(UCSB, CA) 2006.8.23

Visible-light-driven Powdered Photocatalysts for Water Splitting

(Tokyo University of Science, CREST/JST)
Akihiko KUDO

Photocatalyst

Energy conversion

TiO_2
Industrial products

Environmental application

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Superhydrophilicity

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Anti-stain

Self cleaning

Water splitting
H_2 production

Target of our project

Development of new photocatalyst materials

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To make a library of photocatalyst materials

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To achieve artificial photosynthesis

(Solar H_2 production)

Topics

1. Development of highly active tantalate photocatalysts for overall water splitting (UV)

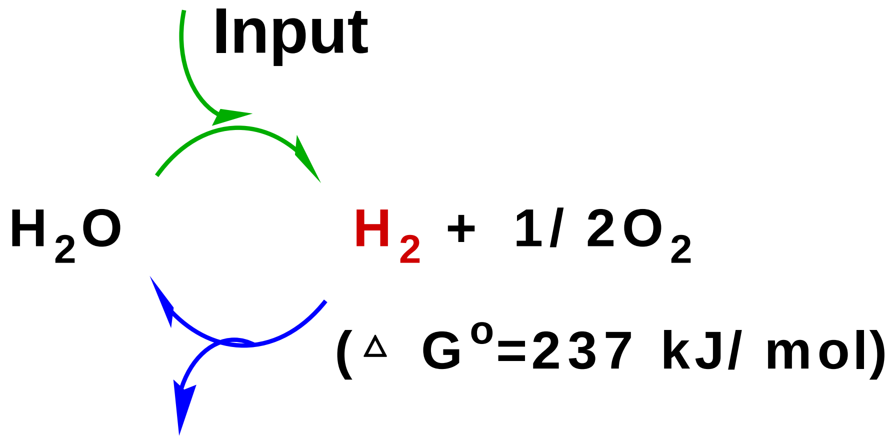
2. Development of visible-light-driven photocatalysts by band engineering (Sacrificial systems)

3. Construction of Z-schemes for overall water splitting under VIS light irradiation

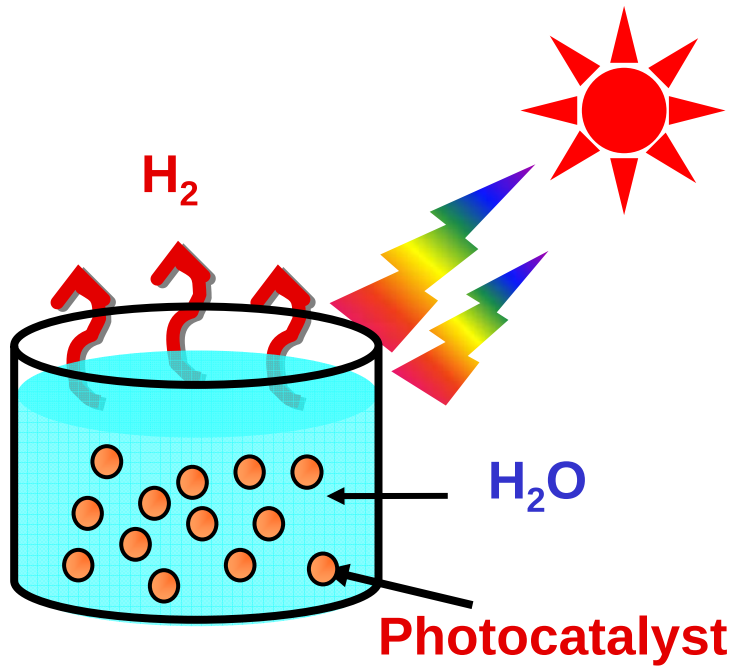
4. Development of highly active metal sulfide photocatalysts for solar hydrogen production (Sacrificial systems)

Photocatalytic water splitting
- Ideal H_2 production, Artificial photosynthesis -

Natural energy (Solar light)



Energy output
For fuel cell, hydrogen engine --



Simple system!
Advantage to
large scale system

An ultimate chemical reaction for solving energy and environmental issues

History of development of photocatalysts for water splitting

1970's-1980's (Honda-Fujishima effect, focused on TiO_2)

TiO_2, $SrTiO_3$, CdS, ZnS

1980's-1990's (Finding of new materials)

Nb,Ta,Zr oxides   Layered compounds

1990's-2000's (Achievement of highly efficient water splitting ,
Finding of various materials)

Ta mixed oxides, d^{10} metal oxides, various oxides,

metal sulfides solid solutions, oxynitrides, oxysulfides

Recent progress (Water splitting under VIS)

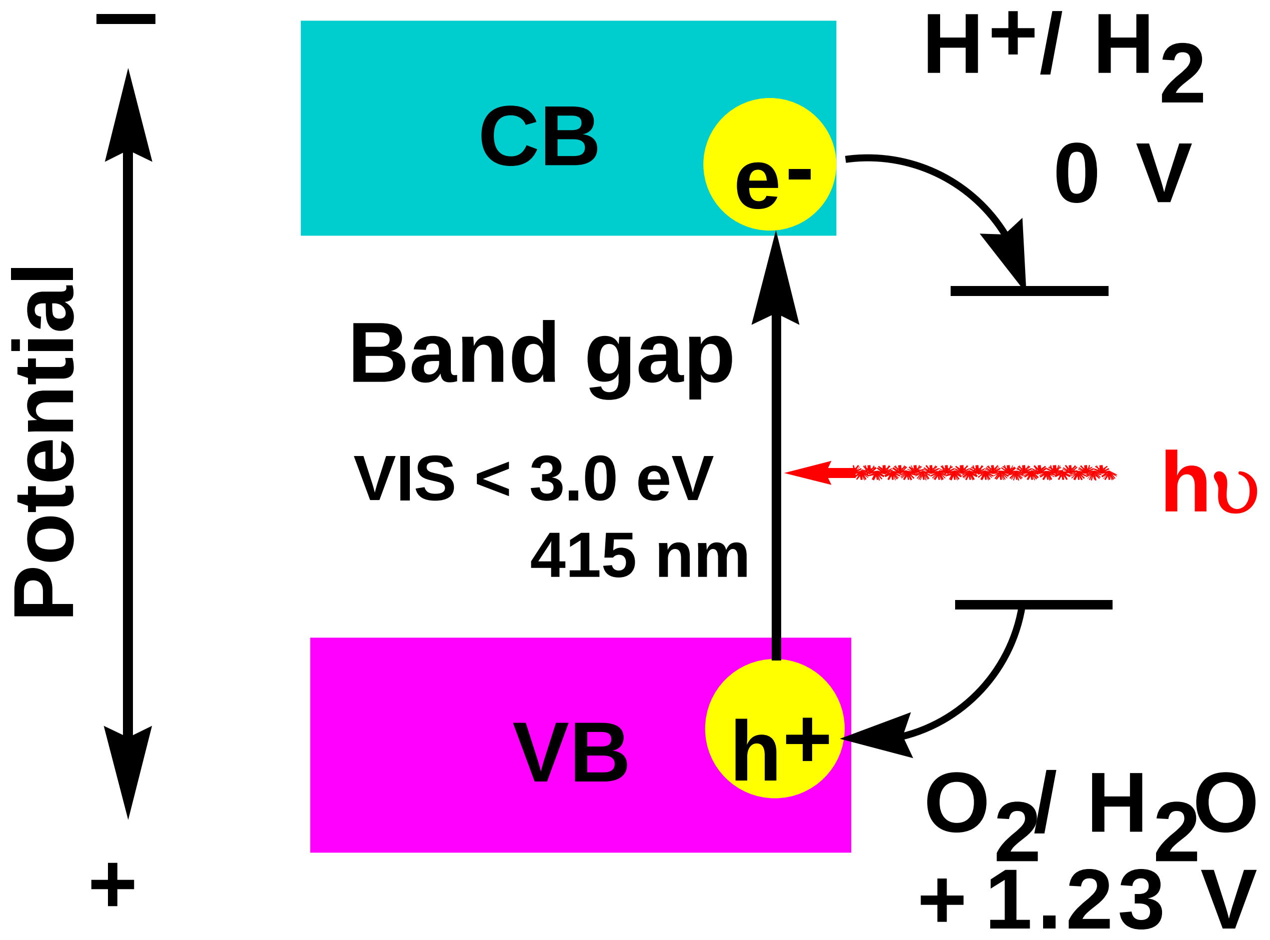
$Pt/SrTiO_3$:Cr,Ta-WO_3 (Sayama) , Pt/TaON-WO_3 (Abe)

$Ru/SrTiO_3$:Rh-$BiVO_4$ (Kudo), Cr-Rh/GaN:ZnO (Domen, Inoue)

Photocatalyst library of Kudo's group

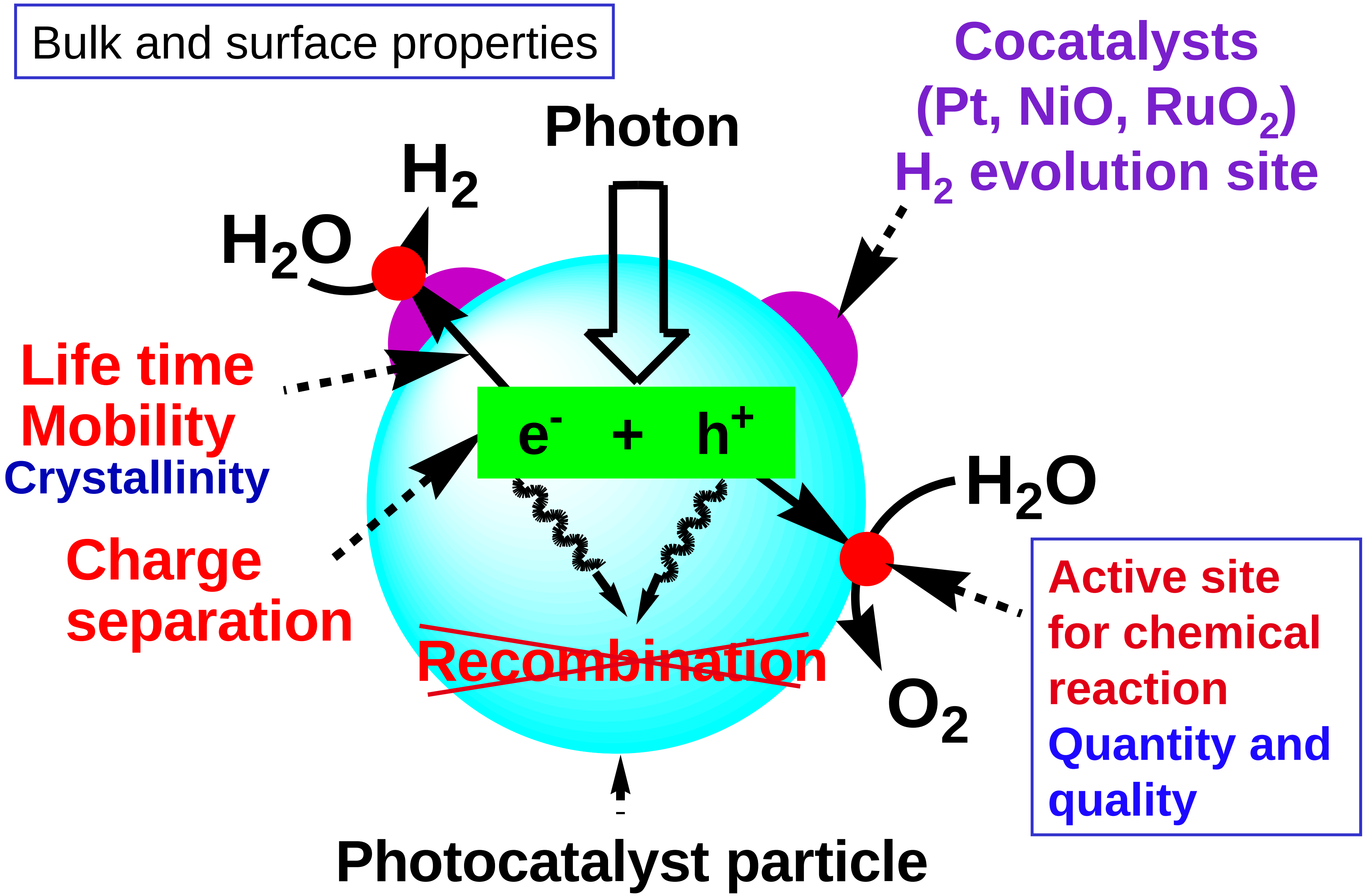
UV-responsive photocatalysts	VIS-responsive photocatalysts		
Overall water splitting	Overall water splitting	H_2 evolution (Sacrificial)	O_2 evolution (Sacrificial)
ANb_2O_6	$SrTiO_3$:Rh-$BiVO_4$	ZnS:Cu	$BiVO_4$
$Sr_2Nb_2O_7$	$SrTiO_3$:Rh-Bi_2MoO_6	ZnS:Ni	Bi_2MoO_6
$Cs_2Nb_4O_{11}$	$SrTiO_3$:Rh-WO_3	ZnS: Pb,Cl	Bi_2WO_6
$Ba_5Nb_4O_{15}$		$NaInS_2$	$AgNbO_3$
$ATaO_3$		$AgGaS_2$	Ag_3VO_4
$NaTaO_3$:La		$CuInS_2$- $AgInS_2$-ZnS	TiO_2:Cr,Sb
ATa_2O_6		$SrTiO_3$:Cr,Sb	TiO_2:Ni,Nb
$K_3Ta_3Si_2O_{13}$		$SrTiO_3$:Cr,Ta	TiO_2:Rh
$K_3Ta_3B_2O_{12}$		$SrTiO_3$:Rh	$PbMoO_4$:Cr
$K_2LnTa_5O_{15}$		$SnNb_2O_6$	$SnNb_2O_6$
$AgTaO_3$			

Mechanism of semiconductor photocatalysts (I)
- band engineering-

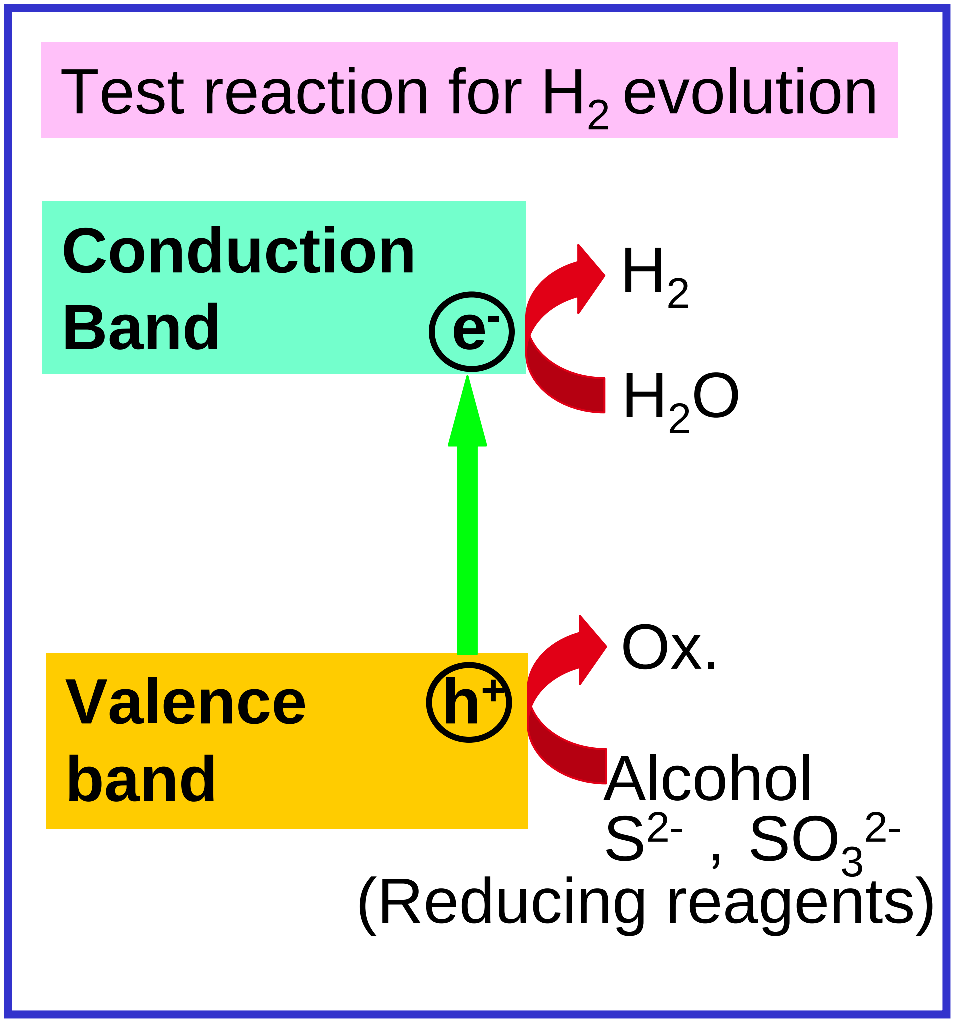


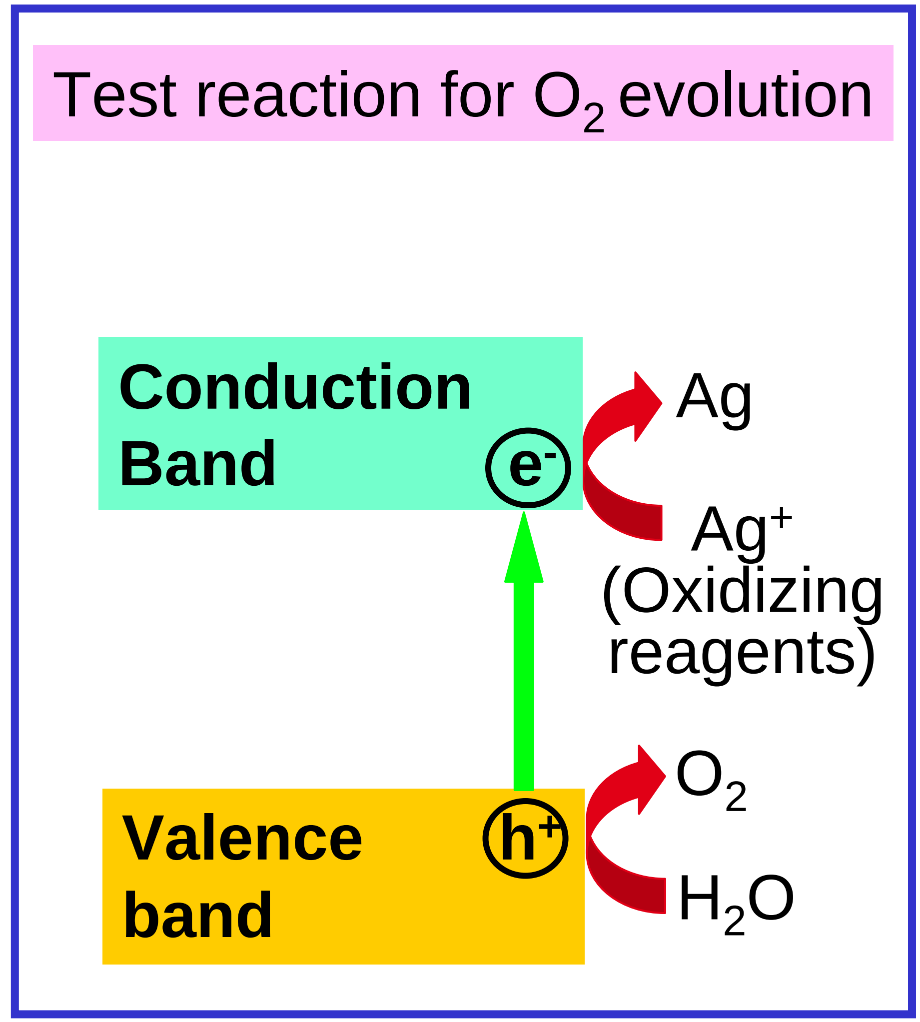
Band structure → Thermodynamic requirement

Mechanism of powdered photocatalysts (II) - kinetic parameters -



H_2 or O_2 evolution reaction in the presence of sacrificial reagents
- Half reactions for water splitting -



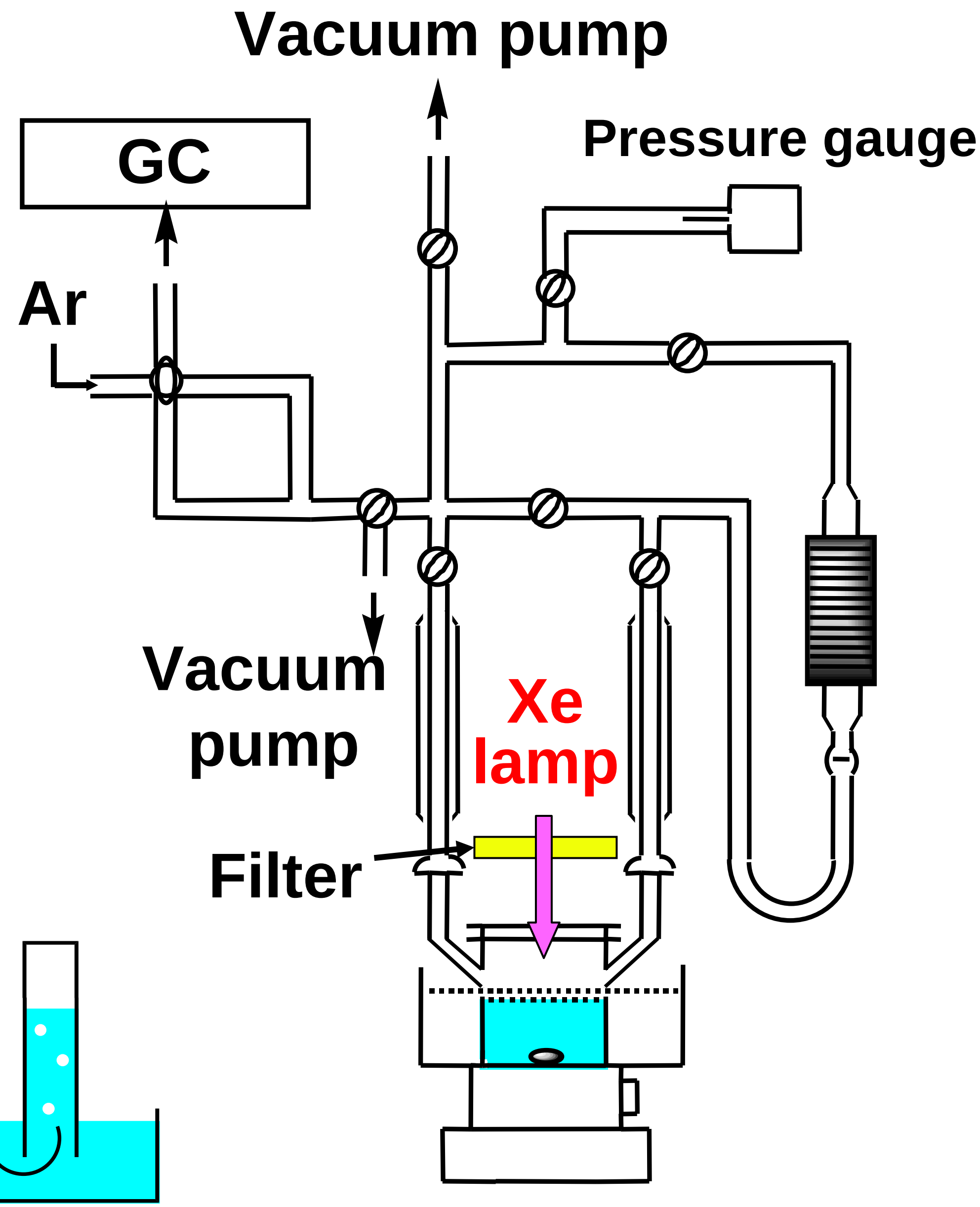


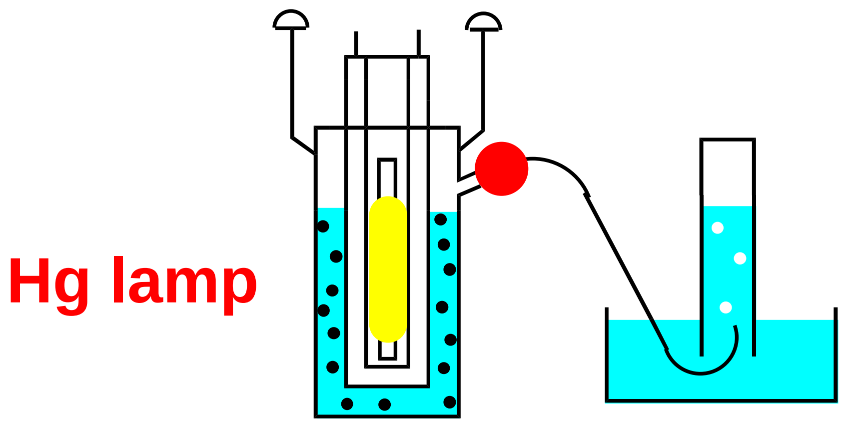
Factors → Band level, reaction site, recombination

Experimental setup for photocatalytic reaction

Gas-closed circulation system

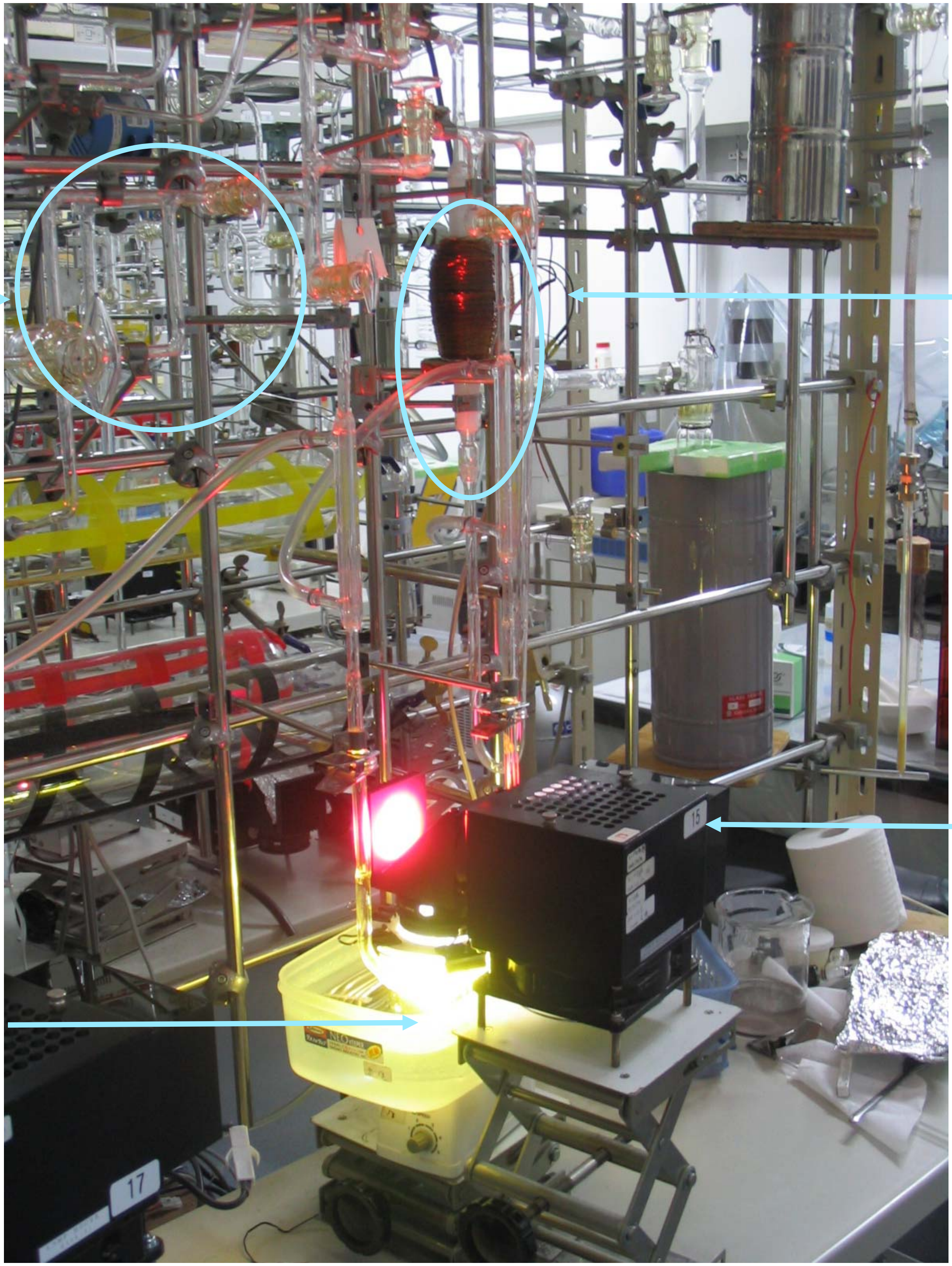
- Light source of UV
  400W High pressure Hg lamp
- Light source of VIS
  300W Xe lamp + filter
- Solar simulator (AM-1.5)



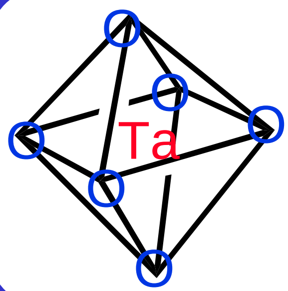


For UV irradiation

For VIS irradiation


Sampling port to GC
Gas circulation pump
300W Xe lamp
Reactor

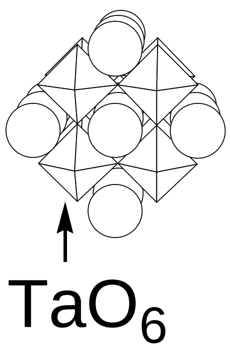
Topic 1 Highly active tantalate photocatalysts for water splitting (UV)

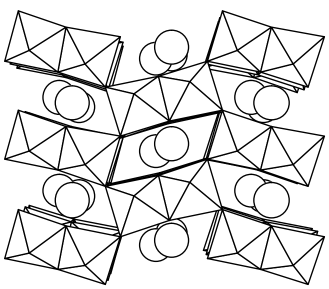


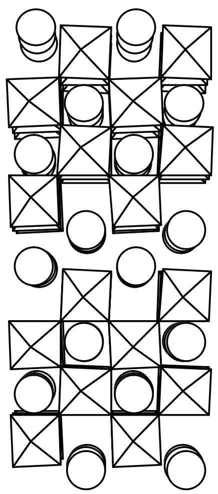
TaO_6
Octahedral units

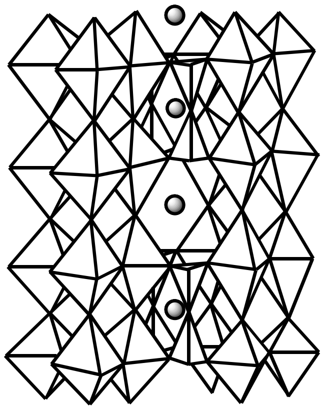
H. Kato and A. Kudo, *Catal. Today*, **78**, 561 (2003).

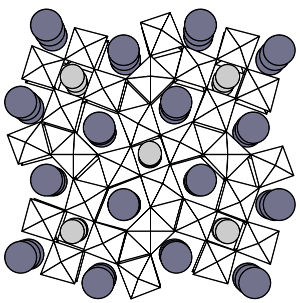
$ATaO_3$ (A=Li, Na, K)	$A'Ta_2O_6$ (A'=Ca, Sr, Ba)	$Sr_2Ta_2O_7$	$K_3Ta_3Si_2O_{13}$	$K_2LnTa_5O_{15}$











Perovskite (ilumenite) | Calcio Columbite | Layered perovskite | Tungsten bronze

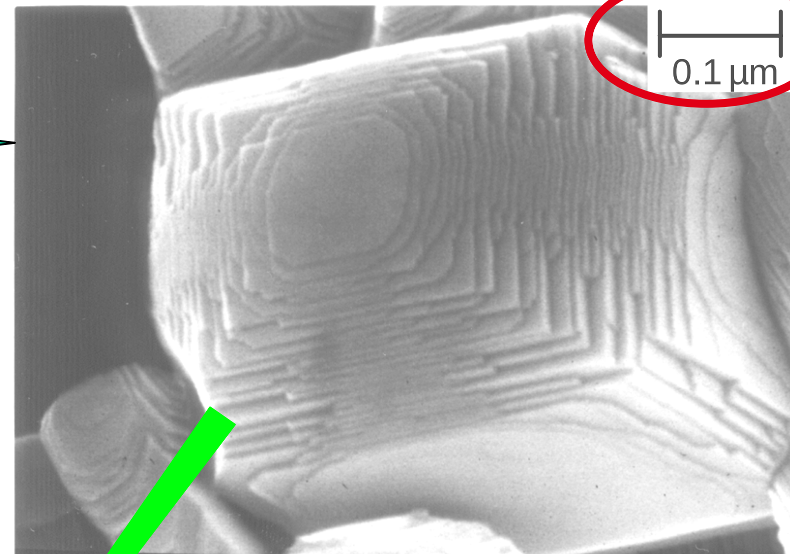
Water splitting over tantalate photocatalysts under UV irradiation

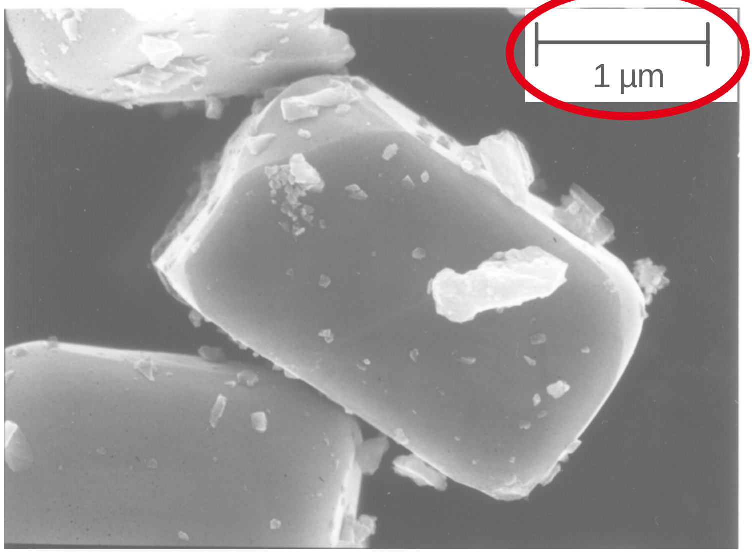
Photocatalyst	Band gap / eV	NiO loaded / mass%	Activity / μmol/h H_2	Activity / μmol/h O_2
$K_3Ta_3Si_2O_{13}$	4.1	None	53	23
$K_3Ta_3Si_2O_{13}$	4.1	1.3	390	200
$LiTaO_3$	4.7	None	430	220
$LiTaO_3$	4.7	0.10	98	52
$NaTaO_3$	4.0	None	160	86
$NaTaO_3$	4.0	0.05	2180	1100
$KTaO_3$	3.6	None	29	13
$KTaO_3$	3.6	0.10	7.4	2.9
$CaTa_2O_6$	4.0	None	21	8.3
$CaTa_2O_6$	4.0	0.10	72	32
$SrTa_2O_6$	4.4	None	140	66
$SrTa_2O_6$	4.4	0.10	960	490
$BaTa_2O_6$	4.1	None	33	15
$BaTa_2O_6$	4.1	0.30	629	303
$Sr_2Ta_2O_7$	4.6	None	57	18
$Sr_2Ta_2O_7$	4.6	0.15	1000	480
$K_2PrTa_5O_{15}$	3.8	None	10	3
$K_2PrTa_5O_{15}$	3.8	0.1	1550	830

Cat.: 1.0 g, H_2O: 390 ml, Inner irradiation quartz cell, 400 W Hg lamp

SEM images of $NaTaO_3$ and $NaTaO_3$:La photocatalysts

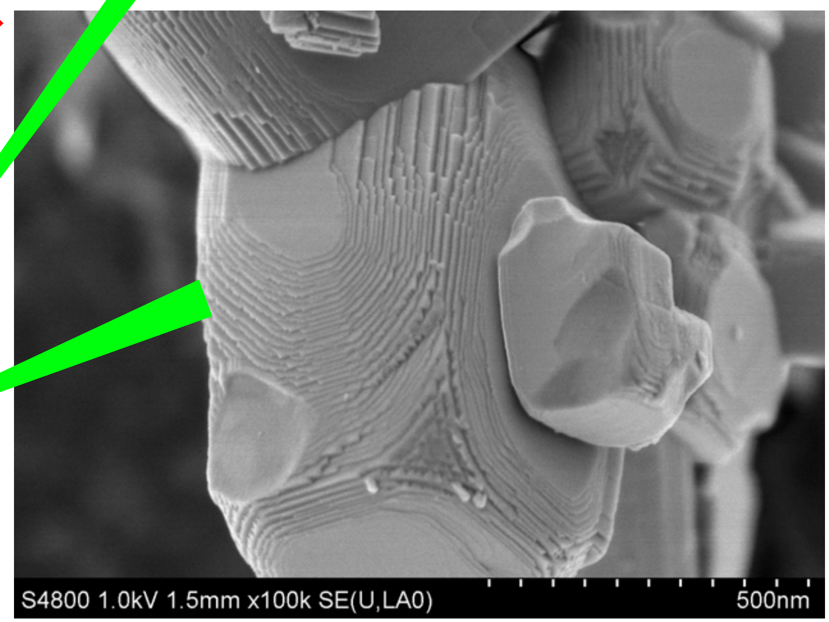
K_2CO_3, Ta_2O_5, La_2O_3 → 1423K





$NaTaO_3$

La doping

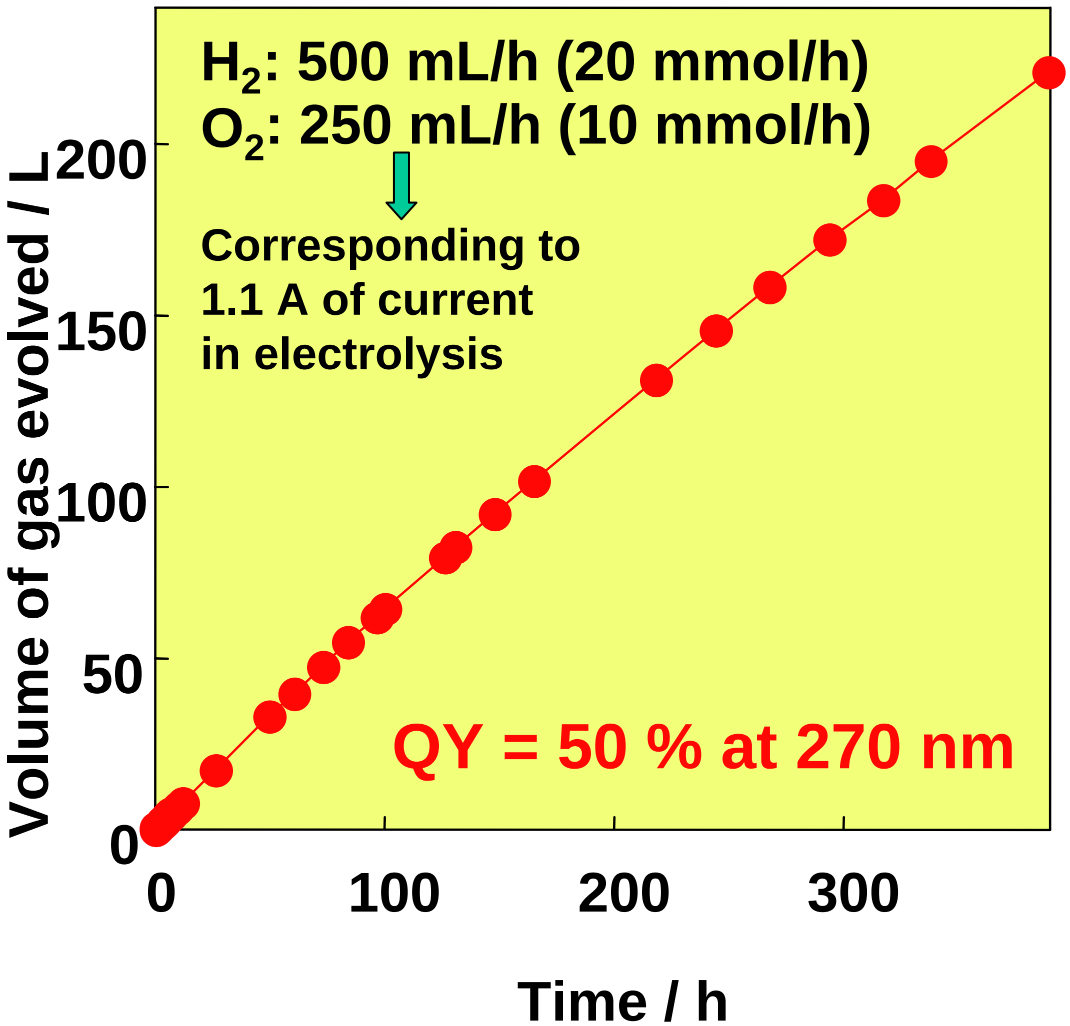


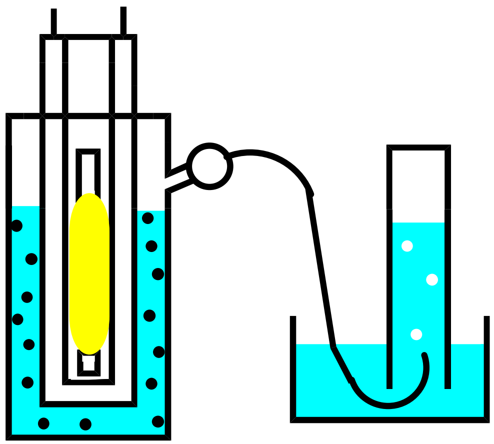
$NaTaO_3$:La

Fine particle with high crystallinity

Surface nano-step structure

Water splitting over NiO(0.2wt%)/$NaTaO_3$:La1.5% photocatalyst



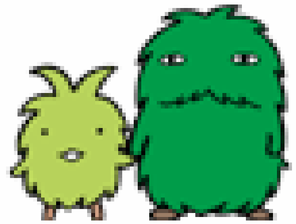


Catalyst:1g,
1mM NaOH:390mL,
inner irradiation quartz cell,
400W high-pressure Hg lamp

Band Gap: 4.1 eV

Kato, Asakura, Kudo, *J. Am. Chem. Soc.*, **125**, 3082 (2003).

Photocatalytic water splitting on NiO/$NaTaO_3$:La



BG:4.1eV
QY:56% (270nm)

Responsive to 300nm

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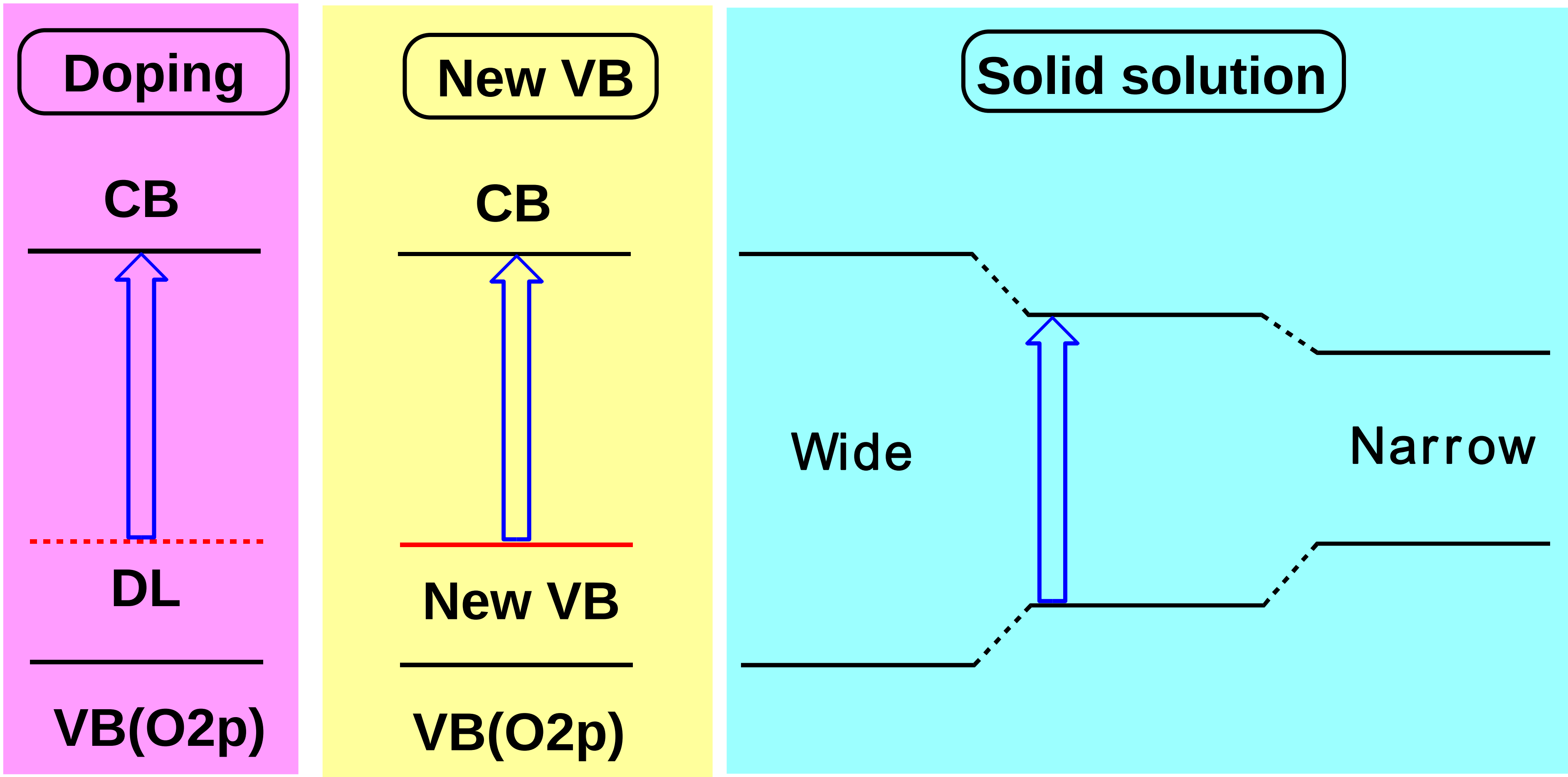
200W Xe-Hg Lamp

Photocatalyst Powdered Layer

Highly efficient water splitting using a powdered photocatalyst is actually possible.

Topic 2 Band engineering for design of visible-light-driven photocatalysts

A. Kudo, H. Kato, and I. Tsuji, *Chem. Lett.*, **33**, 1534 (2004).



TiO_2, $SrTiO_3$
Dopant → recombination center

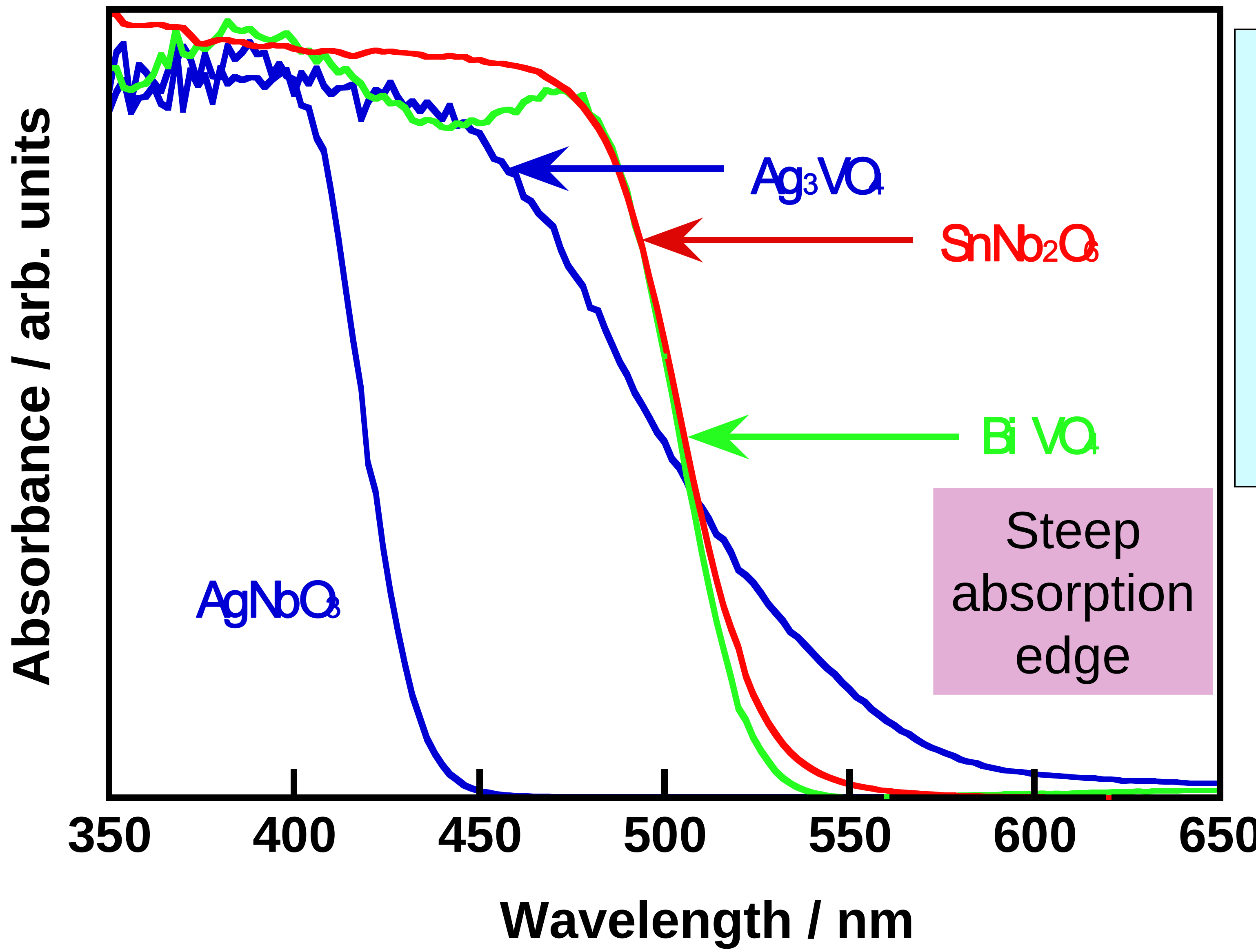
Activities of doped photocatalysts using VIS (Sacrificial systems)

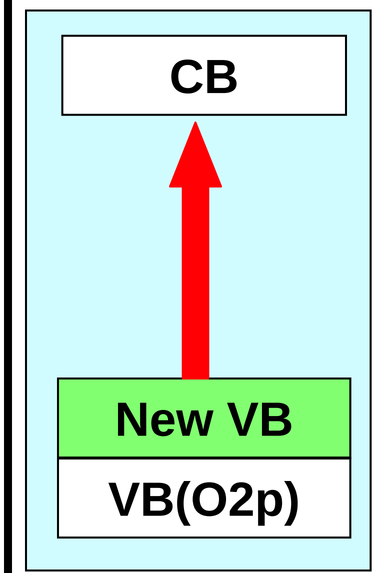
Host	Dopant (ca. 1%)	EG / eV	$h\nu$ / nm	Activity / μmol h^{-1}	
				H_2 [a)]	O_2 [b)]
$SrTiO_3$	Cr/Sb	2.4	>420	78	0.9
	Cr/Ta	2.3	>440	70	0
	Ni/Ta	2.8	>420	2.4	0.5
	Rh	2.3	>440	117	0
TiO_2(rutile)	Cr/Sb	2.2	>420	0	32
	Cr	-	>420	-	0
	Rh/Sb	2.2	>440	0	22
	Rh	-	>440	-	0
	Ni/Nb	2.6	>440	0	13
WO_3	-	2.8	>420	-	48

Catalyst: 0.3g, Light source: 300W Xe lamp + cut off filters
a) 10vol%CH_3OHaq 150mL, b) O_2 0.05mol/L $AgNO_3$aq 150mL

Codoping ➡ charge compensation, suppression of mixed valency

Diffuse reflectance spectra of VB-controlled photocatalysts





Ag4d
Sn5s
Bi6s

Activities of photocatalysts valence-band-controlled with Ag4d, Bi6s, Sn5s under visible light irradiation (λ > 420 nm)

Photocatalyst	BG / eV	Sacrificial reagent	Activity / μmol/h	
			H_2 [a)]	O_2 [b)]
$AgNbO_3$	2.86	$AgNO_3$	---	37
Ag_3VO_4	2.0	$AgNO_3$	---	17
$BiVO_4$	2.4	$AgNO_3$	---	200
$Pt/SnNb_2O_6$	2.3	CH_3OH	14	---
$SnNb_2O_6$	2.3	$AgNO_3$	---	5
WO_3	2.8	$AgNO_3$	---	48

Catalyst: 0.3g, Light source: 300W Xe lamp

a) H_2 evolution reaction: 10vol%CH_3OHaq 150mL (cocatalyst: Pt)

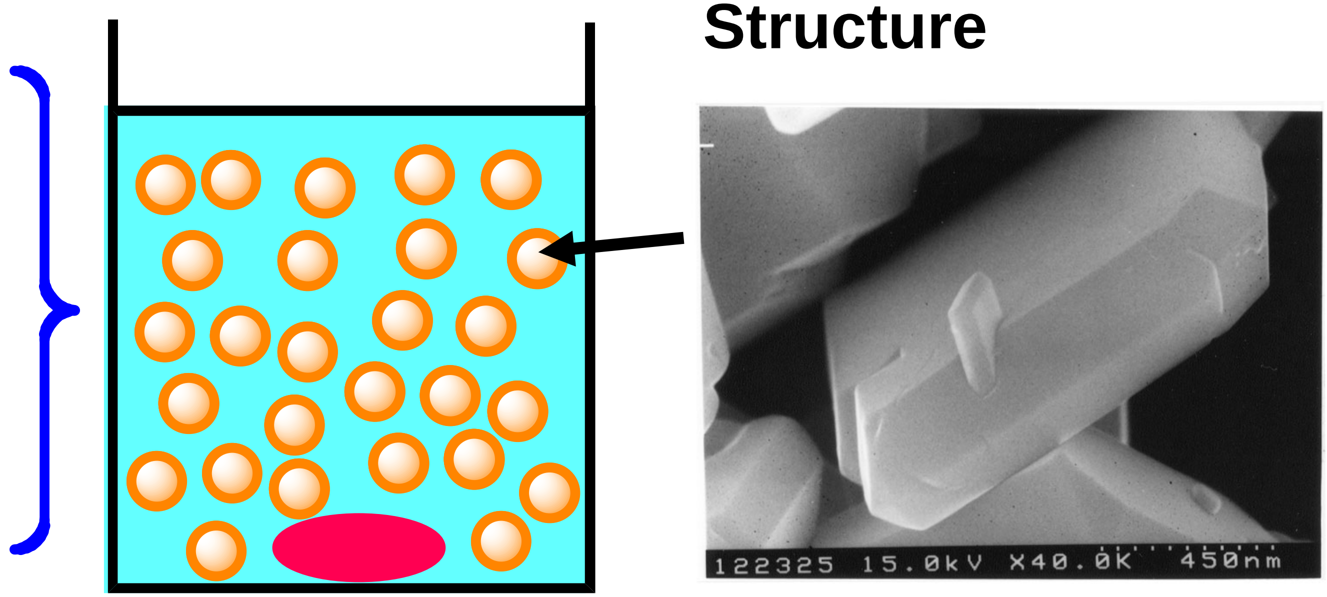
b) O_2 evolution reaction: 0.05mol/L $AgNO_3$aq 150mL

Preparation of $BiVO_4$ photocatalyst

Aqueous process

$Bi(NO_3)_3{\bullet}5H_2O$
+
Vanadates
+
H_2O

Monoclinic Scheelite Structure

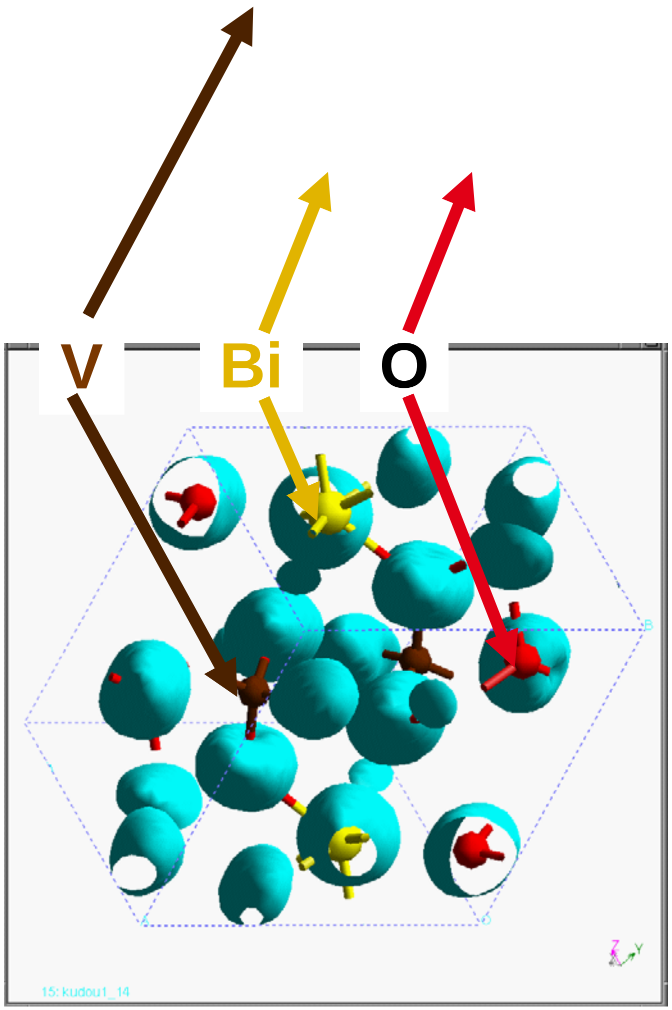


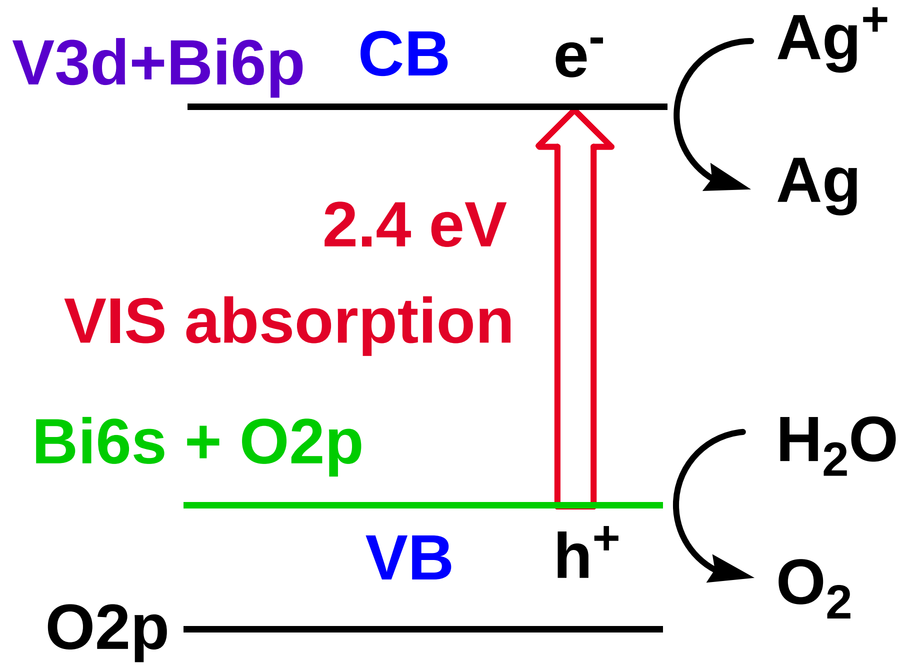
Ambient temperature and pressure in aqueous media
→ Environmentally friendly process

A. Kudo, K. Omori, and H. Kato, *J. Am. Chem. Soc.*, **121**, 11459 (1999).
S. Tokunaga, H. Kato, and A. Kudo, *Chem. Mater.*, **13**, 4624 (2001).

Band structure of $BiVO_4$ photocatalyst

LUMO
(Bottom of CB)

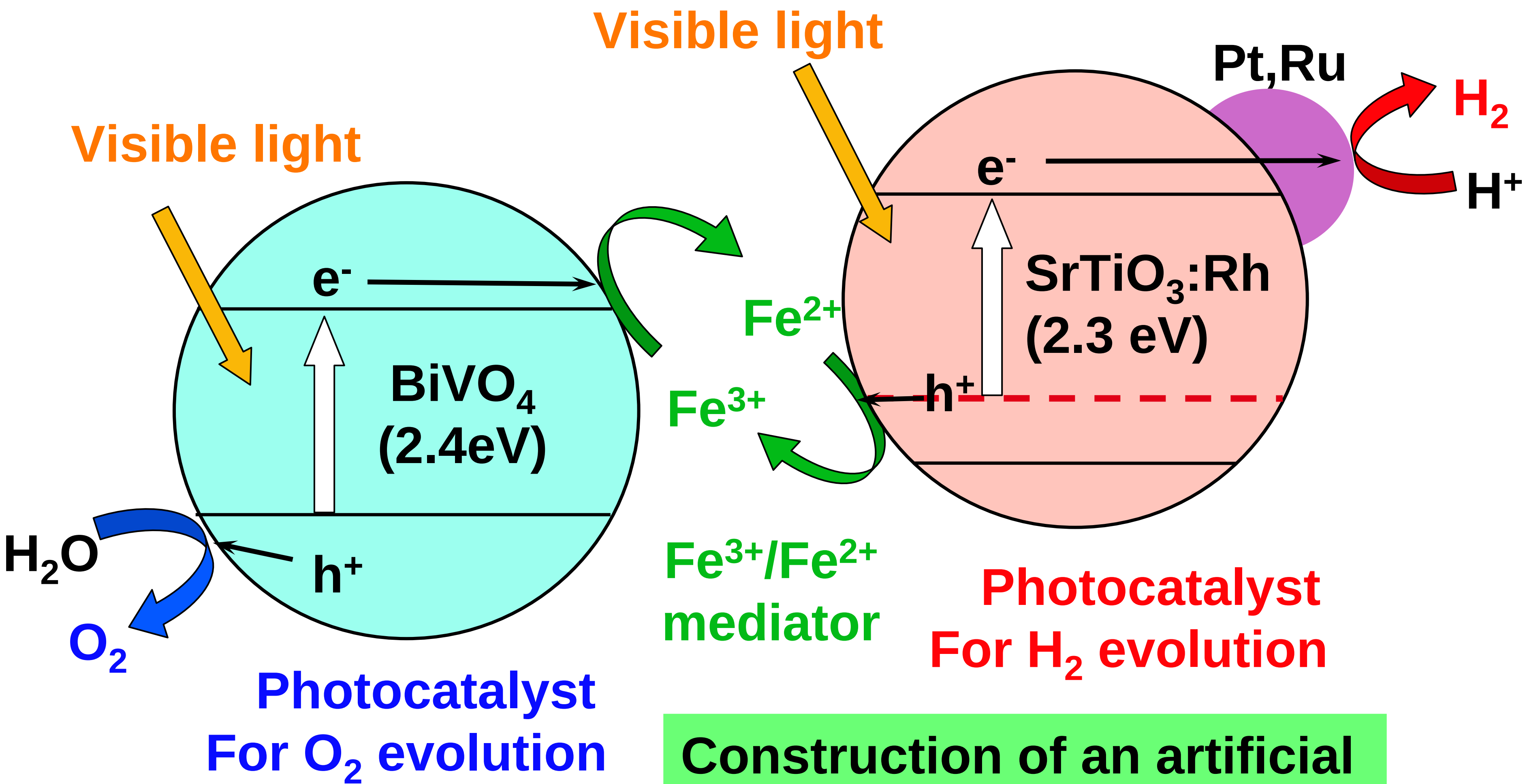




HOMO
(Top ofVB)

Calculated by Prof. Kobayashi
(Kyoto Institute of Technology)

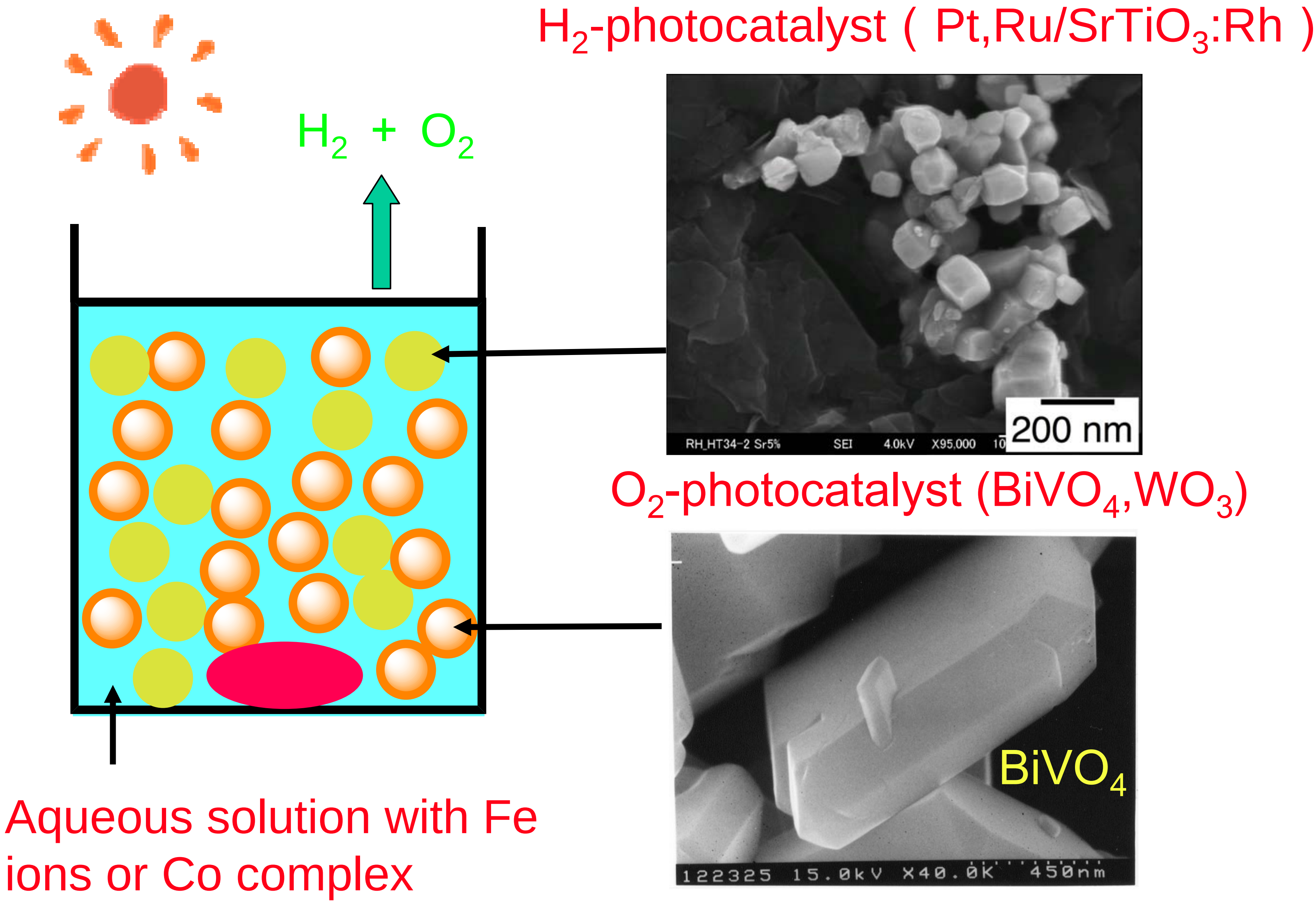
Topic 3 Water splitting using visible light - Two photon process (Z-scheme) -



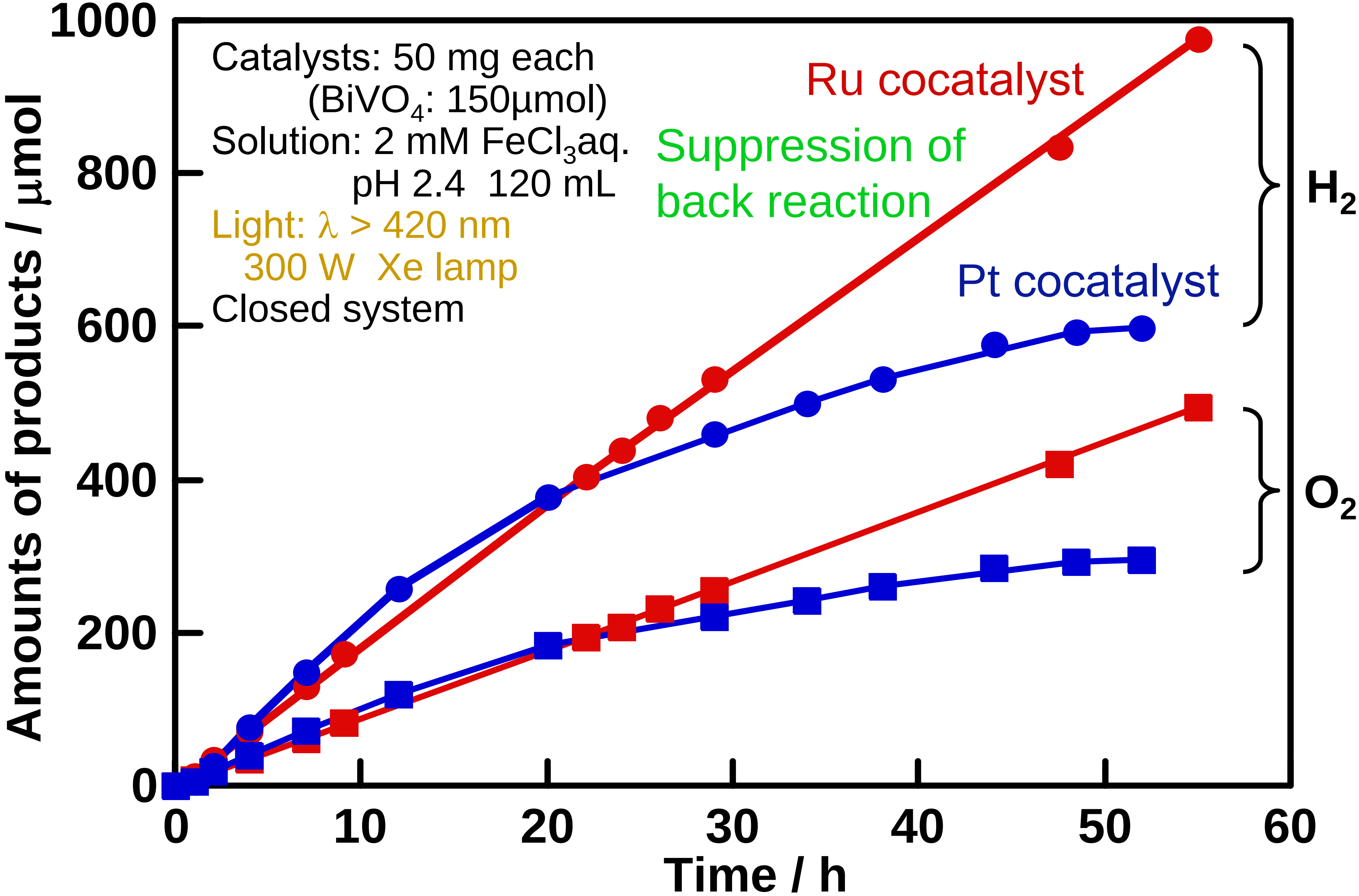
Construction of an artificial photosynthesis system

H. Kato, A. Kudo, *et. al.*, *Chem. Lett.*, **33**, 1348 (2004).

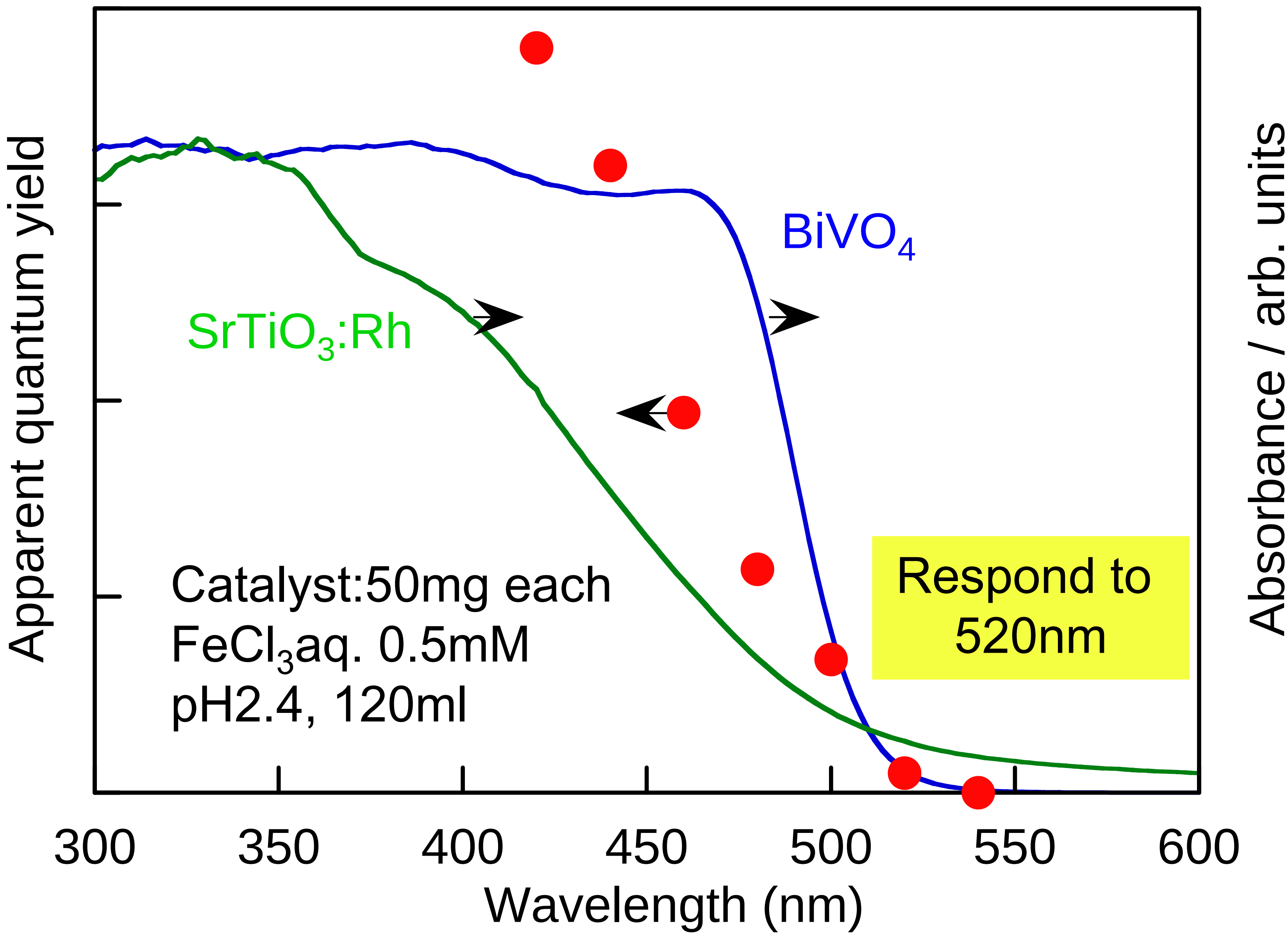
Z-scheme photocatalyst system using nano-oxides for solar hydrogen production



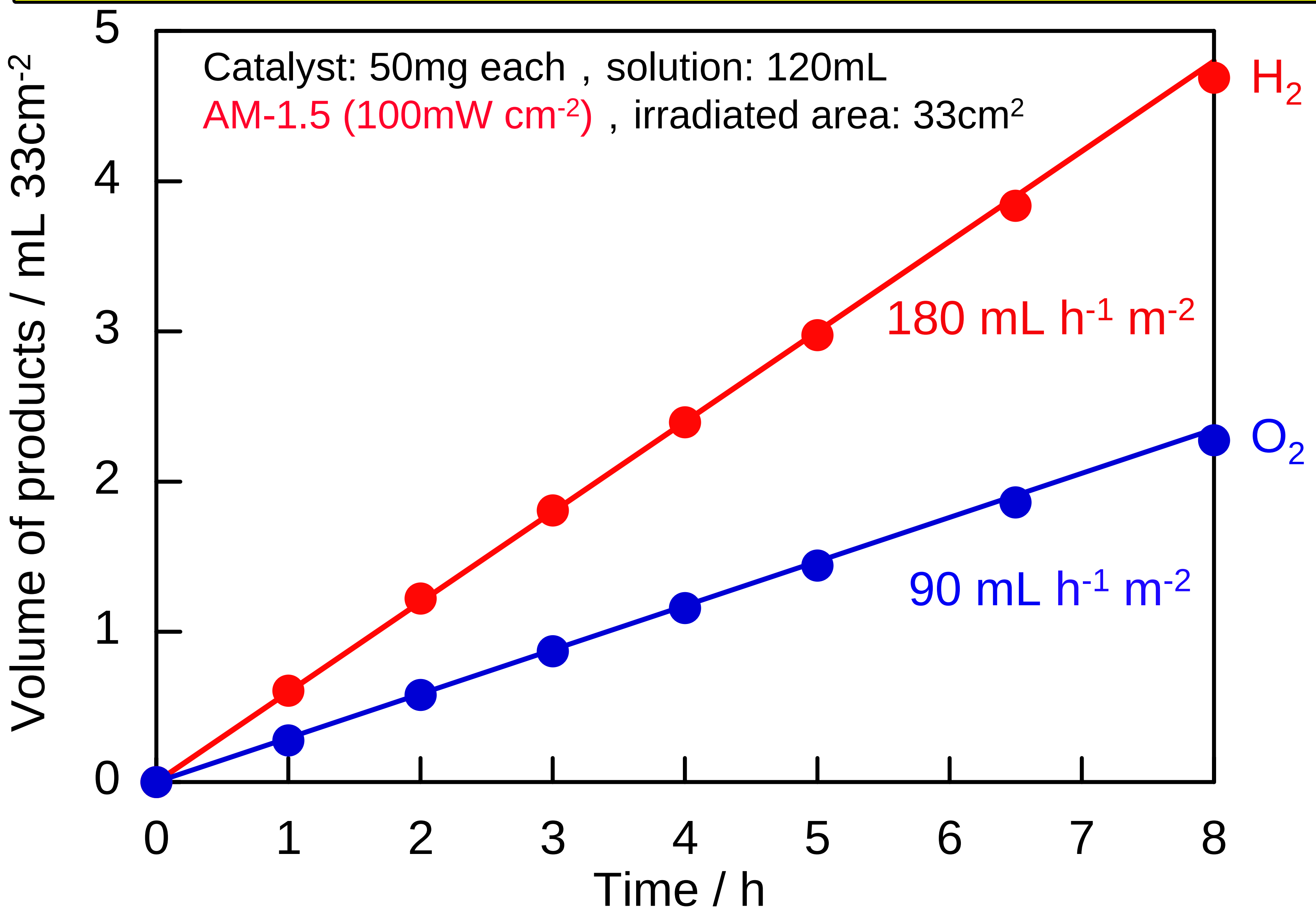
Water splitting by (Ru/SrTiO$_3$:Rh)-(WO$_3$) and (Pt/SrTiO$_3$:Rh)-(WO$_3$) systems under VIS irradiation



Action spectrum of (Ru/$SrTiO_3$:Rh)-($BiVO_4$)-$FeCl_3$ system for water splitting

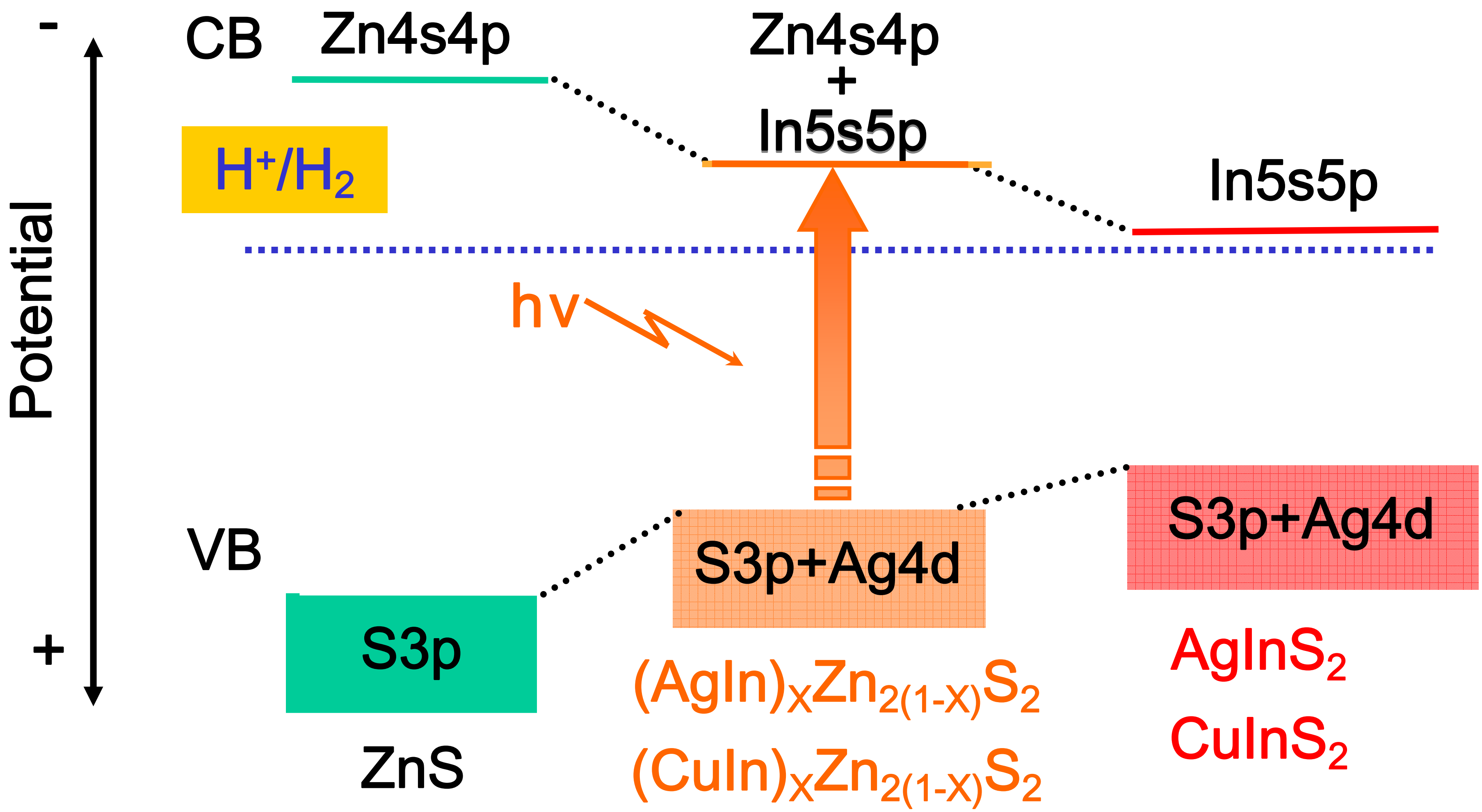


Solar hydrogen production from water
by (Ru/$SrTiO_3$:Rh_HT)-($BiVO_4$)-$FeCl_3$ system



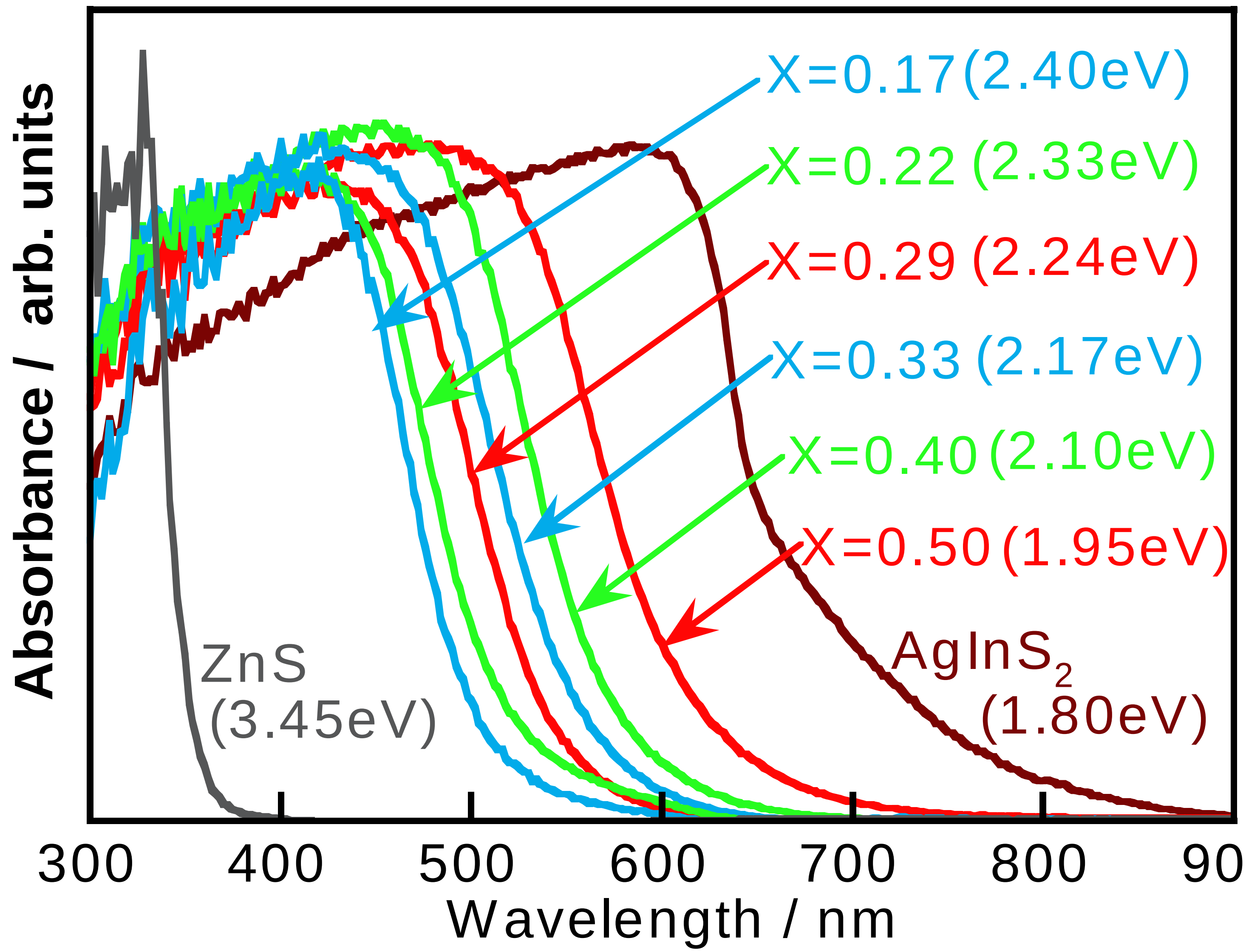
Topic 4 Highly active metal sulfide photocatalysts for solar H_2

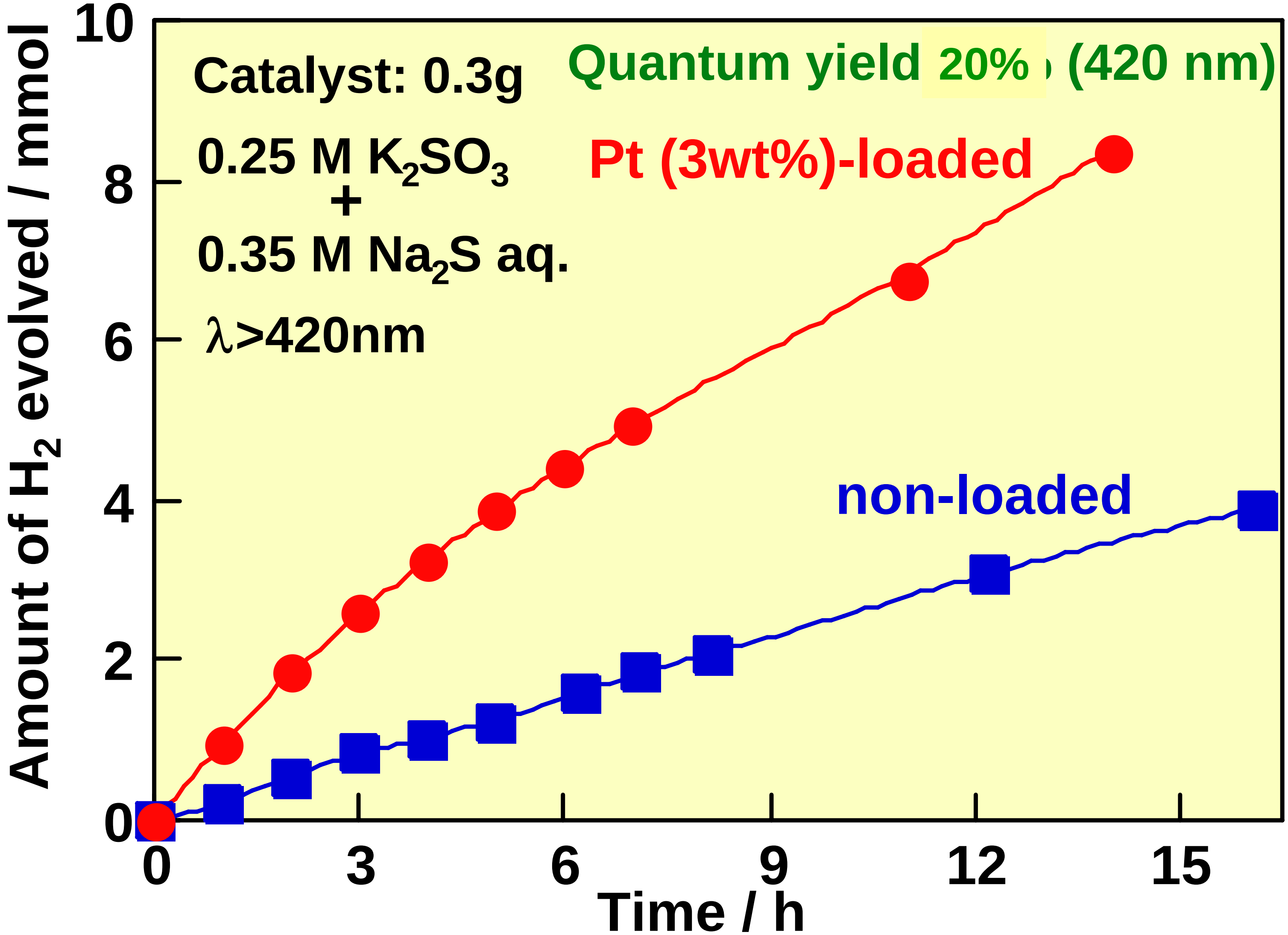
Band engineering by making a solid solution



I. Tsuji, A.. Kudo, *et al.*, *J. Am. Chem. Soc.*, **126**, 13406 (2004).

Diffuse reflectance spectra of $(AgIn)_XZn_{2(1-X)}S_2$ solid solutions

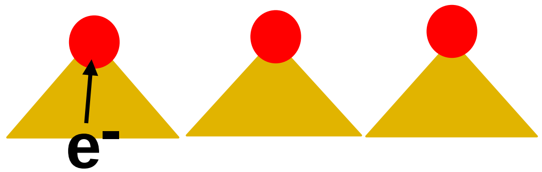




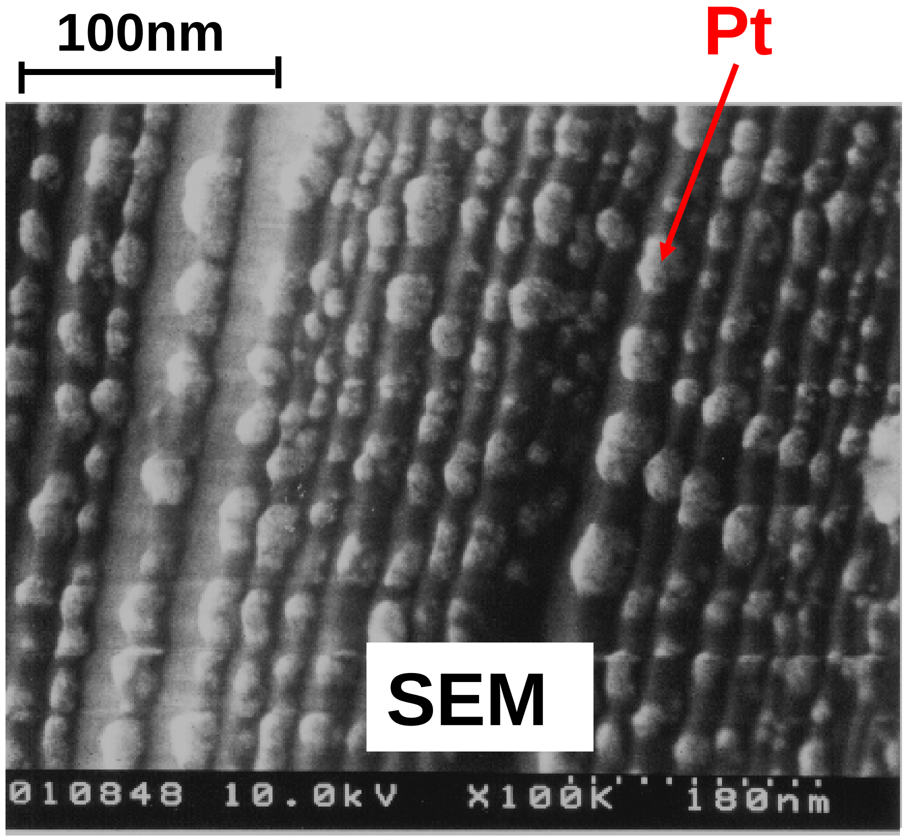
Photocatalytic H_2 evolution from an aqueous K_2SO_3 and Na_2S solution over $AgInZn_7S_9$ powder heat-treated at 1123 K under visible light irradiation

SEM and TEM images of Pt-photodeposited $(AgIn)_{0.22}Zn_{1.56}S_2$

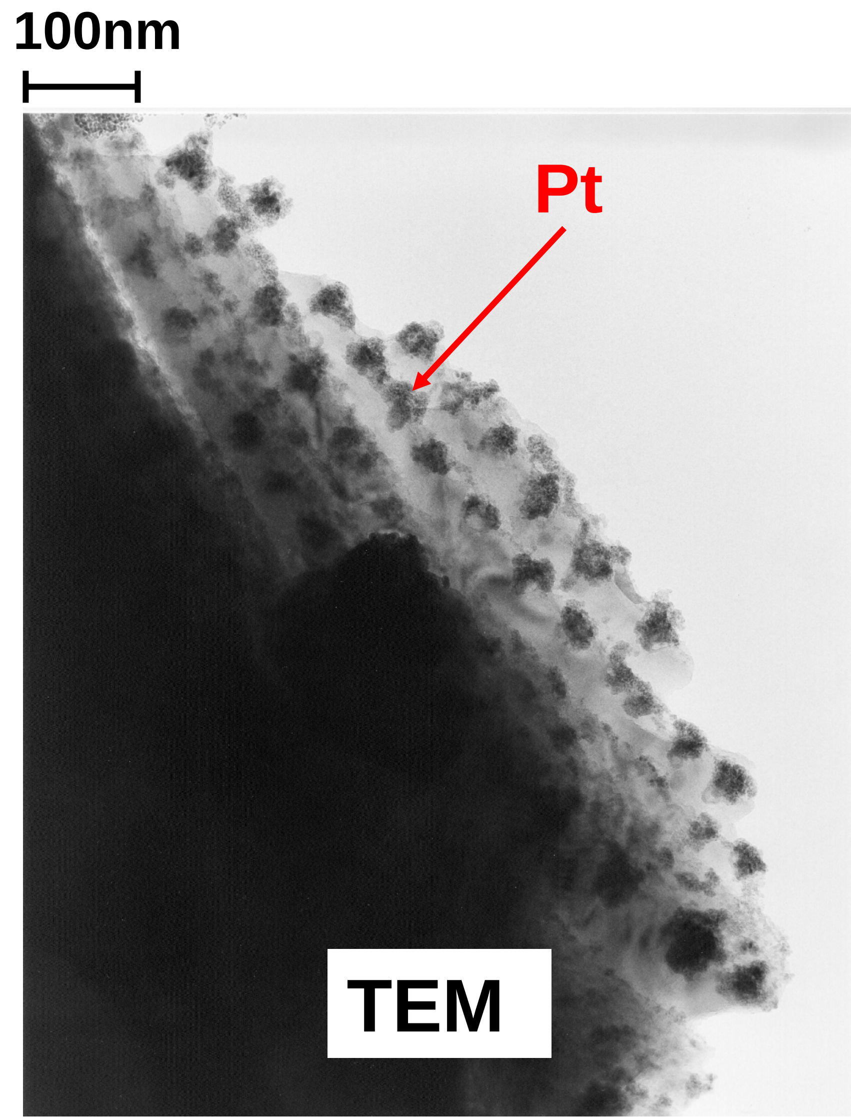
Pt photodeposited



Surface nano-structure



Pt 3wt%



Pt 1wt%

H_2 evolution on $Ru/(CuAg)_{0.25}In_{0.5}Zn_{1.0}S_2$ photocatalyst

Solar simulator(AM-1.5)

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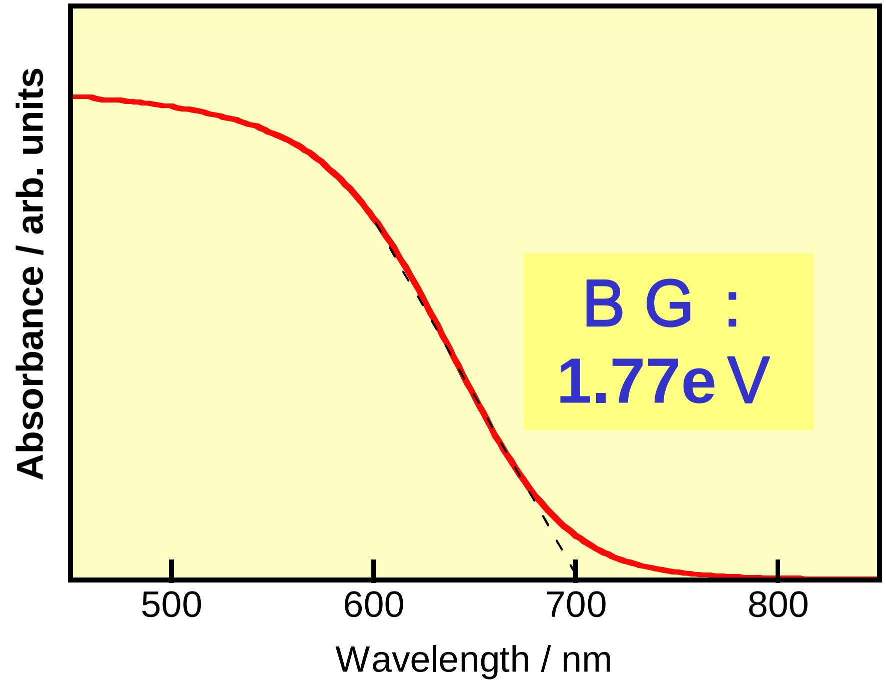
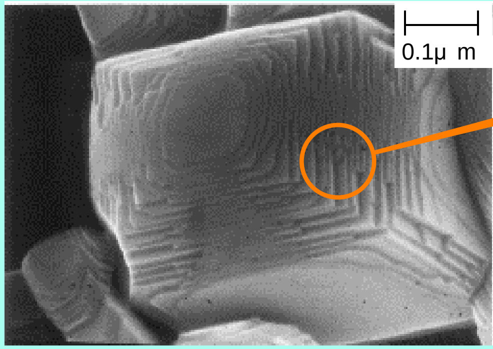
Rate of H_2 evolution
8L/h•m²

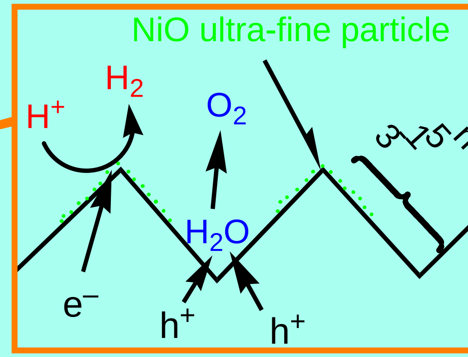


Photocatalyst Reactant: K_2SO_3 + Na_2S

I. Tsuji, H. Kato, and A. Kudo,
Angew. Chem., *Int. Ed.*, 44, 3565 (2005), *Chem. Mater., 18, 1969* (2006).

1 . Highly efficient water splitting

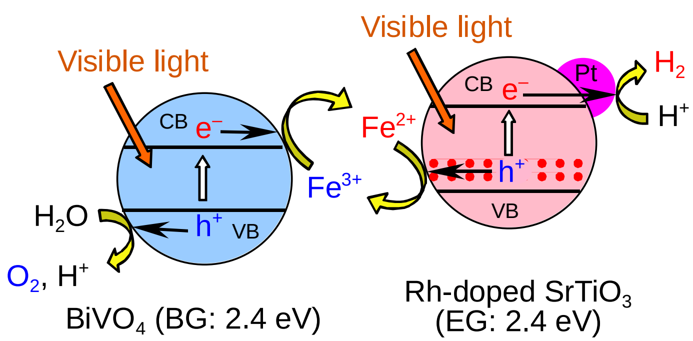


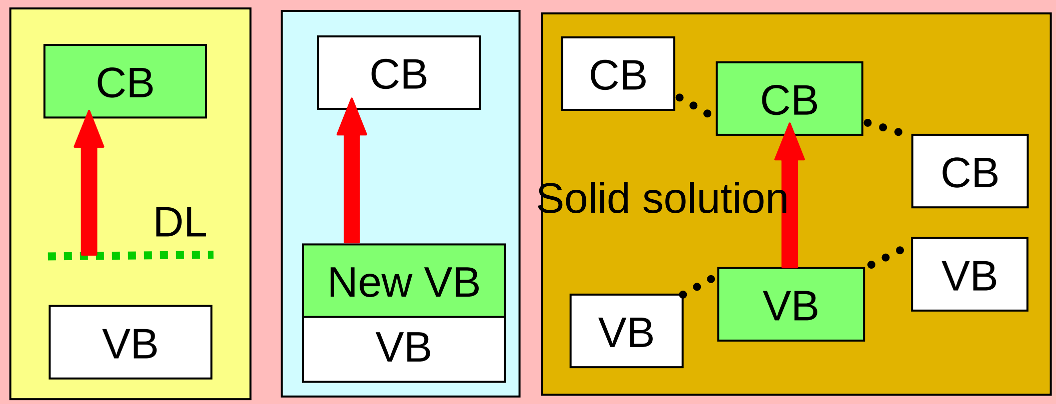


QY: 56%
(270nm)

2 . Visible-light-driven photocatalysts developed by band engineering

Water splitting by Z-scheme





ZnS:Cu or Ni (H_2)
TiO_2:Cr,Sb (O_2)
$SrTiO_3$:Cr,Ta (H_2)
$SrTiO_3$:Rh (H_2)

$SnNb_2O_6$ (H_2)
$AgNbO_3$ (O_2)
Ag_3VO_4 (O_2)
$BiVO_4$ (O_2)

ZnS-Cu,$AgInS_2$ (H_2)

Highly active under solar simulator

A. Kudo, H. Kato, and I. Tsuji, *Chem. Lett.*, **33**, 1534 (2004).