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 hydro- carbons.

- 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

1971

Dr. Akira **Fujishima**

Dr. Kenichi **Honda**

Photocatalysis

Photocatalysis $\xrightarrow{\text{catalyst}}$ reaction assisted by photons

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 hydrophylicity properties

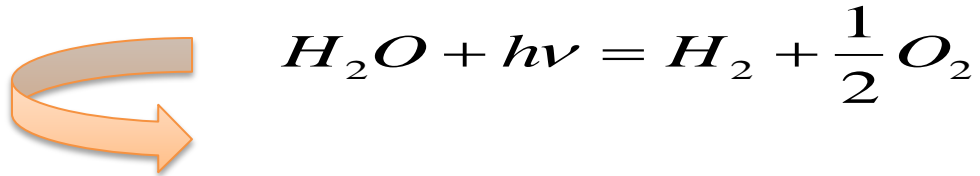Light energy conversion as represented by water splitting

- TiO_2 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
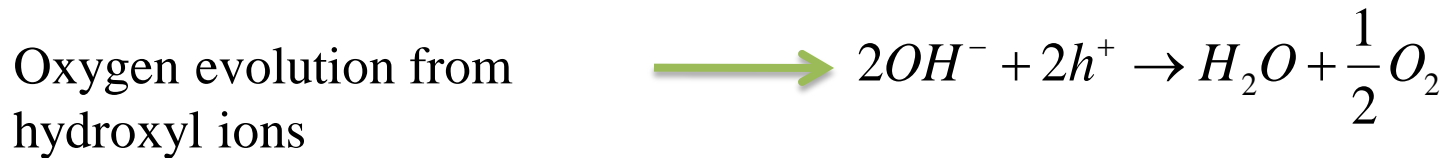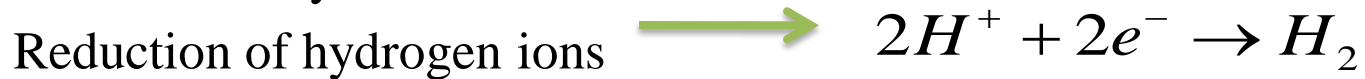
$$H_2O + h\nu = H_2 + \frac{1}{2}O_2$$

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

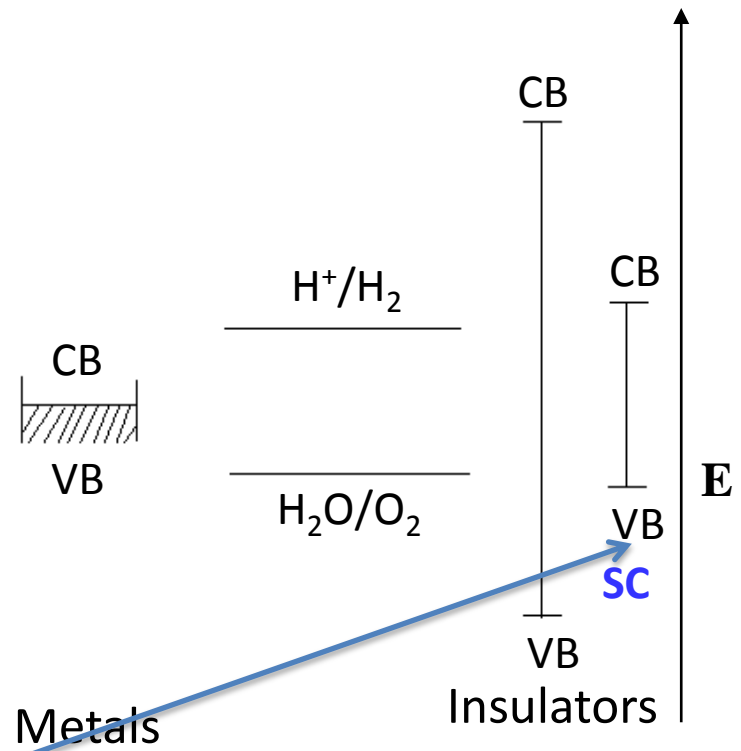# Concepts -why semiconductors are chosen as photocatalysts ?

- 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 $\longrightarrow$ $2H^+ + 2e^- \rightarrow H_2$

Oxygen evolution from hydroxyl ions $\longrightarrow$ $2OH^- + 2h^+ \rightarrow H_2O + \dfrac{1}{2}O_2$
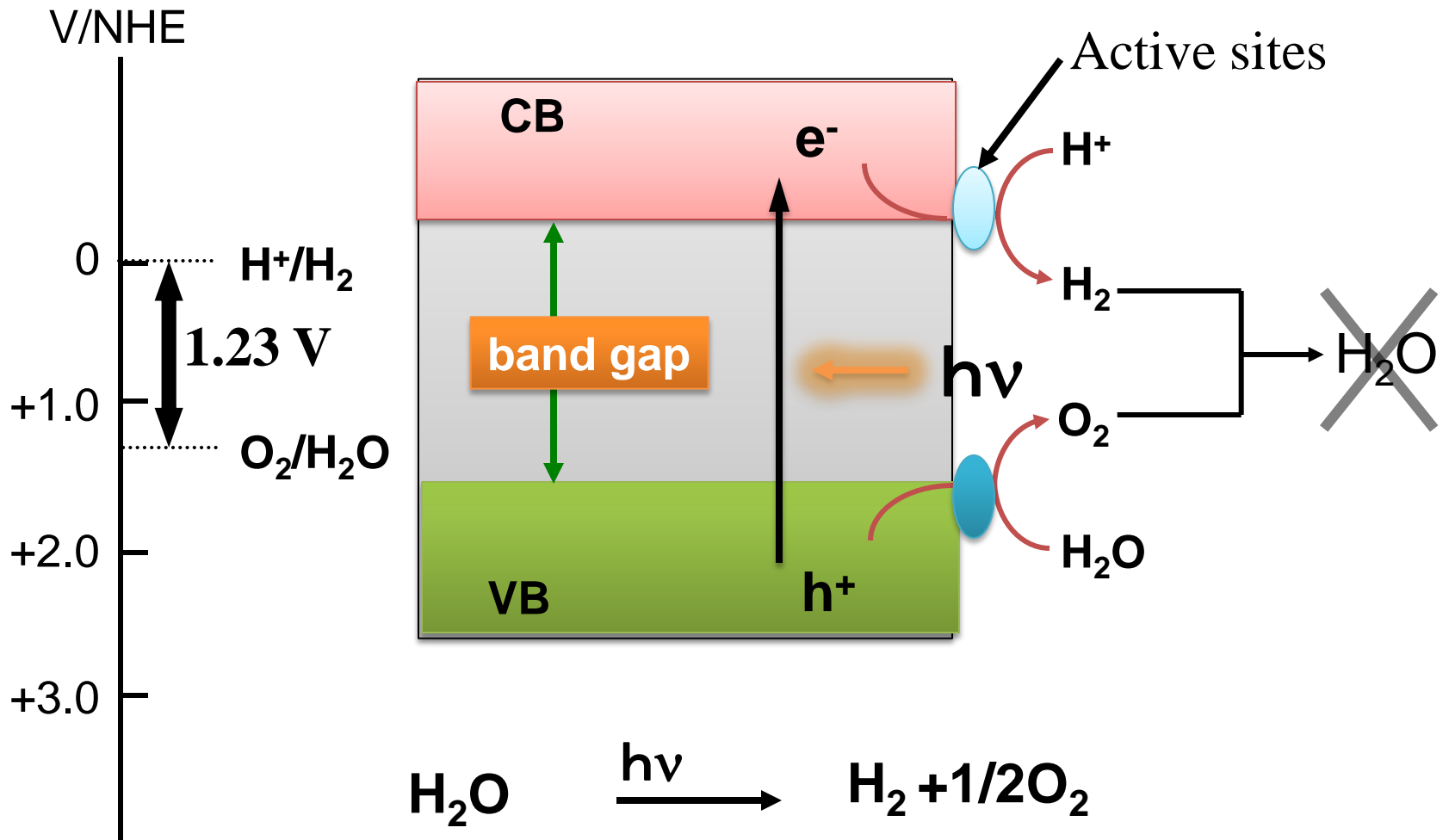
- Band gap is important.

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.

CB

CB

H⁺/H₂ — H^+/H_2

CB

VB

H₂O/O₂ — H_2O/O_2

VB

SC

E

VB

Metals

Insulators

Semiconductor is the best selection

OVERALL WATER SPLITTING

V/NHE

0 — H⁺/H₂

1.23 V

+1.0 — O₂/H₂O

+2.0

+3.0

CB

e⁻

band gap

hν

VB

h⁺

Active sites

H⁺

H₂

O₂

H₂O

H₂O

$H_2O \xrightarrow{h\nu} H_2 + 1/2 O_2$

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

Ref: C H Henry, *J. Appl. Phys*. ,51, 4494 (1980)
    : W. Shockley and H J Queisser, J. Appl.Phys. , 32, 510 (1981)

Depth of light absorption in semiconductors

✓ Absorbance and transmittance of a material is given by Beer's law

$$A = \ln \frac{I}{I_0} = \alpha l \qquad\qquad T = \frac{I}{I_0} = \exp(-\alpha l)$$

Optical path length I, I_0 – transmitted and incident light intensity. α- absorption coefficient

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

$$\alpha = \frac{A(h\upsilon - E_g)^m}{h\nu}$$

Here m is a constant which depends on the optical transition, m=2 for an indirect band gap semi conductor and ½ for a direct band gap semi conductor.

Carrier statistics

✓ Intrinsic carrier concentration in semiconductors is low

$$n_i p_i \propto \exp(-\frac{E_g}{kT})$$

Doping

✓ increases the conductivity and able to control other electronic properties
✓ Crystal defects can also behaves as dopants
✓ Conductivity can be controlled by doping
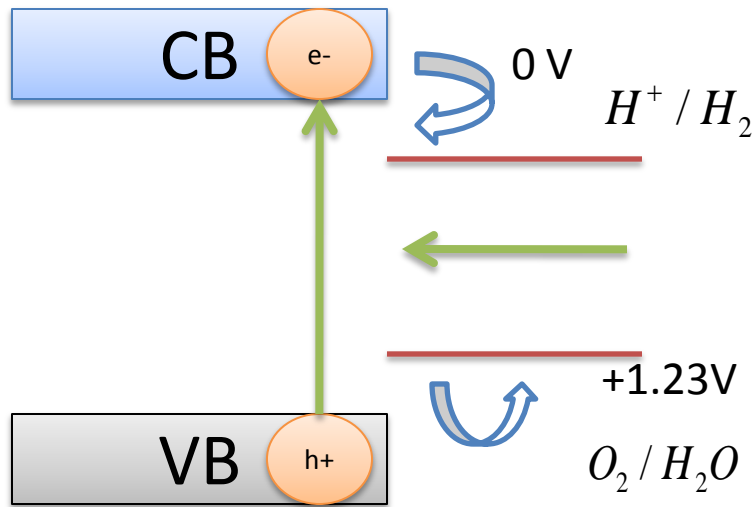
$$\sigma = qn\mu_n + qp\mu_p$$

Fermilevel

✓ Analogy to the Nernst equations-Fermi level of a semiconductor phase
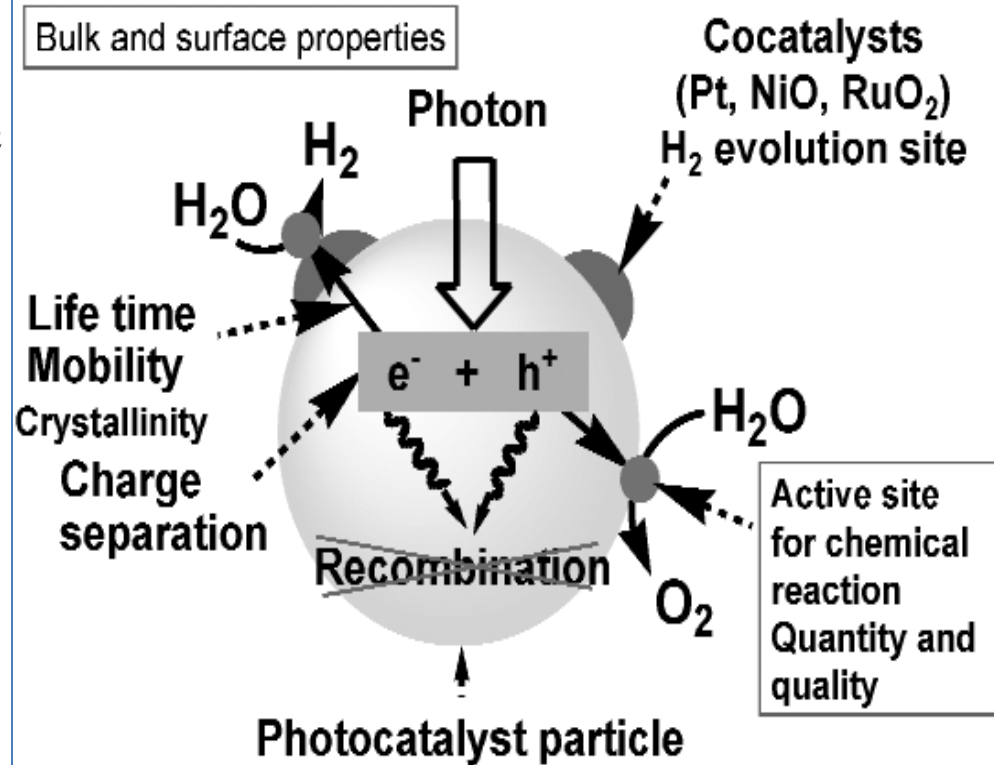
$$E_F = E_{Fi} - kT \ln(n / N_C)$$
$$E_F = E_{Fi} + kT \ln(p / N_V)$$

By doping electrical conductivity and Fermi level can be controlled !!

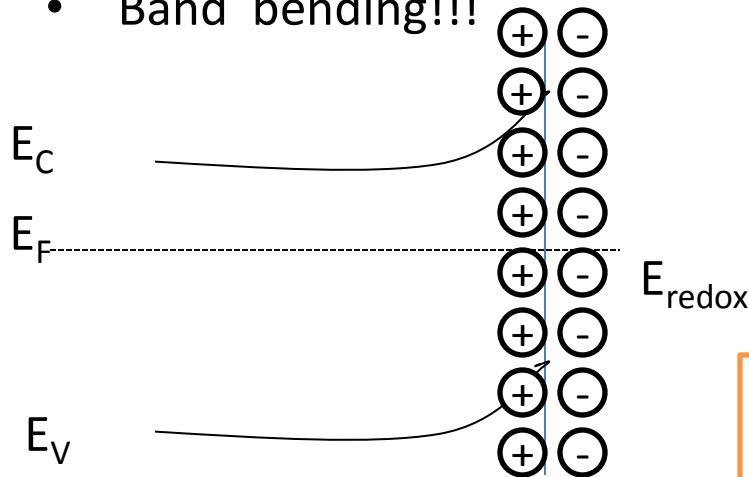# PRINCIPLE OF WATER SPLITTING ON SEMICONDUCTOR PHOTOCATALYSIS

Processes for photocatalytic reaction in electrode system

Processes for photocatalytic reaction in powdered system

ELECTROCHEMISTRY OF SEMICONDUCTORS

- Band bending!!!

E_C

E_F

E_V

E_{redox}

Concept of space charge region

Electrochemical potential difference - charge movement

n- type semiconductor – upward bending of the band

Metal oxide

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

Flat band potential- no band bending
For highly doped semiconductors, this equals the bottom of the conduction band
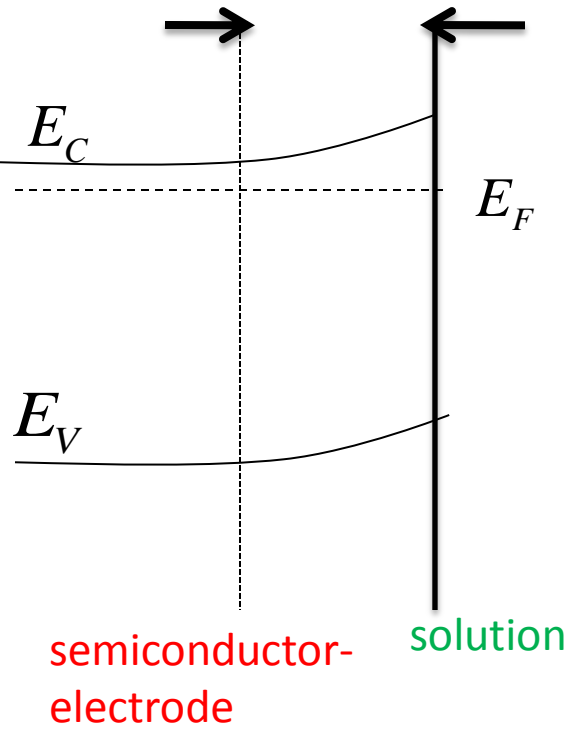
χ Mulliken electronegativity

E_0 free energy of electron in H_2 redox scale

Flat band potential must exceed the proton reduction potential
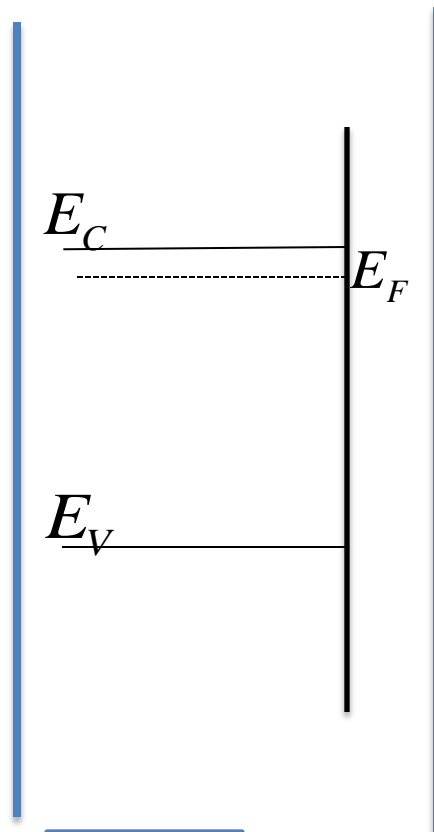
0.0 V at pH=0 and -0.41 t pH=7

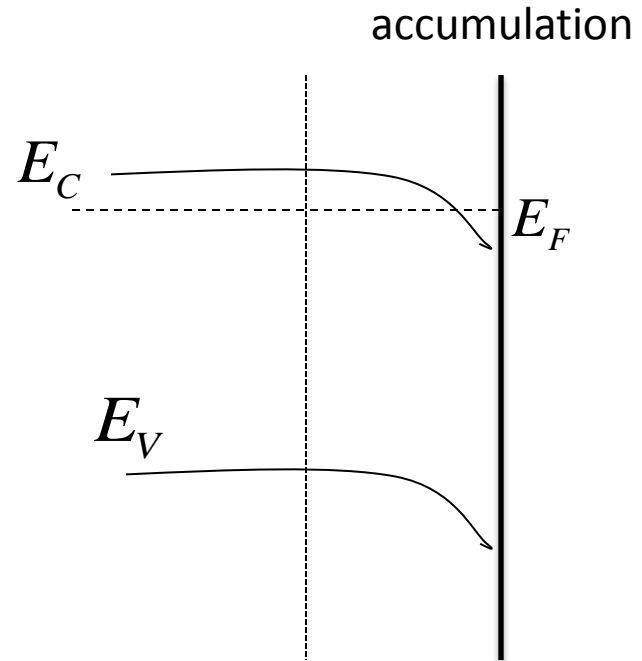Magnitude and direction of the band bending, varies with the applied potential

Space charge region

accumulation

E_C

E_F

E_V

E_C

E_F

E_V

E_C

E_F

E_V

semiconductor-electrode
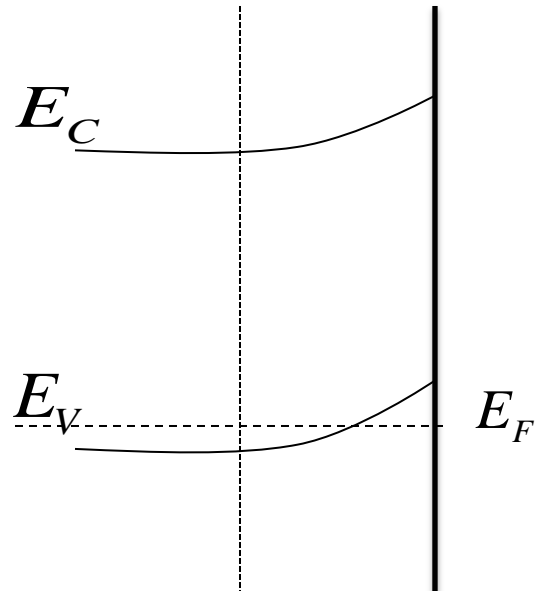
solution

E > E$_{fb}$

E = E$_{fb}$

E < E$_{fb}$

Effect of varying the applied potential (E) on the band edges in the interior of an n type semiconductor

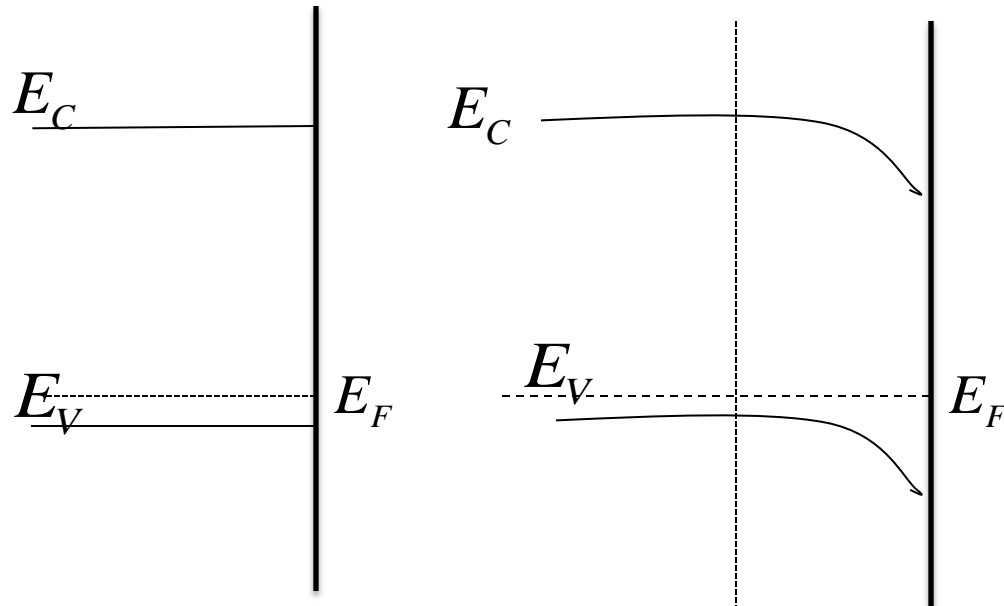Effect of varying the applied potential (E) on the band edges in the interior of a
p- type semiconductor

accumulation

Space charge region

E_C

E_C

E_C

E_V E_F

E_V E_F

E_V 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
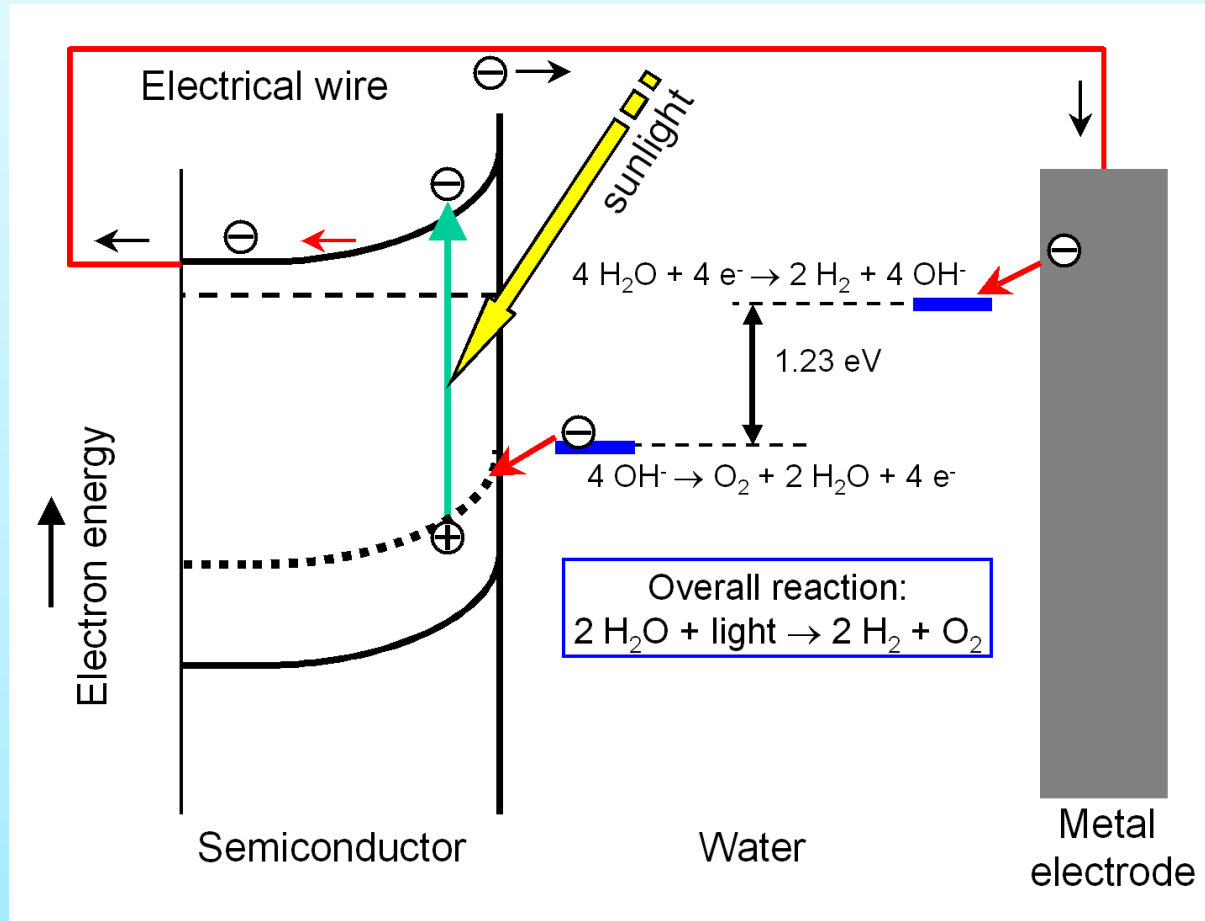
- Width of the depletion layer W depends on donor concentration and the applied potential

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

- The flat band potential relates to the pH as

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

N_D Donor concentration

V Applied potential

V_{fb}^{PZC} pH at the net absorbed charge is zero

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

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

P_{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 semi conductor
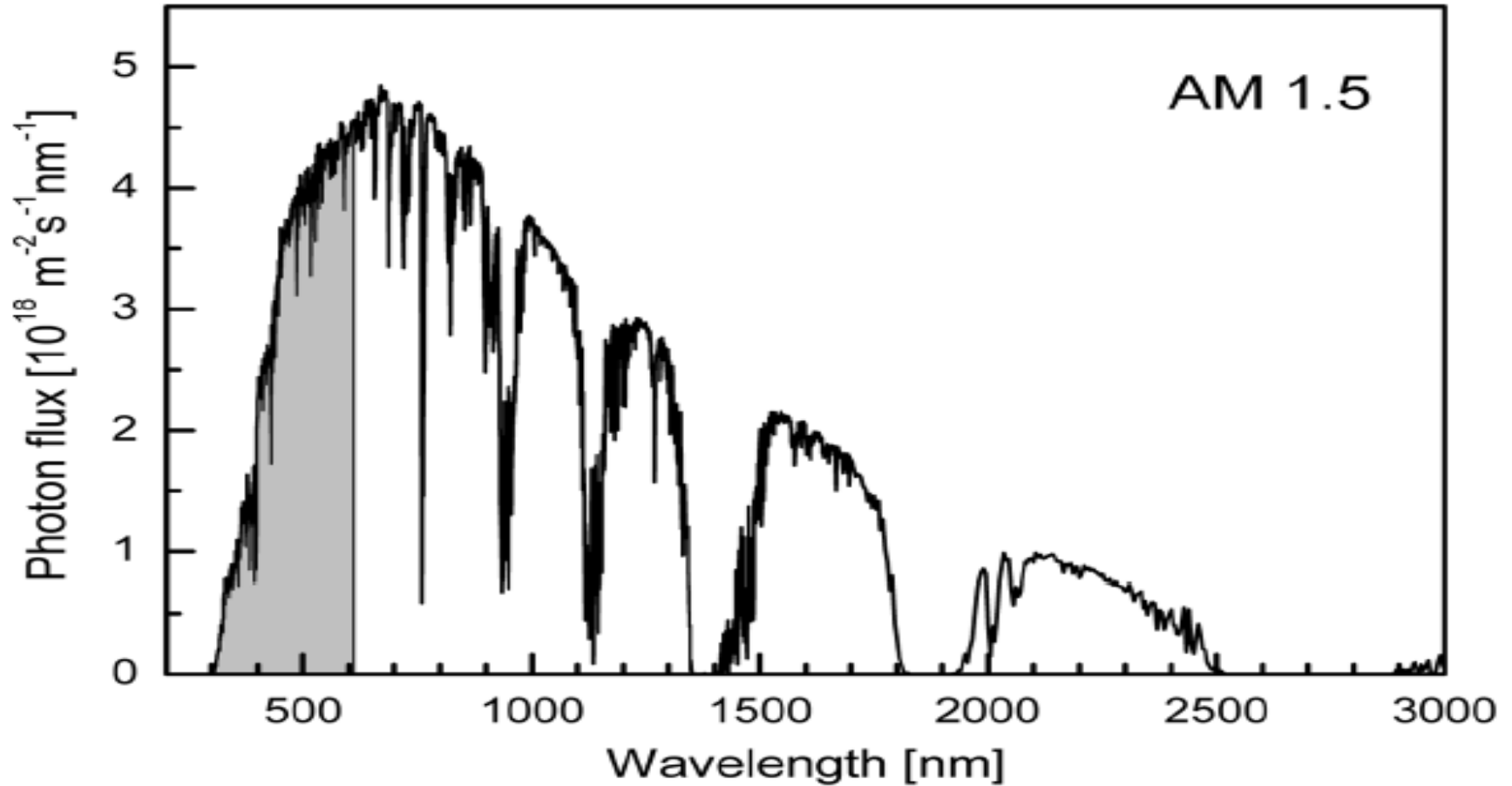
Stability against photo corrosion

Most important property which imits 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_2O_3 shows an intermediate case (pH and oxygen stochiometry)

- Percentage ionic character of some semiconductors

Percentage ionic character

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

| Semiconductor	M-O	Percentage ionic character
TiO_2	Ti-O	59.5
$SrTiO_3$	Ti-O-Sr	68.5
$Fe_2\text{-}O_3$	Fe-O	47.3
ZnO	Zn-O	55.5
WO_3	W-O	57.5
CdS	Cd-S	17.6
$CdSe$	Cd-S	16.5
$LaRhO_3$	La-O-Rh	53.0
$LaRuO_3$	La-O-Ru	53.5
PbO	Pb-O	26.5
$ZnTe$	Zn-Te	5.0
$ZnAs$	Zn-As	6.8
$ZnSe$	Zn-Se	18.4
ZnS	Zn-S	19.5
GaP	Ga-P	3.5
$CuSe$	Cu-Se	10.0
$BaTiO_3$	Ba-O-Ti	70.8
MoS_2	Mo-S	4.3
$FeTiO_{3\text{-}}$	Fe-O-Ti	53.5
$KTaO_3$	K-O-Ti	72.7
$MnTiO_3$	Mn-O-Ti	59.0
SnO_2	Sn-O	42.2
Bi_2O_3	Bi-O	39.6

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_{RED} and E_V should be below E_{OX}
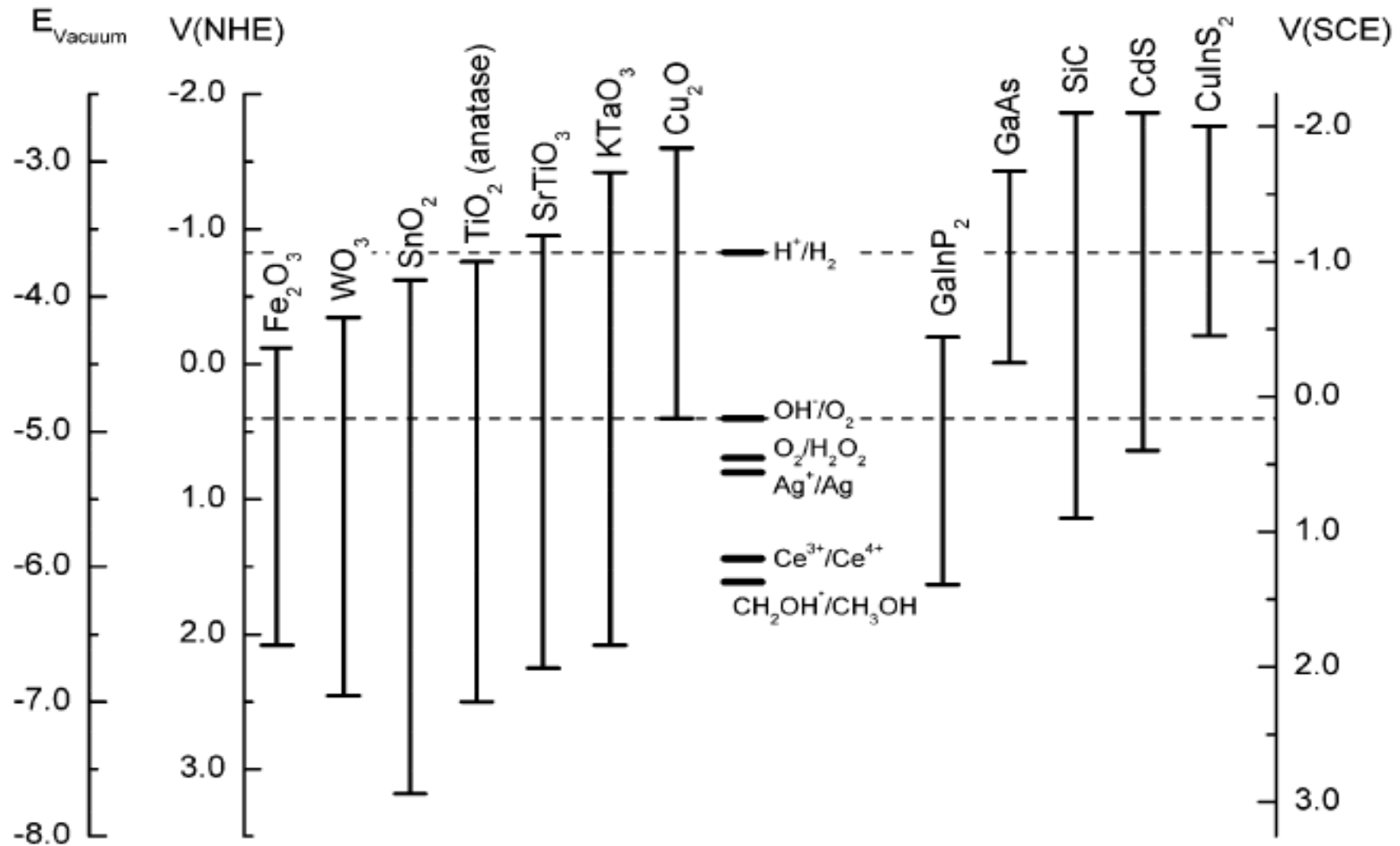
Charge transport

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 straight forward approach towards solar water splitting
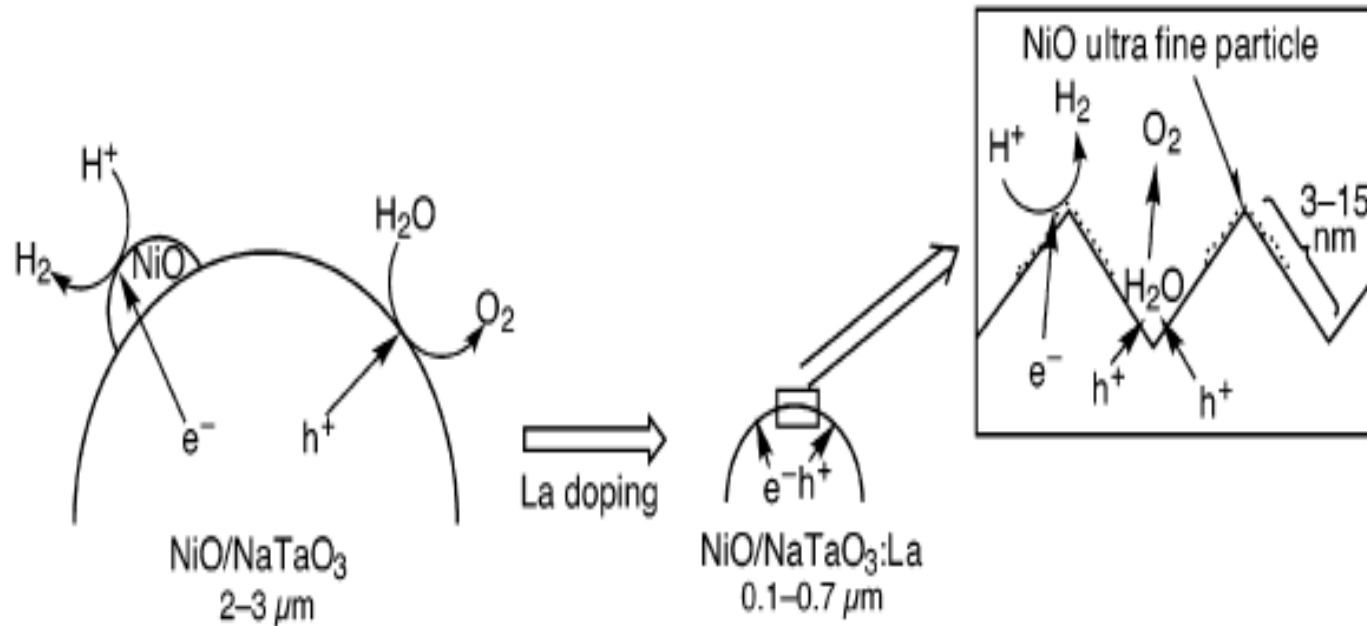- Oxidation and reduction takes place at the surface of the same particle
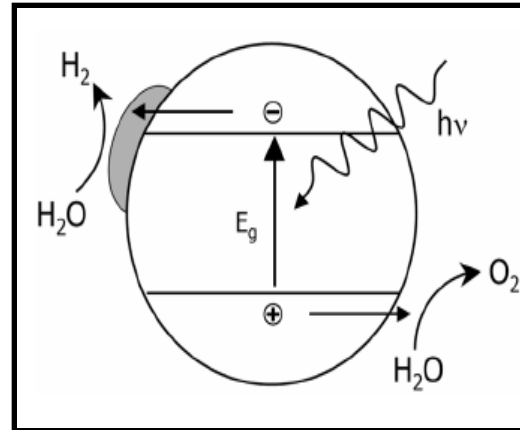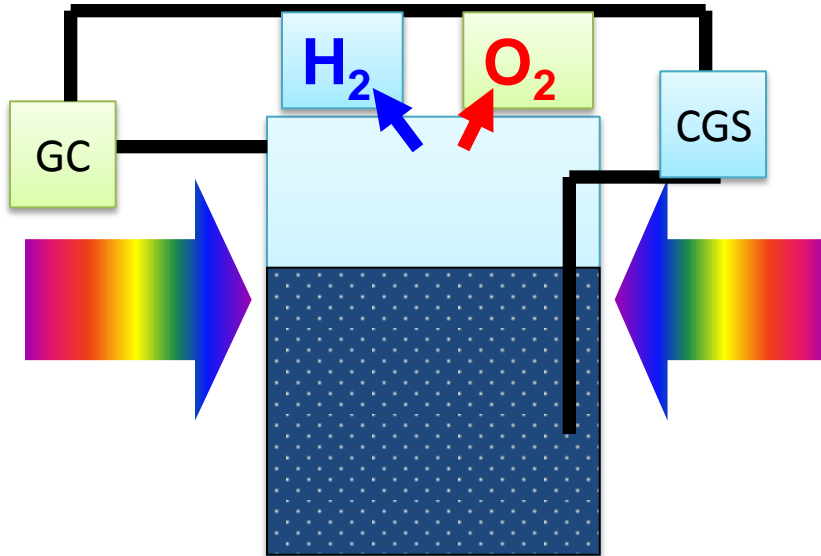
ACTIVITY = [H_2]

QE = 2 [H_2] / I

- Efficiency
- Definition of quantum yield

Driving force to seperatre is ELECTRIC FIELD AT INTERFACE SC/L

- To enhance the kinetics and to avoid recombination of H_2 and O_2 co catalysts can be used
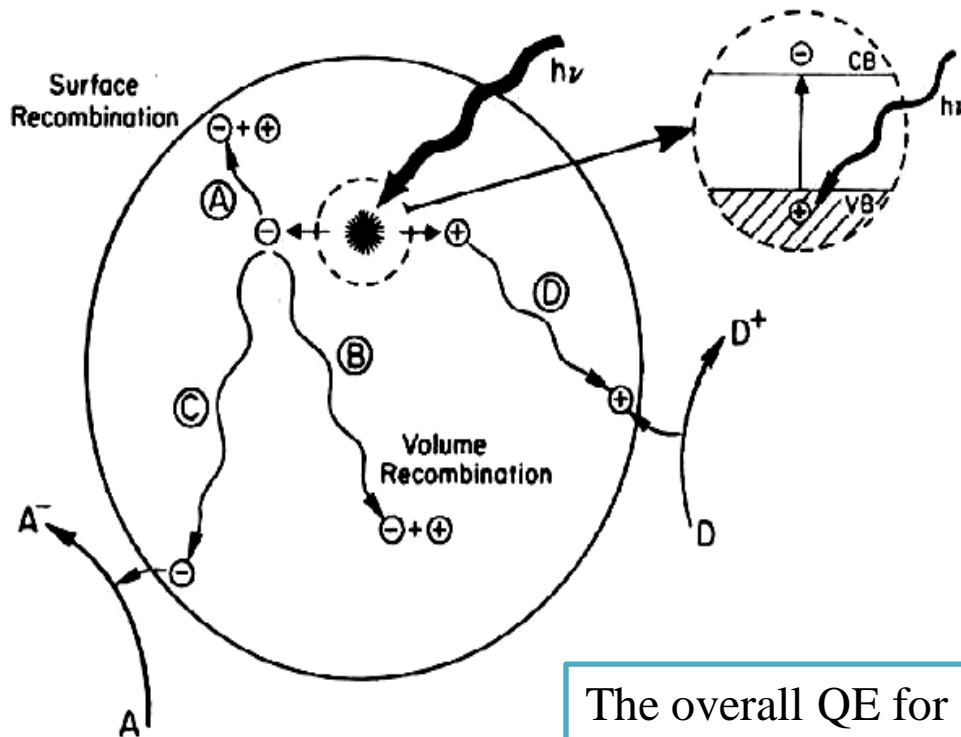

Mechanism of highly efficient photocatalytic water splitting over NiO/NaTaO₃:La photocatalysts.

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

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

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

A. Millis and S. L. Hunte *J. Photochem. Photobiol.* A: *Chem* 180 (1997) 1

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 1.9-3.1eV
- Band edges should straddle the oxidation and reduction potential of H_2O
- Photocatalyst should be stable against photo corrosion
- Metal oxide semiconductors with moderate ionicity are suggested
- Life time of the excitons should be high
- Cocatalyst is needed in most of the cases

THANKS FOR YOUR KIND ATTENTION