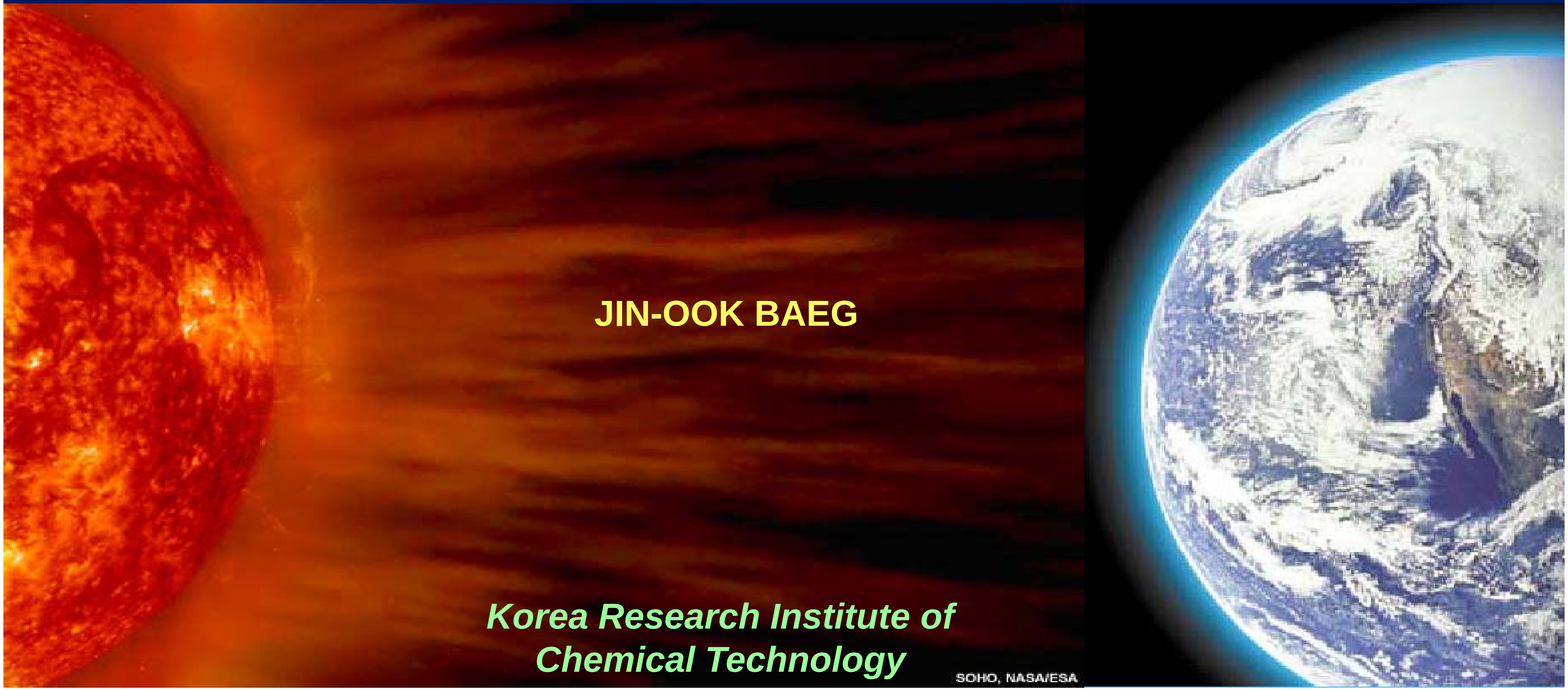
New Nano-structured Semiconductor Photocatalysts for Photocatalytic Solar Hydrogen Production



JIN-OOK BAEG

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Photocatalyst Application

hν

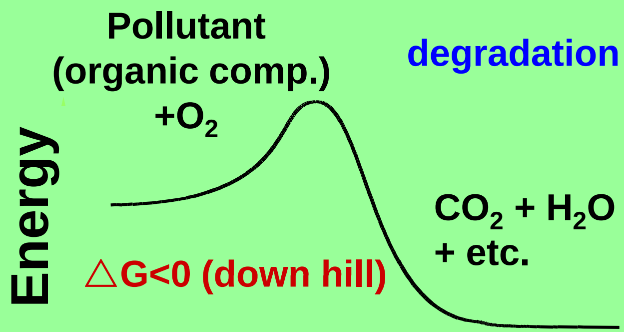
Environmental Remediation

- Pollutant Treatment
- Deodorization
- Sterilization

Solar Energy Conversion

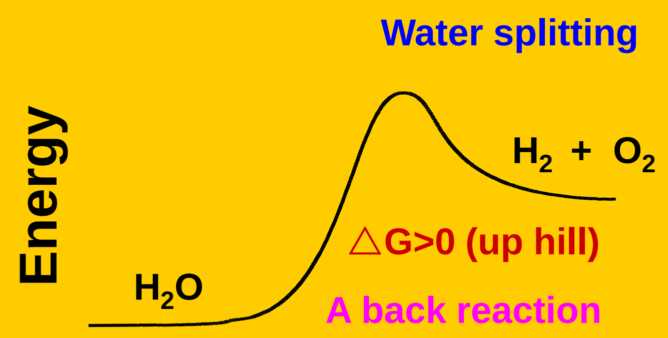
- Water Splitting
- H_2S Splitting

Photo-induced reaction



The reaction irreversibly proceeds.

Light energy conversion reaction



A back reaction easily proceeds.

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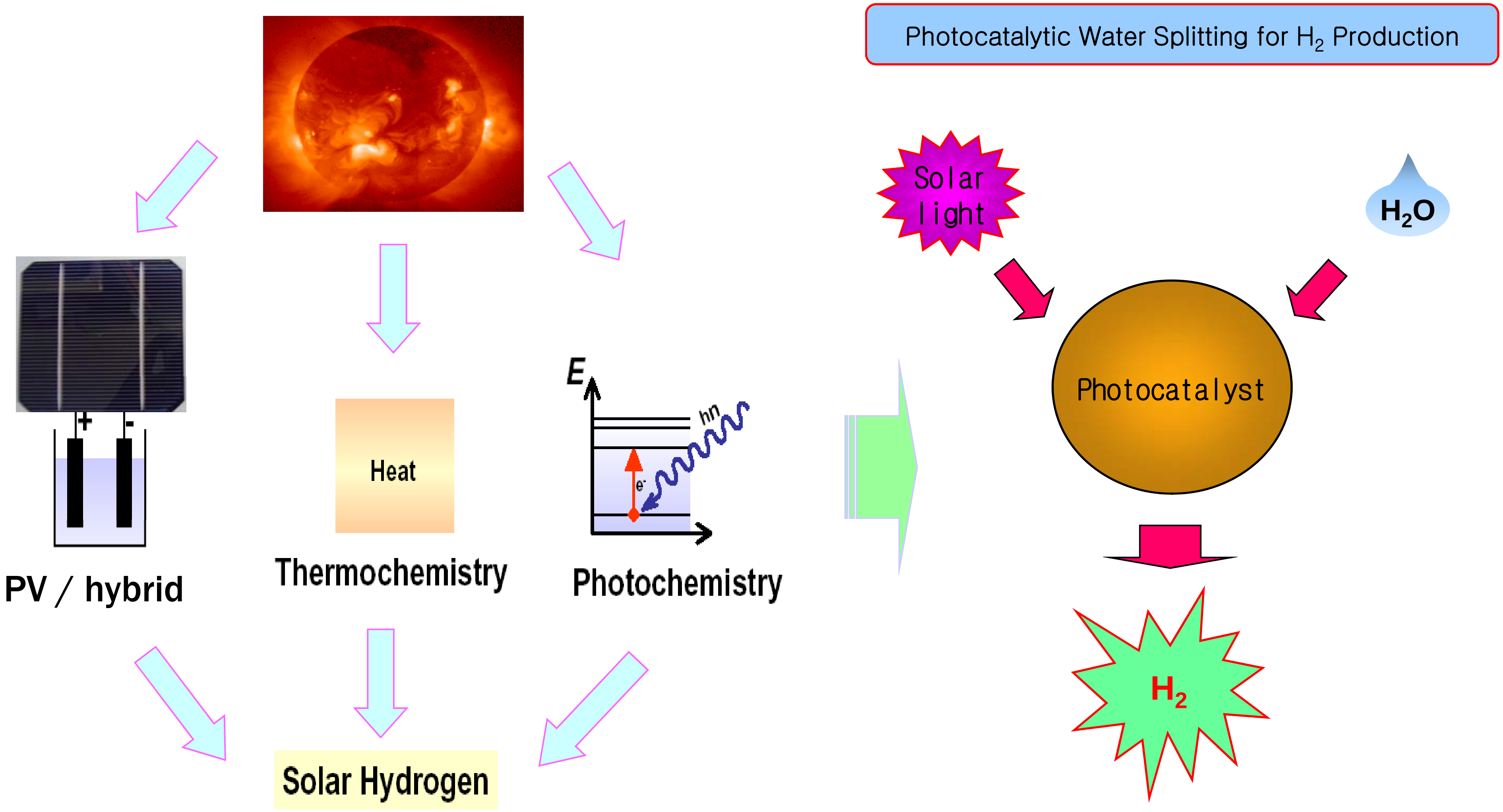
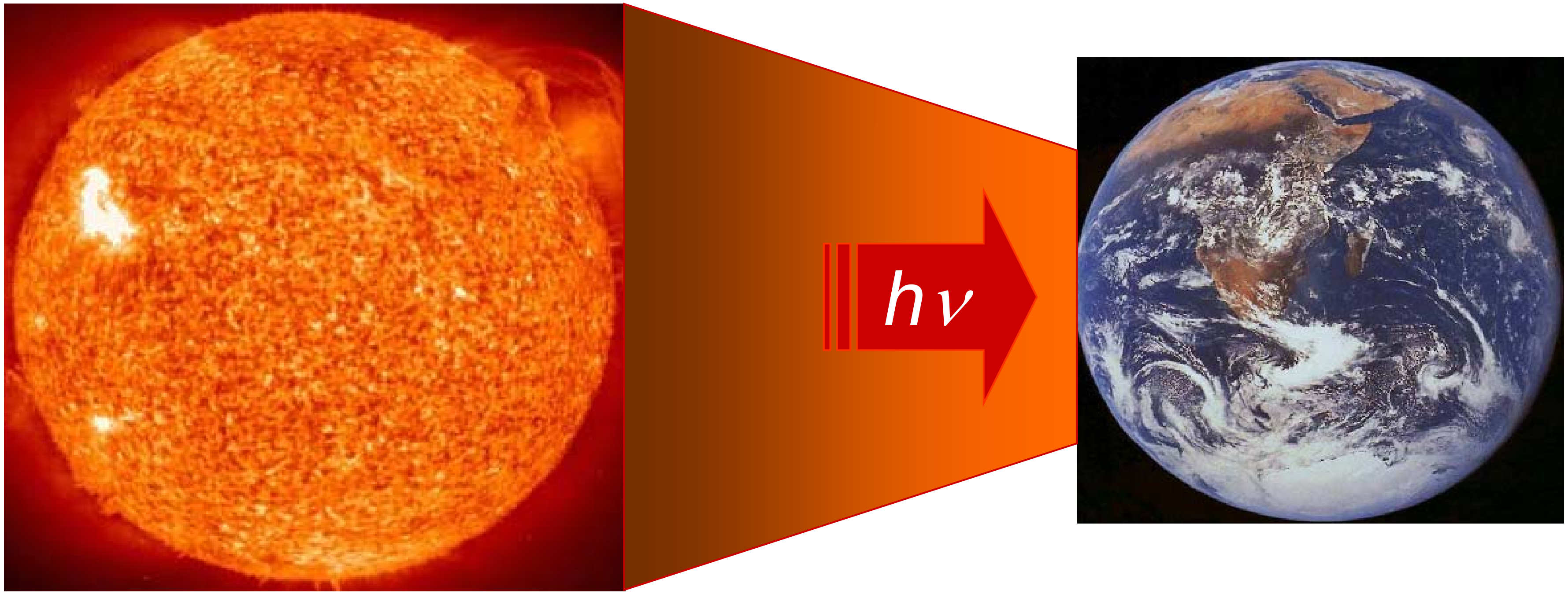
Solar Energy Conversion for Hydrogen Production



Solar Energy

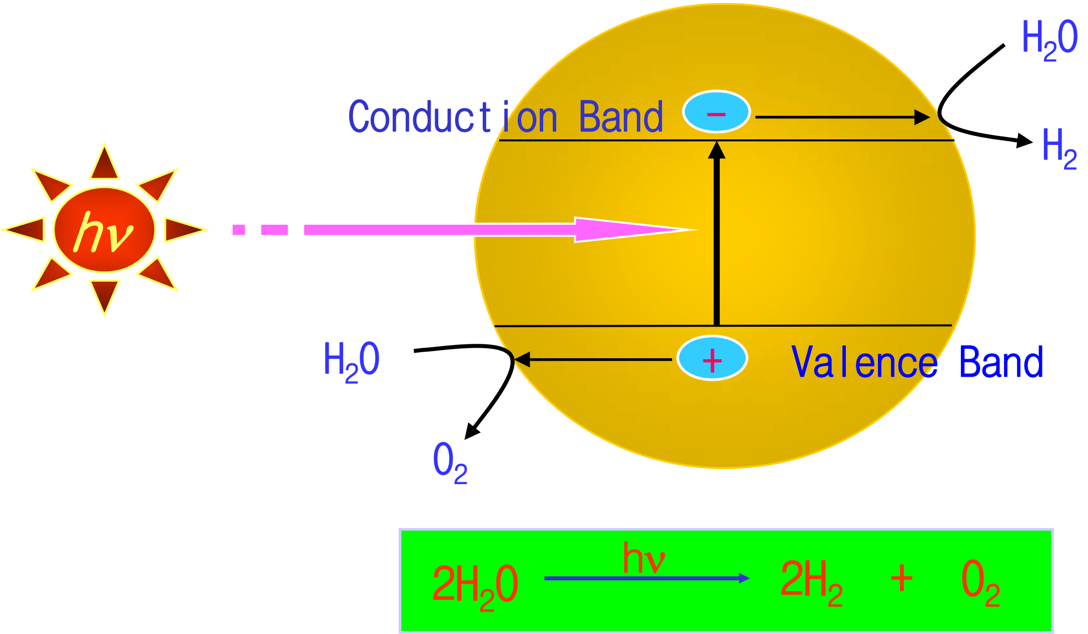


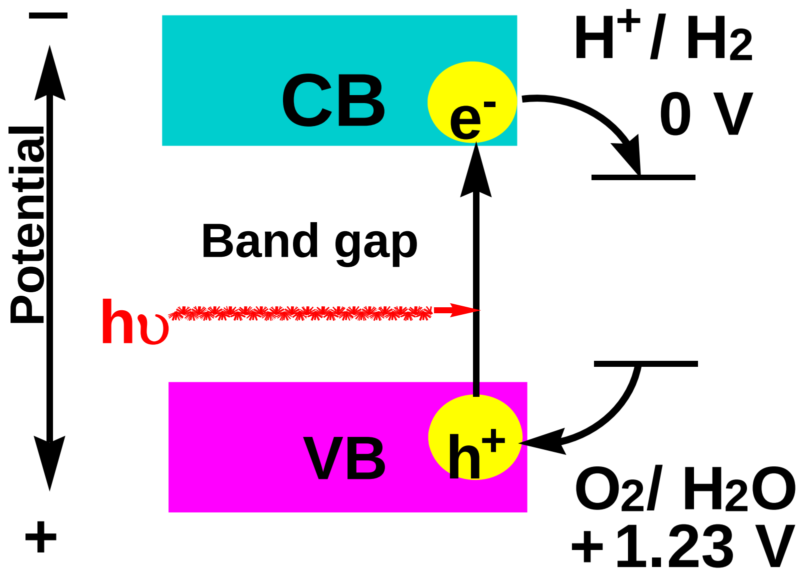
Solar Energy
1.74×10^5 TW

Global need
15.7 TW in 2006

10,000 **times of** ***Current world demands***
(~ 0.1% of the Earth's surface
: 10% conversion efficiency)

Photocatalytic Water Splitting for Hydrogen Production





Energy Requirement for Overall Water Splitting

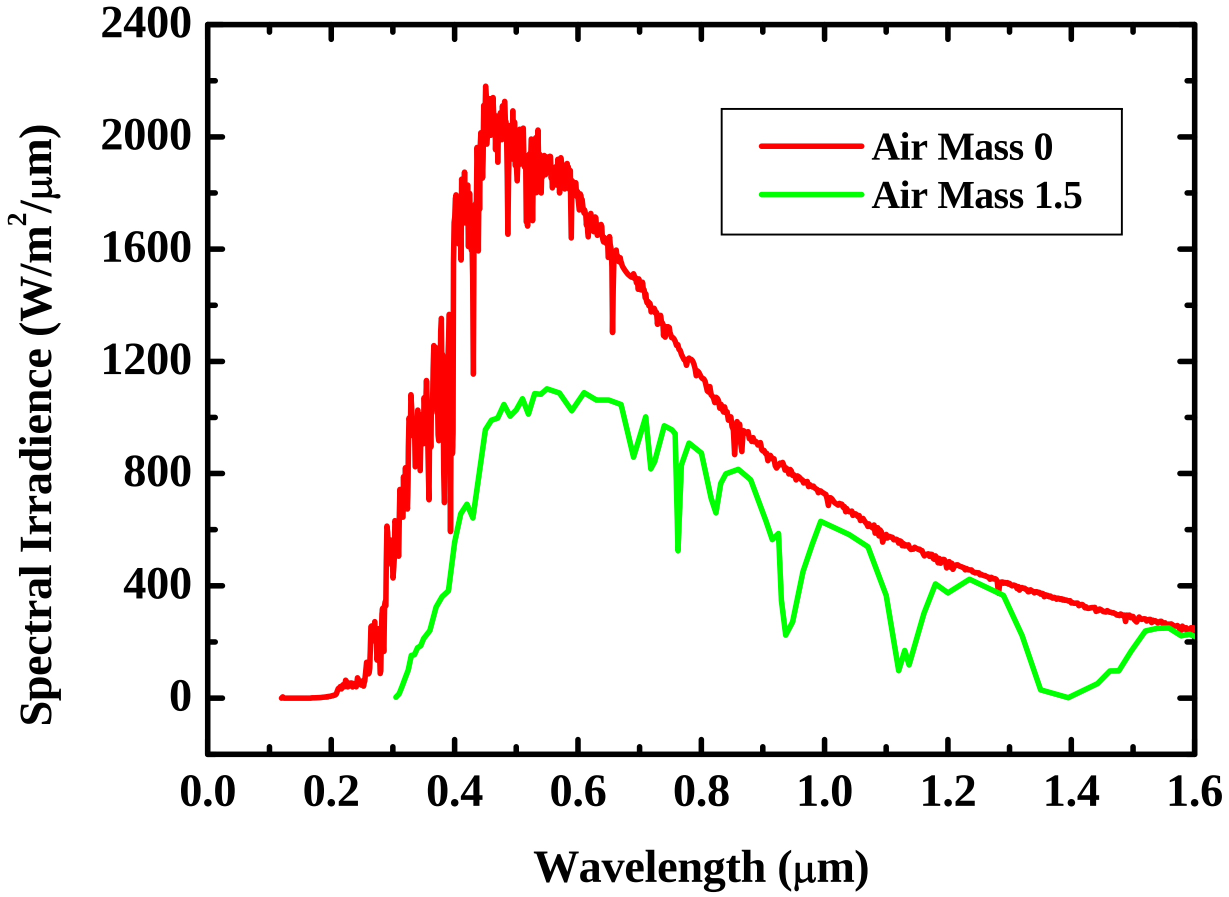
$$2\,H_2O \longrightarrow 2H_2 + O_2$$

$$\Delta G° = 237 kJ/mol \; (E° = -\Delta G°/nF = -1.23V)$$

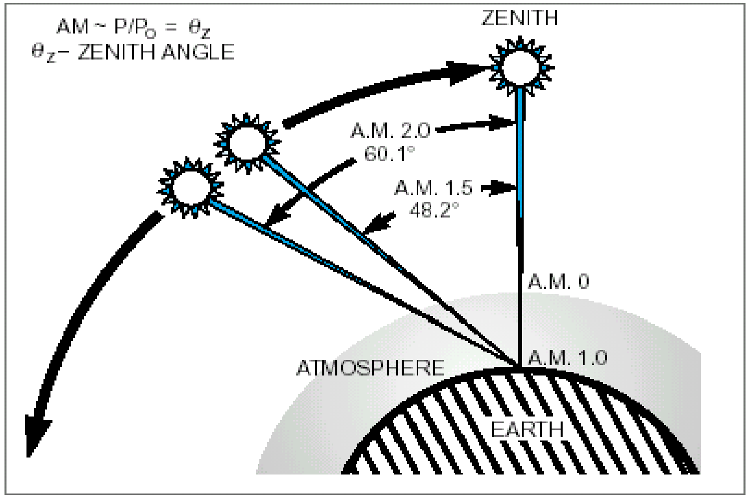
Overpotentials for photo-splitting of water

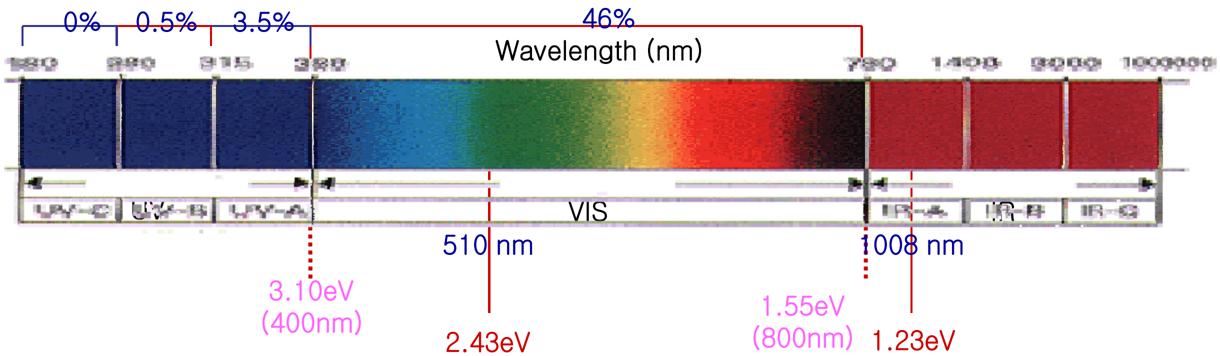
Reaction type Energy required	eV
Electron transfer at a cathode	0.2
Hole transfer at an anode	0.2
H_2 overpotential at a cathode	0.1
O_2 overpotential at an anode	0.5
Band bending for efficient charge separation at an anode	0.2
Total	1.2

Solar Spectrum



AM1.5 ~ 100mW/cm^2





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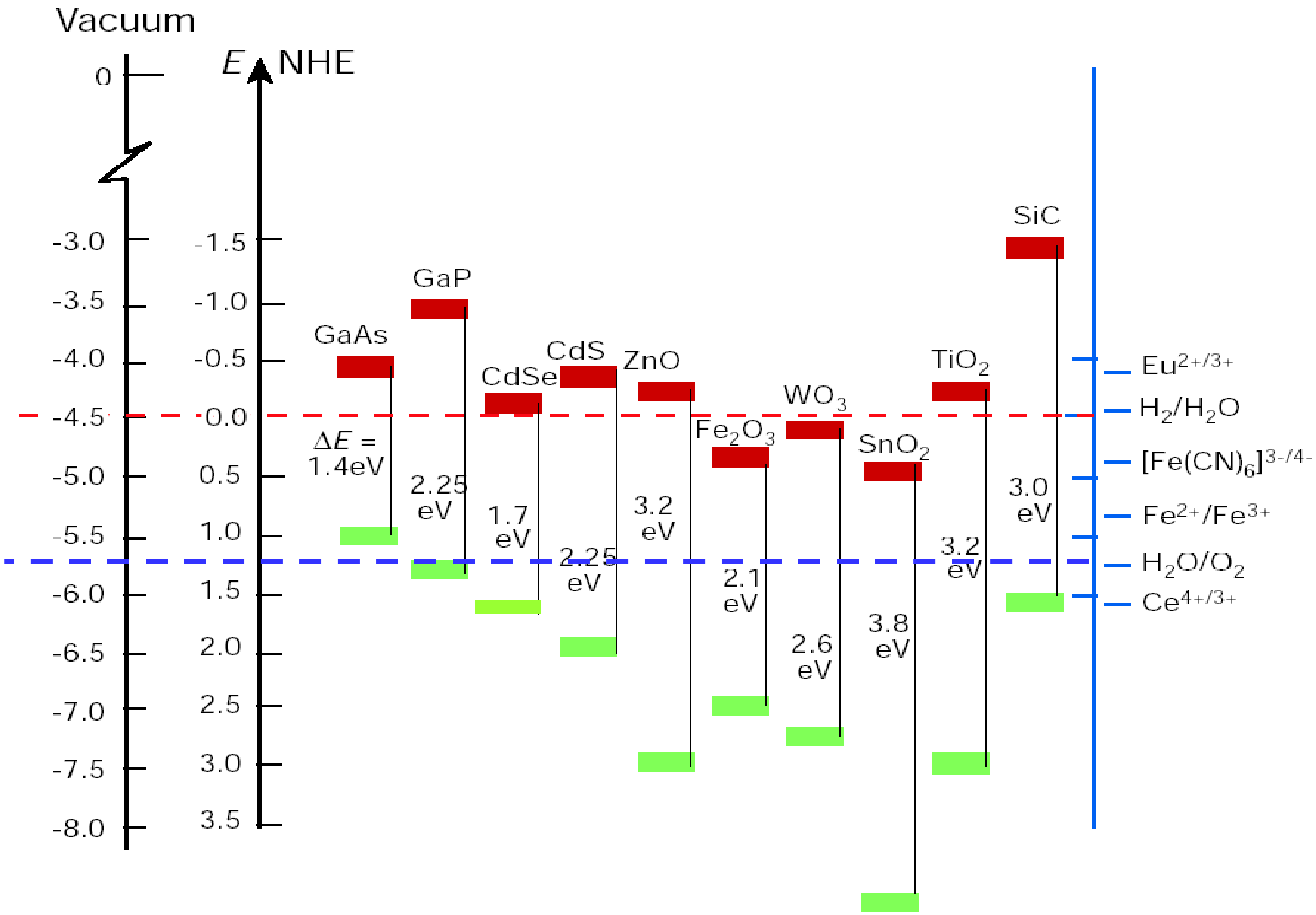
Band Gap Energy and Band Edge Position of Photocatalysts



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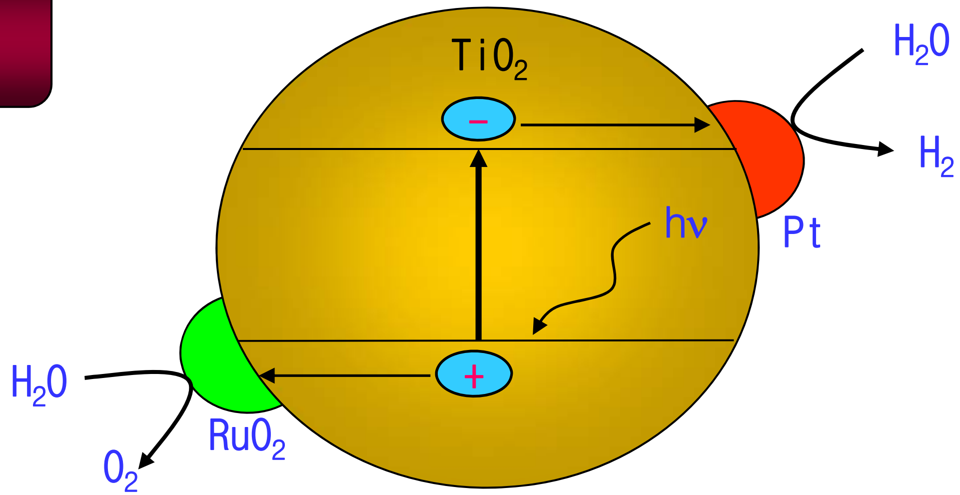
Photocatalysts for Water Splitting (UV Light)

TiO_2 Photocatalyst

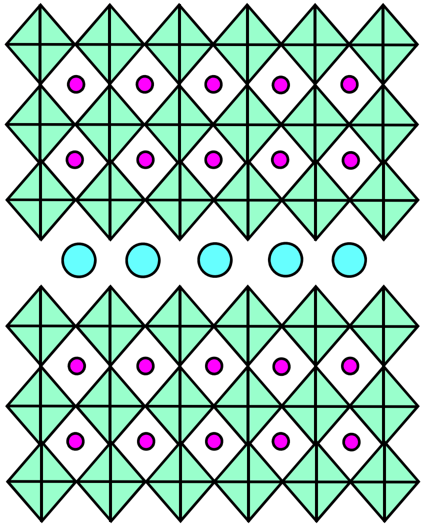


TiO_2 : E_g = 3.2 eV, λ_g = 388 nm

Catalyst	H_2 (μmol/h)
Pt/TiO_2	2
$Pt/TiO_2/RuO_2$	77

- J. C. Escudero *et al.*, *J. Catal.*, 1990, *123*, 319.

Perovskite Photocatalyst (UV Light)



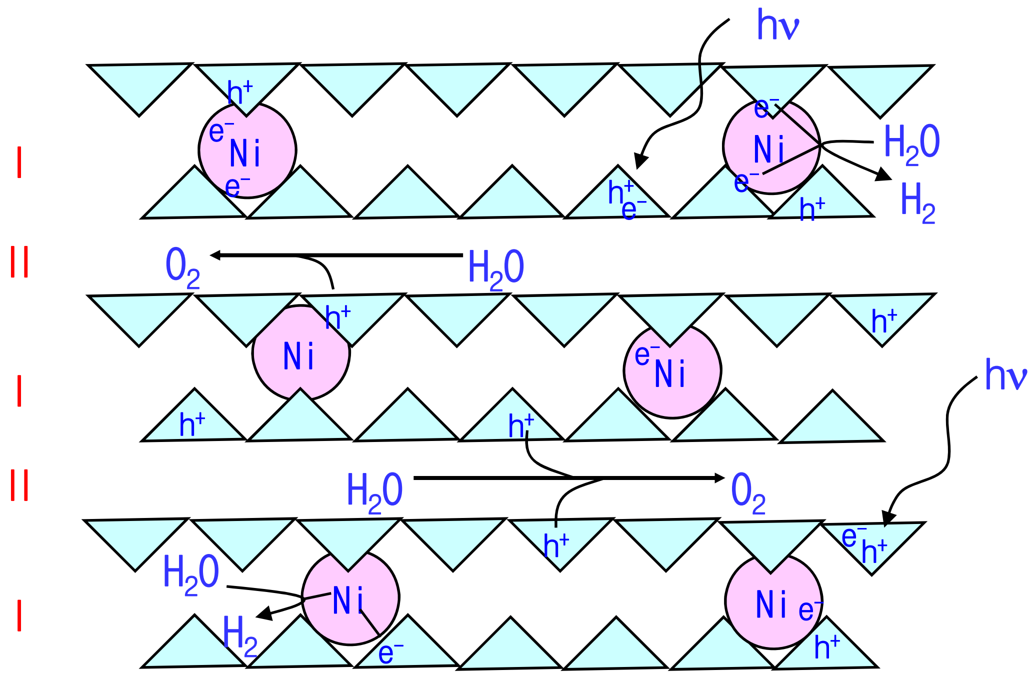
$A\ [M_{n-1}Nb_nO_{3n+1}]$

NbO_6

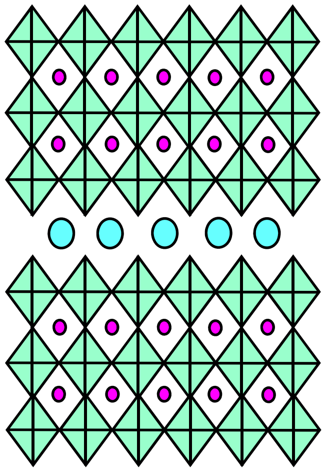
A (Alkali Metals)
= K, Rb, Cs, etc.

M (Alkali Earth Metals)
= Ca, St, etc.

Water splitting mechanism of $K_4Nb_6O_{17}$



Perovskite Photocatalyst (UV Light)



A $[M_{n-1}Nb_nO_{3n+1}]$

X	Catalyst	Rate of Gas evolution (μmol/h)	
		H_2	O_2
0	Ni-$K_4Nb_6O_{17}$	403	197
2	Ni-$K_4Ta_2Nb_6O_{17}$	409	198
3	Ni-$K_4Ta_3Nb_6O_{17}$	233	111
4	Ni-$K_4Ta_4Nb_6O_{17}$	31	12
0	Ni-$Rb_4Nb_6O_{17}$	936	451
2	Ni-$Rb_4Ta_2Nb_4O_{17}$	362	179
3	Ni-$Rb_4Ta_3Nb_4O_{17}$	126	62
4	Ni-$Rb_4Ta_4Nb_4O_{17}$	101	48
6	Ni-$Rb_4Ta_6Nb_4O_{17}$	92	46
6	Ni-$Rb_4Ta_6Nb_4O_{17}$	11	1

0.1 wt% nickel was loaded. Catalyst, 1 g; distilled water, 350 mL; high pressure Hg lamp (400 W); inner irradiation cell (quartz).

- K. Domen *et al.*, *Catal. Today*, 1996, *28*, 175.

Summary of Quantum Efficiency of Overall Water Splitting

Under UV Light

$NiO\text{-}SrTiO_3$

≦~1% (300nm)

$Ni\text{-}Rb_4Nb_6O_{17}$

~ 10% (300nm)

$NiO\text{-}Ni\text{-}Rb_2La_2Ti_3O_{10}$

~ 30% (300nm)

→

$NiO\text{-}NaTaO_3{:}La$

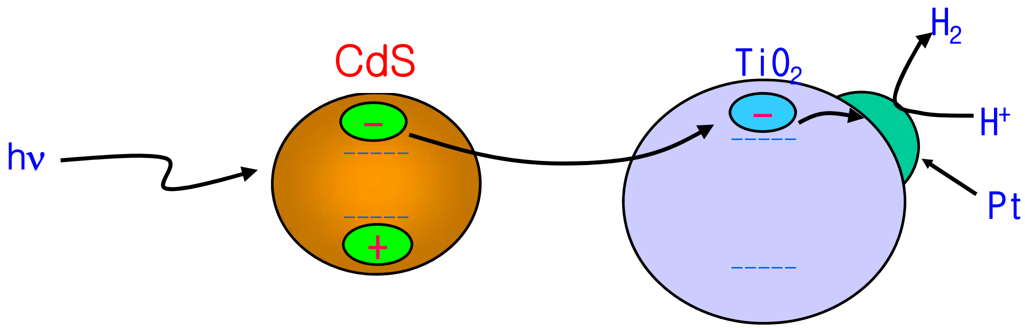
~ 56% (270nm)

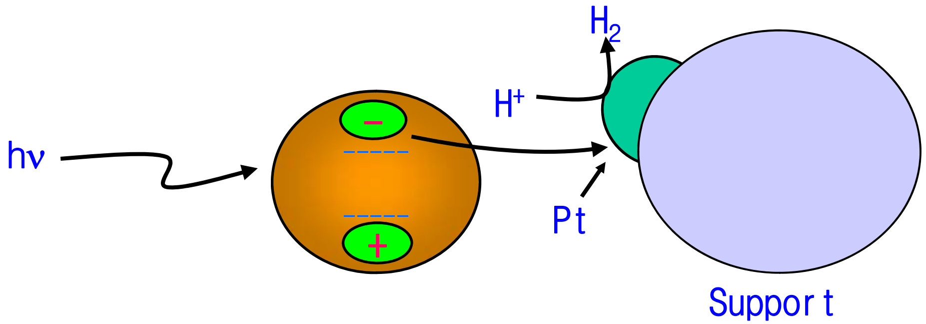
Photocatalyst for Water Splitting (Visible Light)

CdS : Eg = 2.4eV, λg = 517nm

- CdS has ideal band gap & band edge position for water splitting for H_2 production under visible light irradiation.

➡ *But it undergoes photocorrosion!*





Interparticle electron transfer:
(A) Mediated by the conduction band of TiO_2;
(B) Direct electron transfer to separately supported platinum.

Catalyst	Calcination Temp.(℃)	H_2 yield, μmol 1h
$Pt/TiO_2/SiO_2$	400	2.0
CdS/SiO_2	110	
$Pt/TiO_2/SiO_2$	400	3.4
CdS/SiO_2	300	
$Pt/TiO_2/SiO_2$	400	3.8
CdS/SiO_2	400	
$Pt/TiO_2/SiO_2$	110	1.3
CdS/SiO_2	400	
$Pt/TiO_2/SiO_2$	300	2.2
CdS/SiO_2	400	

[a] Reaction conditions: 10 mg of TiO_2/SiO_2; 0.4 wt% Pt (in situ photoplatinization); 10 mL of 1:1 H_2O-MeOH 0.01 M KOH; light source: 450W Xe lamp, 420 nm cut-off filter

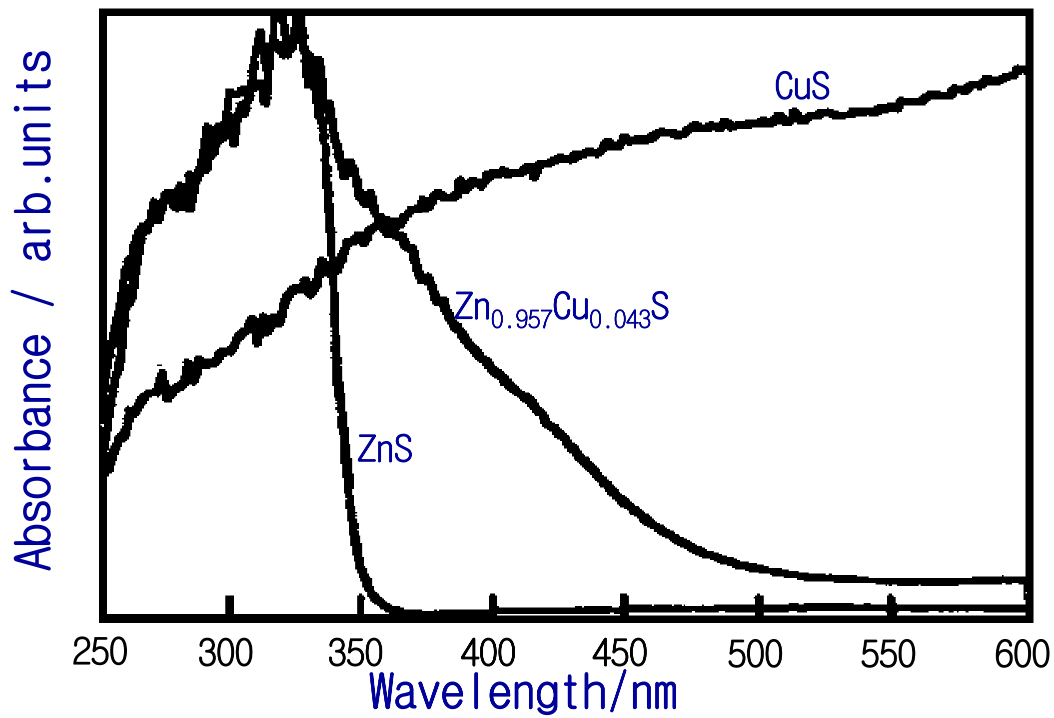
- J. M. White *et al.*, *J. Phys. Chem.*, **1987**, *91*, 3316.

ZnCuS Photocatalyst

$ZnS \longrightarrow Zn_{0.957}Cu_{0.043}S$

E_g = 3.7eV E_g = 2.5eV

λ_g = 335nm λ_g = 496nm



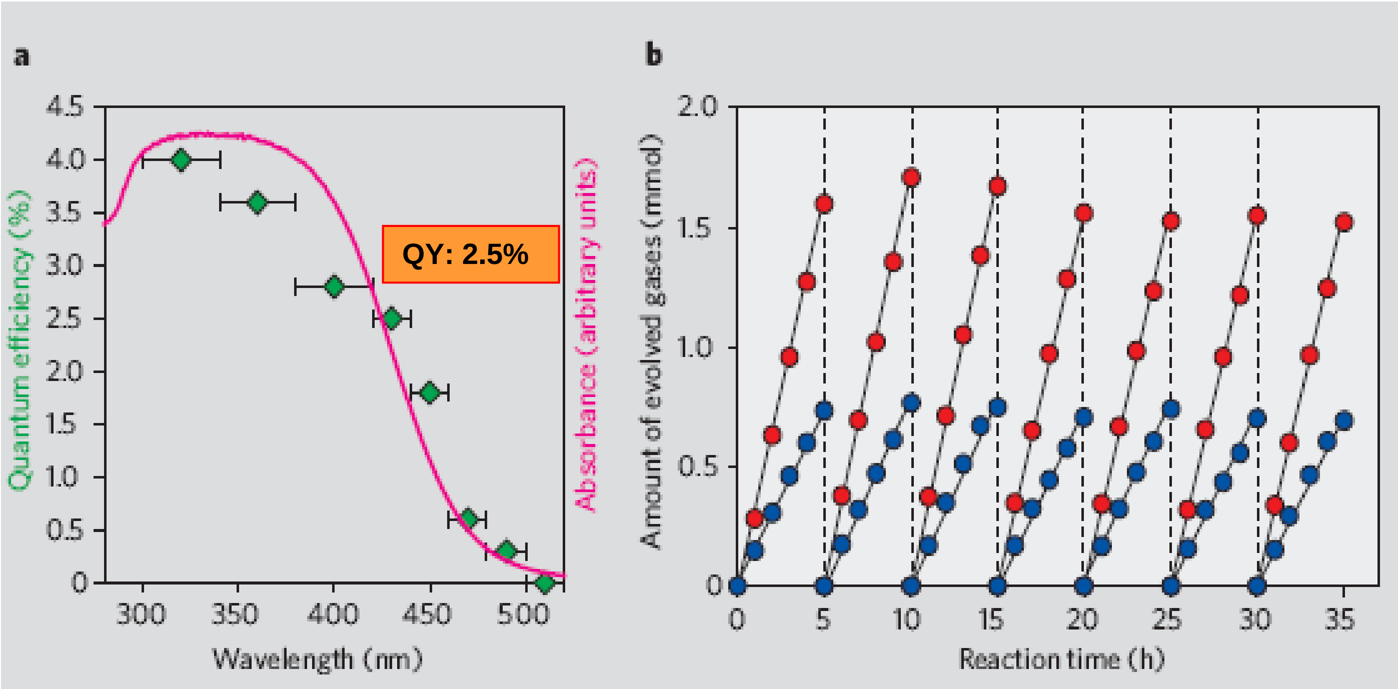
* Quantum yield:
  3.7% (λ > 420 nm)
  (Photocorrosion)

* Rate of H_2 revolution:
  430 μmol/g.cat.hr
  (0.5M Na_2SO_3)

- A. Kudo *et al. Catal Letter*, **1999**, 58, 241.

Rh_2O_3: Cr_2O_3 /$(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ Photocatalyst for Water Splitting

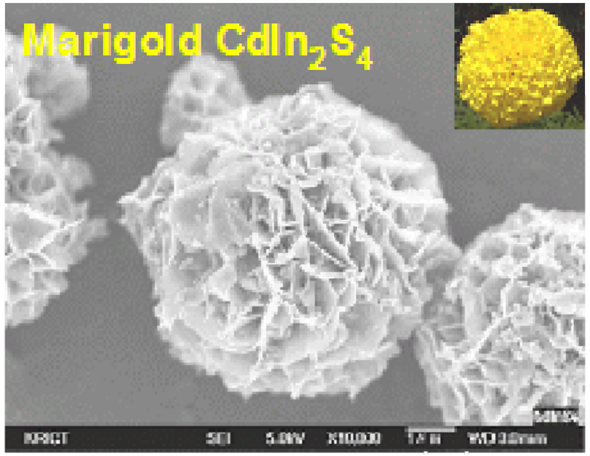
(λ = 420~440 nm; pH=4.5)



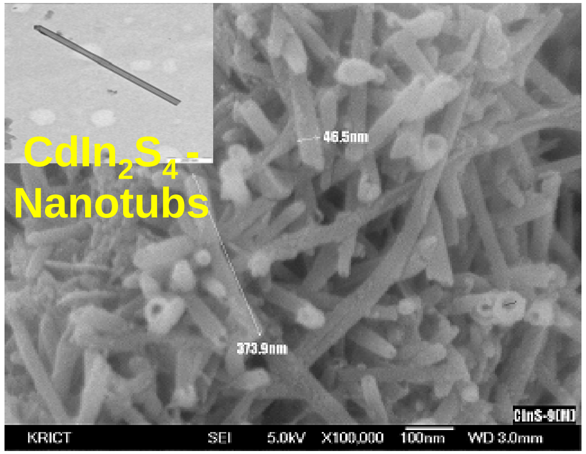
Catalyst: 0.3 g, Rh_2O_3: Cr_2O_3 5 wt.%,

Domen, *et. al.*, *Nature*, **440**, 295 (2006).

$CdIn_2S_4$ Nanotube and Marigold Nanostructure Photocatalyst

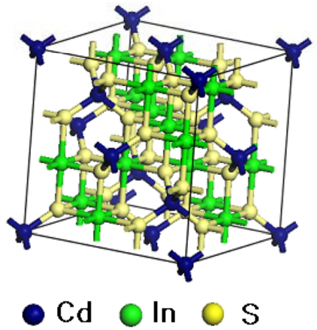


Marigold(aq.) : 3~5㎛

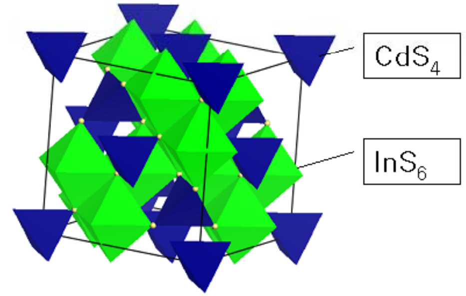


Nanotube(MeOH) : 25nm X 780nm

Cubic spinel nanostructured $CdIn_2S_4$



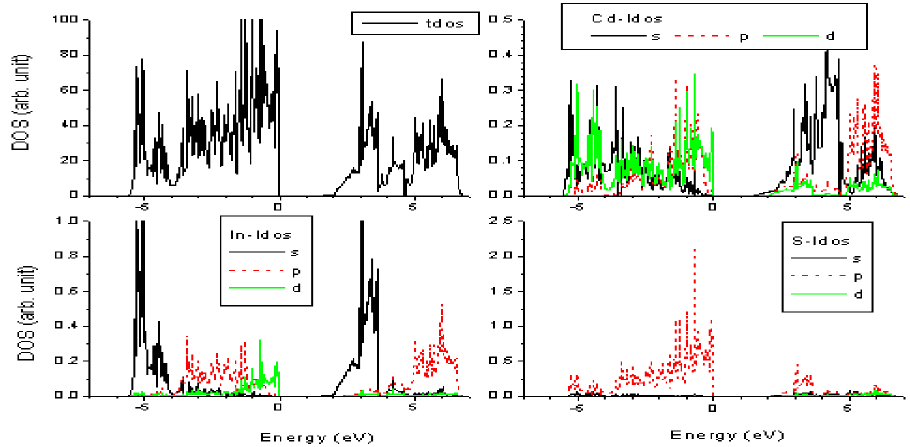
a = 10.84 Å



Bond lengths

Cd-S : 2.52 Å

In-S : 2.61, 2.62 Å In-In : 3.83 Å



Density of states (DOS) for $CdIn_2S_4$ (Calc. Eg = 1.90 eV)
VB (S 3p) ; CB (In 5s, 5p major & Cd 5s, 5p)

Advanced Functional Materials, **2006,*16*, 1349.**

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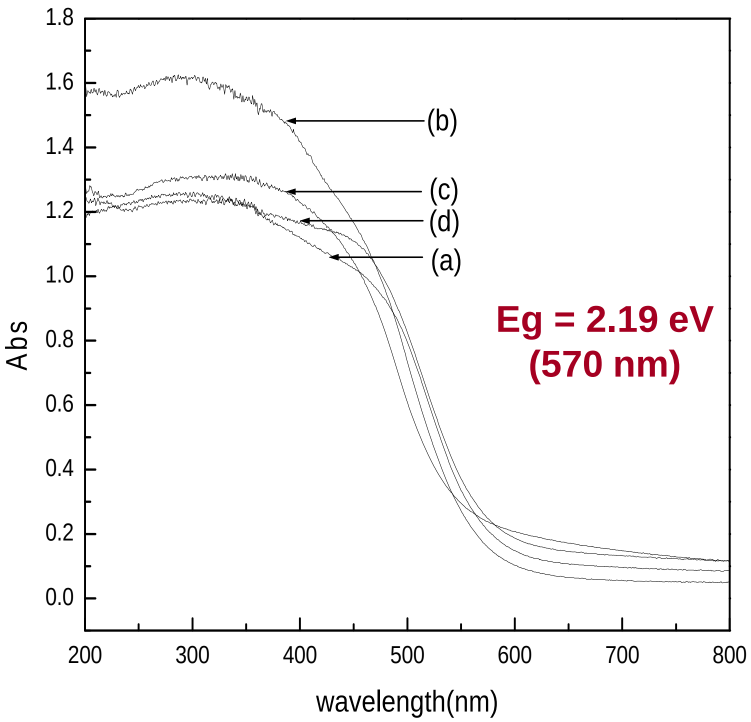
$CdIn_2S_4$ Nanotube and Marigold Nanostructure Photocatalyst



Diffuse Reflection Spectra's (a) aqueous (b) methanol (c) ethylene glycol (d) polyethylene glycol (5%) mediated $CdIn_2S_4$.

$CdIn_2S_4$ Photocatalyst for Hydrogen production

- *High quantum yield!*

– Nanotube(MeOH) : <u>17.1%</u> (@ λ = 500 nm)
– Marigold(aq.) : <u>16.8%</u> (@ λ = 500 nm)

Quantum yield (%) =

$$\frac{[\text{Number of } H_2 \text{ molecules evolved x 2}]}{[\text{Number of incident photons}]} \times 100$$

•Rate of H_2 revolution:

– Nanotube : 3480 μmol/hr
– Marigold : 3476μmol/hr

***Advanced Functional Materials*, 2006,*16*, 1349.**

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Nano-CdS Q.D. Photocatalyst in Glass Matrix

Procedure of Preparation for Powder of Q-CdS in glass matrix

SiO_2 + Na_2O + K_2O + ZnO, B_2O_3 + TiO_2 + BaO & CdS(0.5 wt%)

↓

Ball-milled mixing for 6h

↓

Reaction at 1500~1600°C for 3h

↓

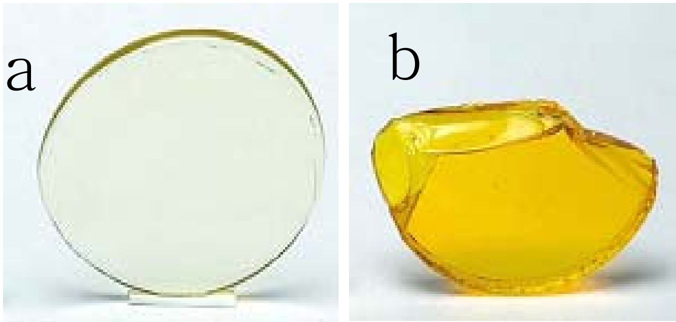
Annealing at 500-600°C (Tg = 570-580) for 72h

↓

Grinding

↓

Powder of Q-CdS in glass matrix



Typical photographs of glass matrix,
a) host glass
b) after crystal growth of Q-CdS

Journal of Material Chemistry, 2007, *17*, 4297.

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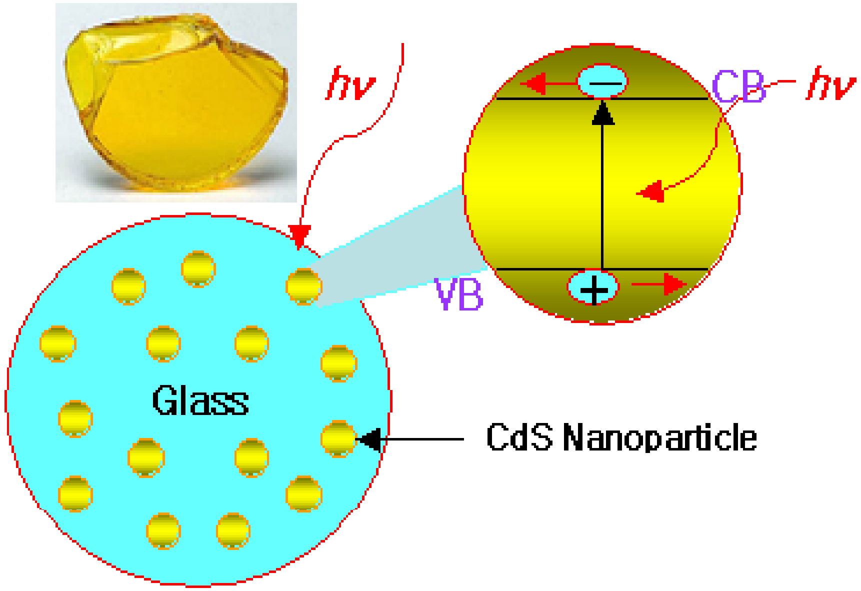
Nano-CdS Q.D. Photocatalyst in Glass Matrix

Q-CdS (1% amount) has 300% higher photocatalytic activity than bulk CdS!!



Photocatalytic Activity for H_2 Production (Visible)

High quantum yield (@ λ = 470 nm) *!!*

- Q-CdS-glass: 17.5%
  (1g of powder contains 0.005g of Q-CdS)
- CdS: 5.5% (0.5 g of CdS)

$$\text{Quantum yield (\%)} = \frac{[\text{Number of } H_2 \text{ molecules evolved x 2}]}{[\text{Number of incident photons}]} \times 100$$

Journal of Material Chemistry , 2007, *17*, 4297.

Octahedrally Coordinated d^0 Transition Metal Oxide Photocatalysts

Octahedrally Coordinated d^0 Transition Metal Oxide Photocatalysts

TiO_2, $SrTiO_3$, $A_2Ti_6O_{13}$ (A = Na, K, Rb)
$BaTi_4O_9$, $A_2La_2Ti_3O_{10}$ (A = K, Rb, Cs)
$K_2Ti_4O_9$, $Na_2Ti_3O_7$

Ti^{4+}	V	Cr
Zr^{4+}	Nb^{5+}	Mo
Hf	Ta^{5+}	W

ZrO_2

Ta_2O_5, $ATaO_3$(A = Na, K)
MTa_2O_6(M = Ca, Sr, Ba)
$Sr_2Nb_2O_7$

$A_4Nb_6O_{17}$(A=K, Rb)
$Sr_2Nb_2O_7$

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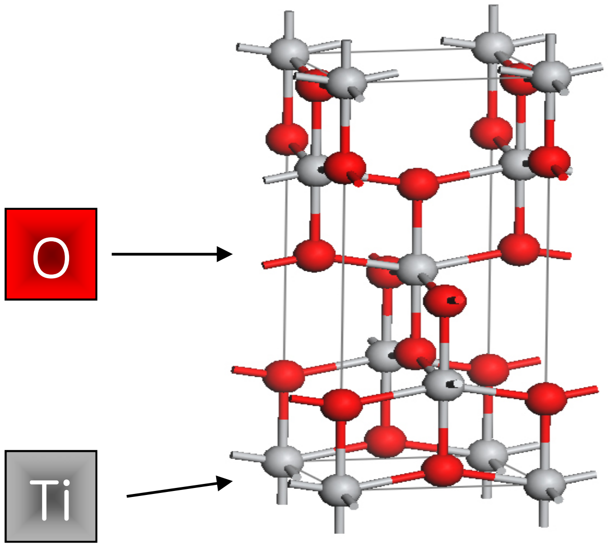
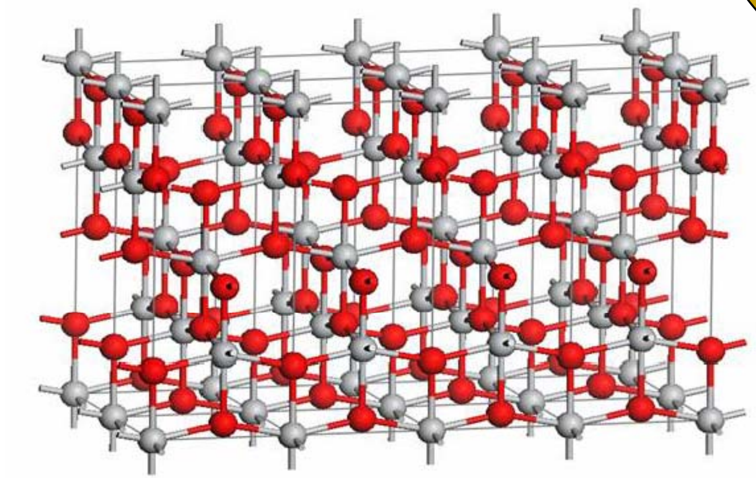
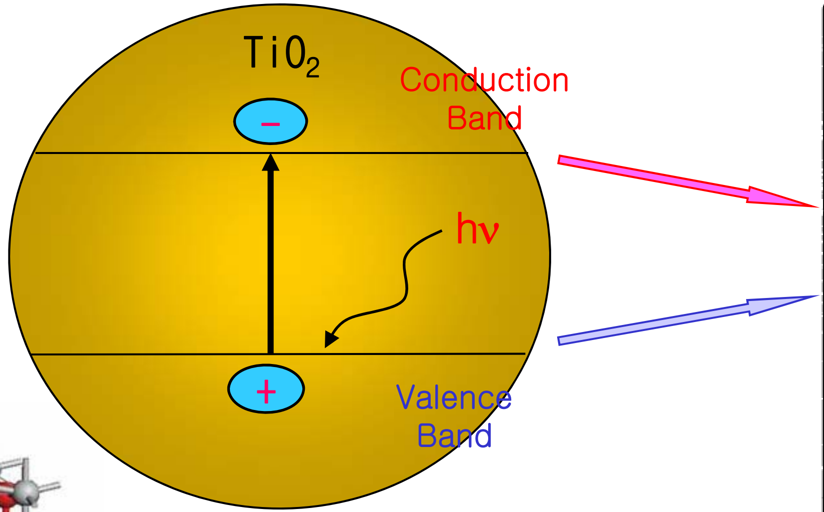
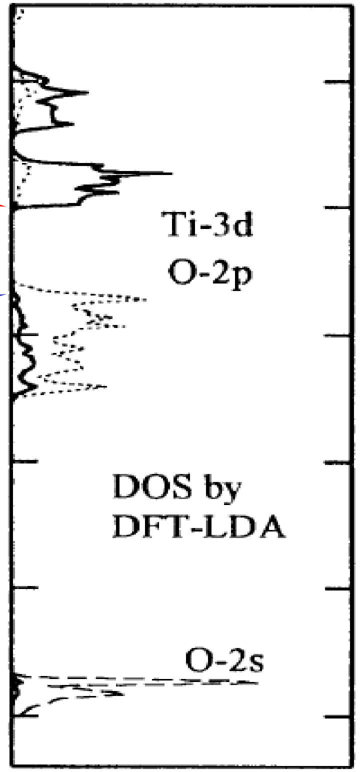
Density of States of TiO_2 by First Principle Calculation





TiO_2

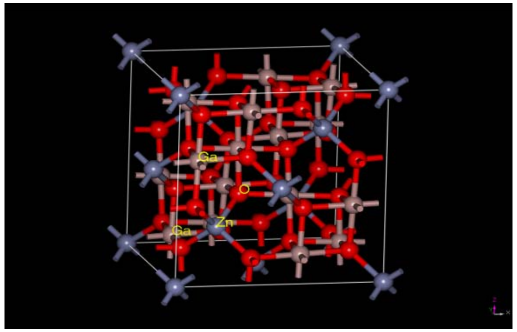


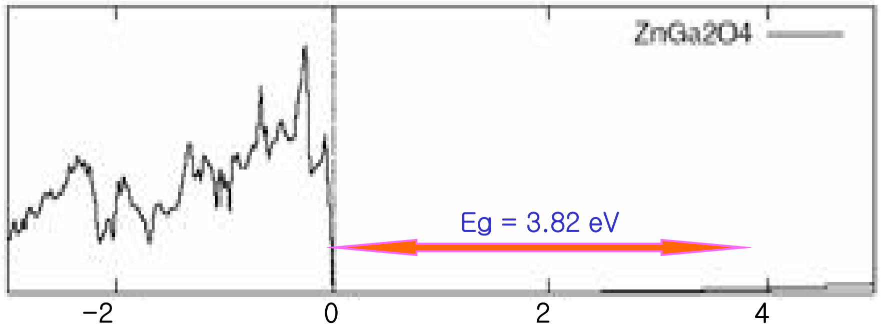


Density of states of TiO_2

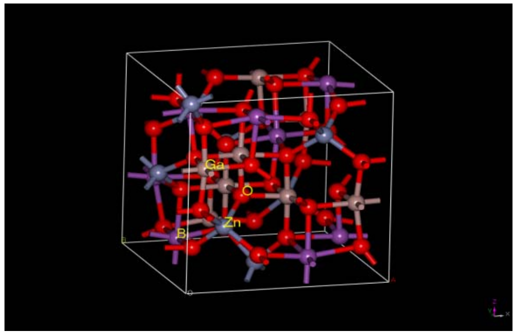
Density of States of $ZnBiGaO_2$ by First Principle Calculation

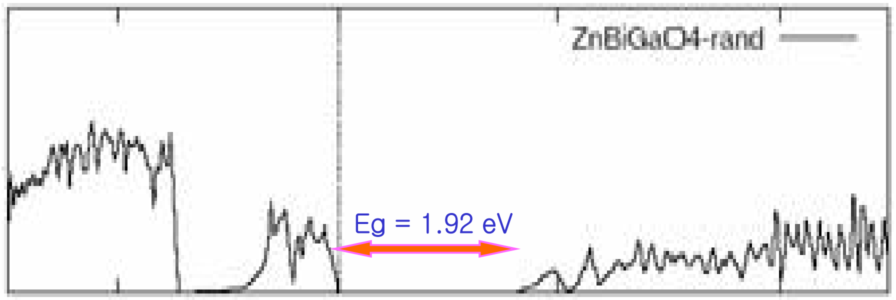
Zn_2GaO_4





$ZnBiGaO_4$





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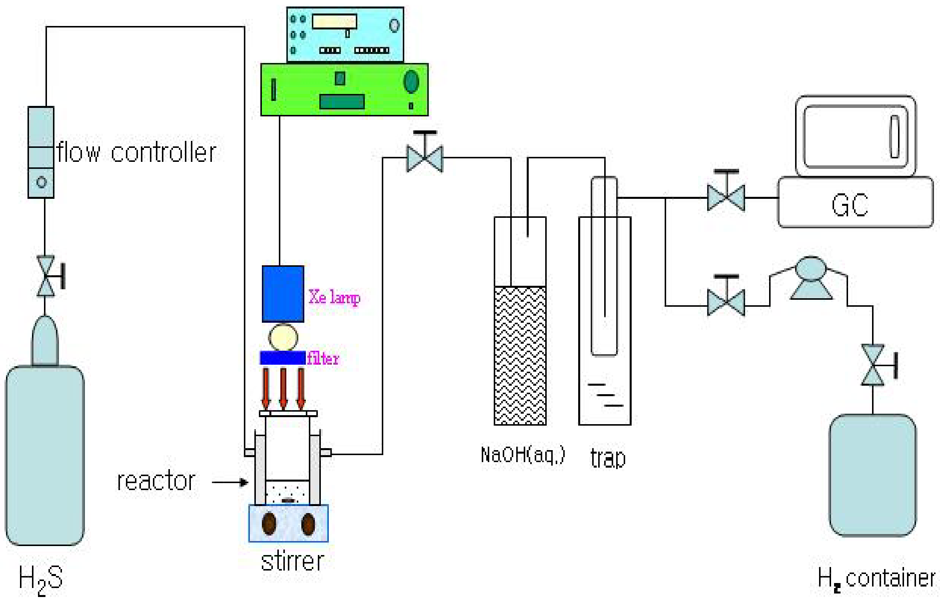
Photocatalytic Activities of New Photocatalysts (Visible)

Photocatalytic H_2 Production System(Visible)



Catalyst	Band gap energy (eV)	H_2 evolution rate[a] (μmol/hr)
$ZnBiGaO_4$	2.80(440nm)	3,030
$CdBiGaO_4$	2.43(510nm)	2,454

[a] Catalyst 0.5g, 250mL(H_2O) + KOH(0.5M), H_2S(2.5mL/min), Xe lamp(450W), light filter(>420nm).

Development of Synthetic Method for New Metal Oxide Photocatalyst

Low temperature economical photocatalyst preparation method!

Procedure of Preparation for $ZnBiVO_4$ by Solid State Method

Zn(II)-oxide | **Bi(III)-oxide** | **V(III)-oxide**

↓

Mixing & Tableting

↓

Reaction at 670°C for 15h

↓

Grinding

↓

Reaction at 725°C for 12h

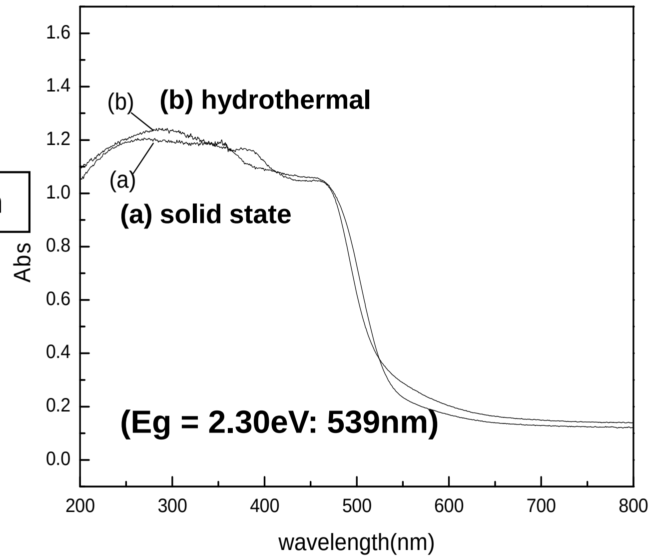
↓

Grinding

↓

$ZnBiVO_4$

Specific surface Area BET (m^2/g) : 0.27



Procedure of Preparation for $ZnBiVO_4$ by Hydrothermal Method

$Zn(NO_3)_2 \cdot 5H_2O$ + $Bi(NO3)_3 \cdot 6H_2O$ + NH_4VO_3 + Urea & water

↓

Reaction at 130°C for 60-72h

↓

Wash & Dry at 250°C for 5h

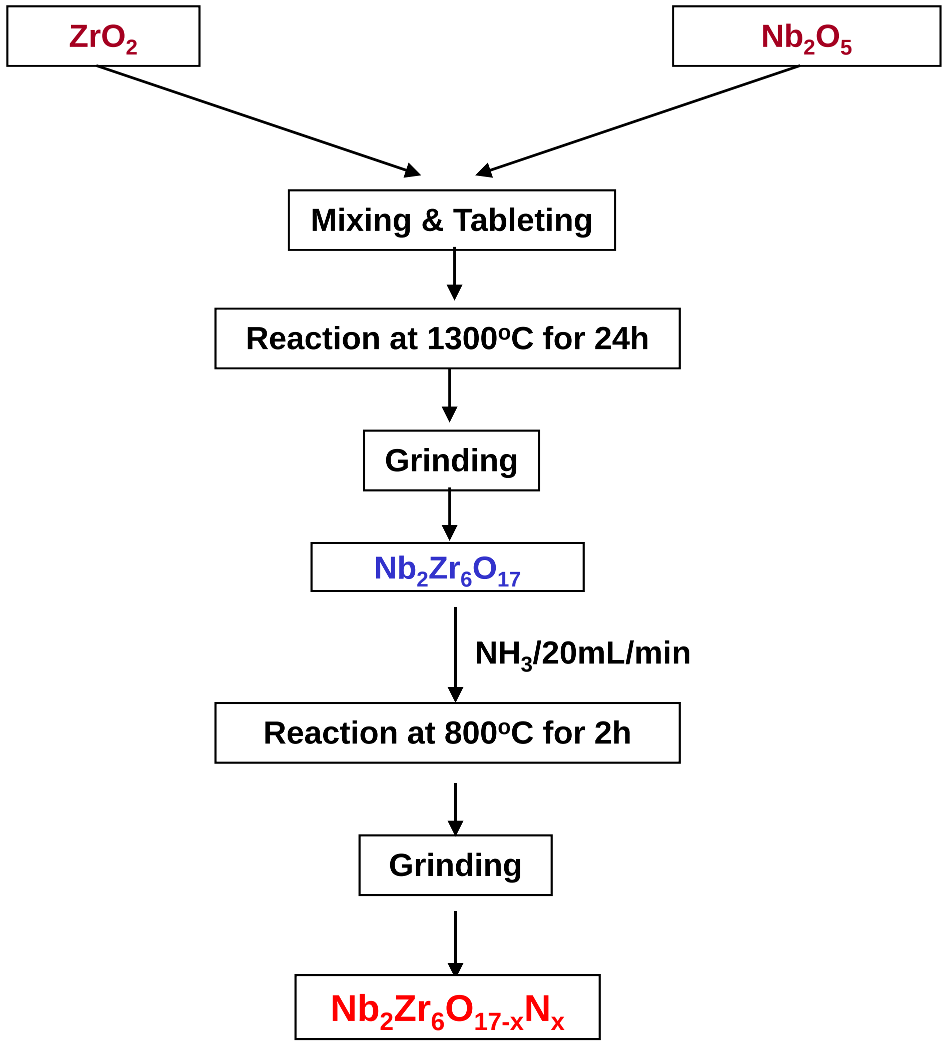
↓

$ZnBiVO_4$

Specific surface Area BET (m^2/g) : 2.50

Preparation of Visible Light Photocatalyst by N-doping

Procedure of Preparation for $Nb_2Zr_6O_{17-x}N_x$



New Visible Light Photocatalyst Synthesis by Molten Salt Method

Procedure of Preparation for $Ga_2Pb_2Nb_2O_7$

Pb(II)-oxide + **Ga(III)-oxide** + **Nb(V)-oxide**

↓

Mixing & Tableting ← **NaCl (10eq.)**

↓

Reaction at 1093°K for 4h

↓

Grinding & Washing

↓

Reaction at 1473°C for 12h

↓

Grinding

↓

$Ga_2Pb_2Nb_2O_7$

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Conclusions

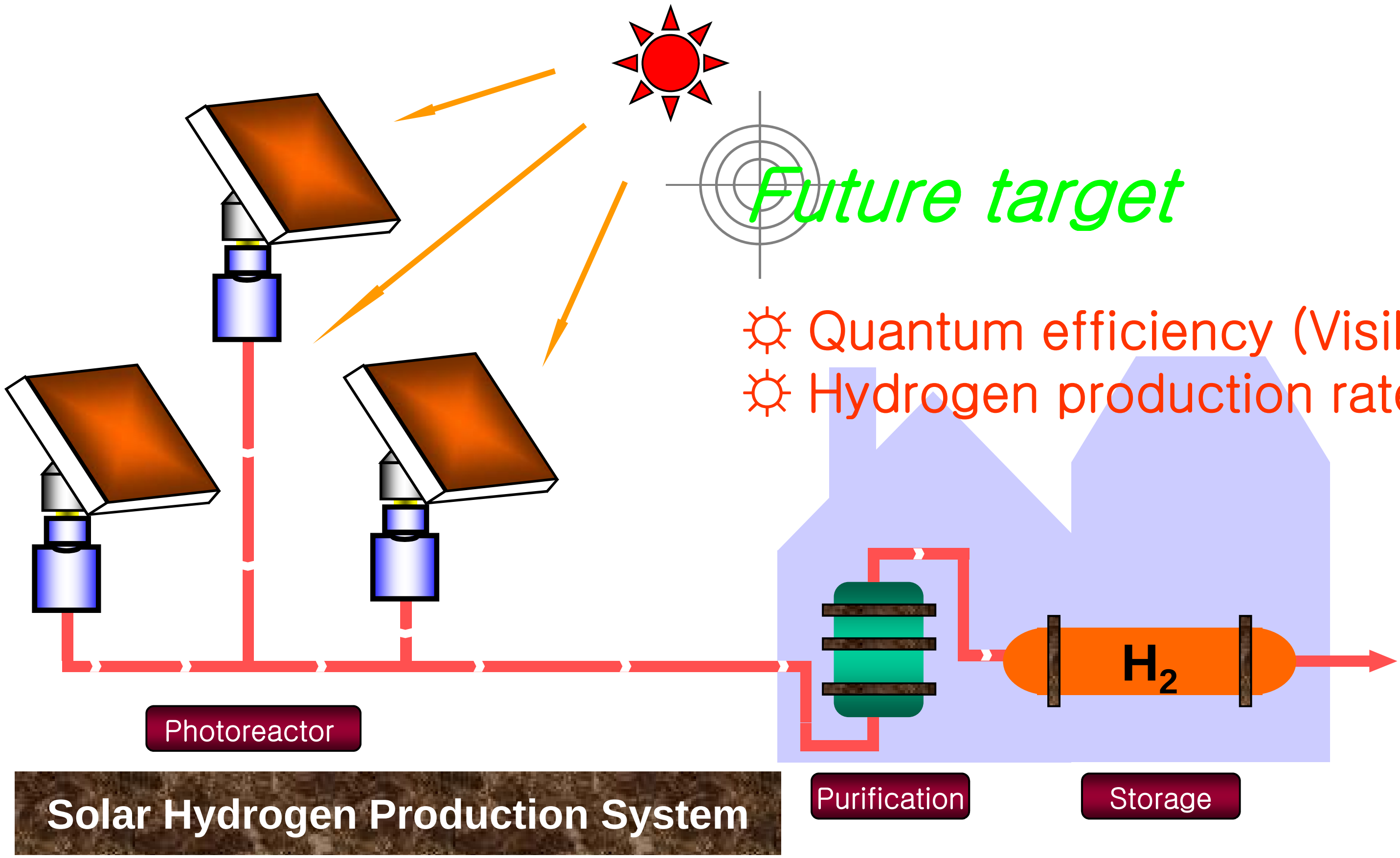
Present Status

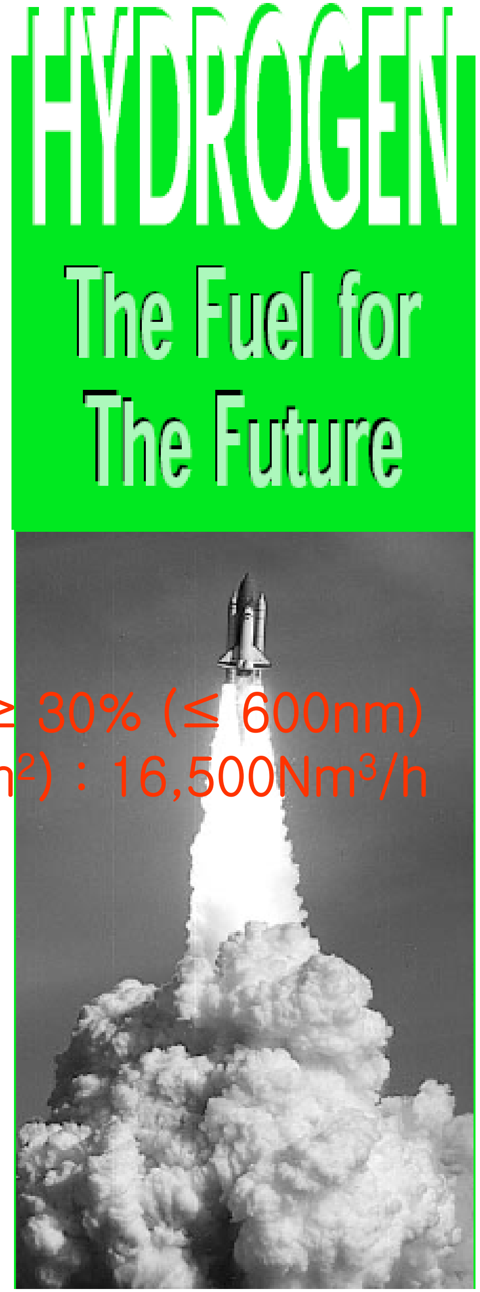
- Quantum efficiency (UV) : ~ 56%(270nm: H_2O)
- Quantum efficiency (Visible) : ~ 5.2%(410nm: H_2O)
- Quantum efficiency (Visible) : *~ 20%(500nm: H_2S)*

Future target

☼ Quantum efficiency (Visible) : ≥ 30% (≤ 600nm)

☼ Hydrogen production rate (1 km^2) : 16,500Nm^3/h





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