \( m=2 \) for an indirect band gap semiconductor and \( \frac{1}{2} \) for a direct band gap semiconductor.
Carrier statistics

✓ Intrinsic carrier concentration in semiconductors is low

\[ n_i p_i \propto \exp\left(-\frac{E_g}{kT}\right) \]

Doping

✓ increases the conductivity and able to control other electronic properties
✓ Crystal defects can also behave as dopants
✓ Conductivity can be controlled by doping

\[ \sigma = qn\mu_n + qp\mu_p \]

Fermilevel

✓ Analogy to the Nernst equations-Fermi level of a semiconductor phase

\[ E_F = E_{Fi} - kT \ln(n / N_C) \]
\[ E_F = E_{Fi} + kT \ln(p / N_V) \]

By doping electrical conductivity and Fermi level can be controlled!!
PRINCIPLE OF WATER SPLITTING ON SEMICONDUCTOR PHOTOCATALYSIS

Processes for photocatalytic reaction in electrode system

Processes for photocatalytic reaction in powdered system
ELECTROCHEMISTRY OF SEMICONDUCTORS

• Band bending!!!

Concept of space charge region

Electrochemical potential difference - charge movement

n- type semiconductor – upward bending of the band

Metal oxide

\[ V_{fb} = E_0 - \chi + \frac{1}{2} E_G \]

\( \chi \) Mulliken electronegativity

\( E_0 \) free energy of electron in H\(_2\) redox scale

Flat band potential must exceed the proton reduction potential

0.0 V at pH=0 and -0.41 t pH=7
Effect of varying the applied potential (E) on the band edges in the interior of an n type semiconductor

- Magnitude and direction of the band bending varies with the applied potential (E).
- **E > E_{fb}**: Accumulation region.
- **E = E_{fb}**: Space charge region.
- **E < E_{fb}**: Solution region.
Effect of varying the applied potential (E) on the band edges in the interior of a p-type semiconductor

- **Accumulation**
  - $E_C$<br>$E_V$<br>$E_F$

- **Space charge region**
  - $E_C$<br>$E_V$<br>$E_F$

- $E > E_{fb}$
- $E = E_{fb}$
- $E < E_{fb}$
The charge transfer abilities of a semiconductor electrode depends on whether there is an accumulation or depletion layer.

If there is an accumulation layer – behaves as metallic electrode-since excess of majority charge carriers available for charge transfer.

If there is a depletion layer - there are few charge carriers available and the electron transfer reaction occur slowly.

However if the electrode is exposed to radiation of sufficient energy electron hole pairs are produced.

If the process occurs within the interior of the semiconductor – recombination-heat.

If it occur in the space charge region, the electric field in this region will cause the separation of the charge.
SEMICONDUCTORS AS PHOTO ANODE IN THE PHOTO ELECTROCHEMICAL CELL (PEC) PRODUCTION OF HYDROGEN

Electrical wire

4 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 2 \text{H}_2 + 4 \text{OH}^- \quad (4.0 \text{ eV})

4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \quad (1.23 \text{ eV})

Overall reaction:

2 \text{H}_2\text{O} + \text{light} \rightarrow 2 \text{H}_2 + \text{O}_2

Electron energy

Semiconductor

Water

Metal electrode
• Width of the depletion layer $W$ depends on donor concentration and the applied potential:

$$W = \left( \frac{2\varepsilon_0\varepsilon_r}{eN_D} \right)^{\frac{1}{2}} \left( V - V_{fb} - \frac{kT}{e} \right)^{\frac{1}{2}}$$

where $N_D$ is the Donor concentration, $V$ is the Applied potential, and $V_{fb}$ is the flat band potential.

• The flat band potential relates to the pH as

$$V_{fb} = V_{fb}^{PZC} + \frac{2.3RT}{F} (PZC - pH)$$

At room temperature, $V_{fb}$ changes with $-59$ mV per unit of pH.
The overall solar–to-hydrogen conversion efficiency of the device can be determined from the electrical characteristics of the device

\[ \eta_{STH} = \frac{j(V_{\text{redox}} - V_B)}{P_{\text{light}}} \]

- \( P_{\text{light}} \) Incident light intensity (W/m\(^2\))
- \( V_B \) Photocurrent density (A/m\(^2\))
- \( V_B \) Bias voltage

Activity of catalyst - rate of evolved gas per catalyst amount

Apparent quantum efficiency \( QE = 2[H_2] / I \)
SUITABLE PHOTO ELECTRODE MATERIALS IN PEC

- Required criteria's!
  - Sufficiently high (visible) light absorption
  - High stability in dark and under illumination (no photo corrosion)
  - Suitable band edge positions to enable the reduction/oxidation of water by the photo generated holes /electrons
  - Efficient charge transport in the semiconductor
  - Low over potentials for the reduction/oxidation reaction (high catalytic activity)
Light absorption

The spectral region depends on the band gap of the semiconductor. Minimum band gap $-1.23 \, \text{eV} + (\text{Thermodynamic losses} \approx 0.4 \, \text{eV}) + \text{Overpotentials required to ensure the fast reaction kinetics} \approx 0.3-0.4 \, \text{eV})$. So at least $1.19 \, \text{eV}$, which corresponds to a wavelength of $650 \, \text{nm}$. Below $400 \, \text{nm}$ the intensity of sunlight falls rapidly, imposing an upper limit $\approx 3.1 \, \text{eV}$. Hence the optimum value of the band gap should be somewhere between $1.9-3.1 \, \text{eV}$, which is in the visible range of the solar spectra!
Stability against photo corrosion

Most important property which limits the usefulness of many photo active materials

Many non oxide semiconductors (Si, Ga As, GaP, etc) either dissolve or form a thin oxide film which prevents the electron transfer across the interface

Almost all M-O photo anodes are thermodynamically unstable!

Eg; TiO$_2$ and SnO$_2$ show excellent stability over a wide range of pH and applied potential

ZnO always decomposes, Fe$_2$O$_3$ shows an intermediate case (pH and oxygen stochiometry)
- Percentage ionic character of some semiconductors

<table>
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<tr>
<th>Semiconductor</th>
<th>M-O</th>
<th>Percentage ionic character</th>
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<tbody>
<tr>
<td>TiO₂</td>
<td>Ti-O</td>
<td>59.5</td>
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<tr>
<td>SrTiO₃</td>
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<td>Cd-S</td>
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<tr>
<td>Bi₂O₃</td>
<td>Bi-O</td>
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</tbody>
</table>

Percentage ionic character

$$\frac{-(\chi_A-\chi_B)^2}{(1-e^{-\frac{4}{4}})} \times 100$$

Most of these have bond character 50-60% and modulating them will only lead to increased ionic character!!

20-30% ionic character with suitable band positions are suggested.
Requirement of band positions

• Conduction and valence band edges should straddle the reduction and oxidation potential of water

Specifically $E_C$ should be above $E_{\text{RED}}$ and $E_V$ should be below $E_{\text{OX}}$
Charge transport

The exciton life time is a very important criteria

- The hole transfer across the n type semi conductor-electrolyte interface
- Should be fast enough 1) to compete with photocorrosion 2) to avoid accumulation

Catalytically active surface species can be added
Usually metals or hole trapping agents
Photocatalytic particle in suspension

- Most straightforward approach towards solar water splitting
- Oxidation and reduction takes place at the surface of the same particle

ACTIVITY = \([H_2]\]
QE = 2 \([H_2] / I\)

Driving force to separate is ELECTRIC FIELD AT INTERFACE SC/L
• To enhance the kinetics and to avoid recombination of $\text{H}_2$ and $\text{O}_2$ co catalysts, co-catalysts can be used.

The presence of sacrificial electron donor or acceptor ensure the stoichiometric conception of electrons or holes.

All metal sulfides including CdS and ZnS undergo photo chemical decomposition in the absence of sacrificial electron donors.
More aspects

The overall QE for interfacial charge transfer is determined by two critical processes:

- Competition between charge carrier recombination and trapping
  - Picoseconds – nanoseconds

- Competition between trapped carrier recombination and interfacial charge transfer
  - Microseconds - milliseconds

An increase in either the recombination lifetime or interfacial charge transfer rate constant is expected to result in higher efficiencies.

Enhancement of photocatalytic activity

- Loading of metals like Cu, Ag, Au, Ni, Pd, Rh and Pt over a variety of metal oxide semiconductors results efficient charge separation!
- Pt is well known as an excellent co catalyst for hydrogen evolution
- The addition of carbonated salts or other electron mediators enhance the hydrogen production by preventing backward reaction

Mixed metals oxide semiconductors
- NiO over SrTiO$_3$ – NiO(H$_2$), SrTiO$_3$ (O$_2$)
  - RuO$_2$ over TiO$_2$ -30 times bigger activity than TiO$_2$ alone
- But if the concentration of RuO$_2$ exceeds a limit- act as electron hole recombination centers !!!
- In the presence of co -catalysts such as NiO –highly active niobates, titanates and tandalates are reported (NiO/NaTaO$_3$)
Visible light activity

- There are methods by which photocatalysts can be fabricated, by which they respond in the visible light
  - Valence band formation using elements other than oxygen
    [BiVO$_4$, AgNbO$_3$, Ag$_3$VO$_4$, Ca$_2$Bi$_2$O$_4$ .......
  - Ion doping

**Cation doping** - transition metals (V, Cr, Fe, Mo, Ru, Os, Re, Rh, V, etc.)
  - rare earth metals
  doped ion create new (impurity) energy levels.
  metal ion dopants act as electron or hole traps
Anion doping

- Doping of anions such as N, F, C, Si in metal oxides or mixed metal oxides can shift in photo response into the visible region

  ➢ little tendency to form recombination centers - remarkable thing

Z-scheme construction

Dual semiconductor system

Dye-sensitization

Dye molecules absorb light with the transfer of an electron from the ground state to excited state. The excited electron goes to the conduction band of an appropriate metal oxide
SUMMARY

- Optimum value of band gap is 1.9-3.1 eV
- Band edges should straddle the oxidation and reduction potential of H₂O
- Photocatalyst should be stable against photo corrosion
- Metal oxide semiconductors with moderate ionicity are suggested
- Lifetime of the excitons should be high
- Cocatalyst is needed in most of the cases
THANKS FOR YOUR KIND ATTENTION