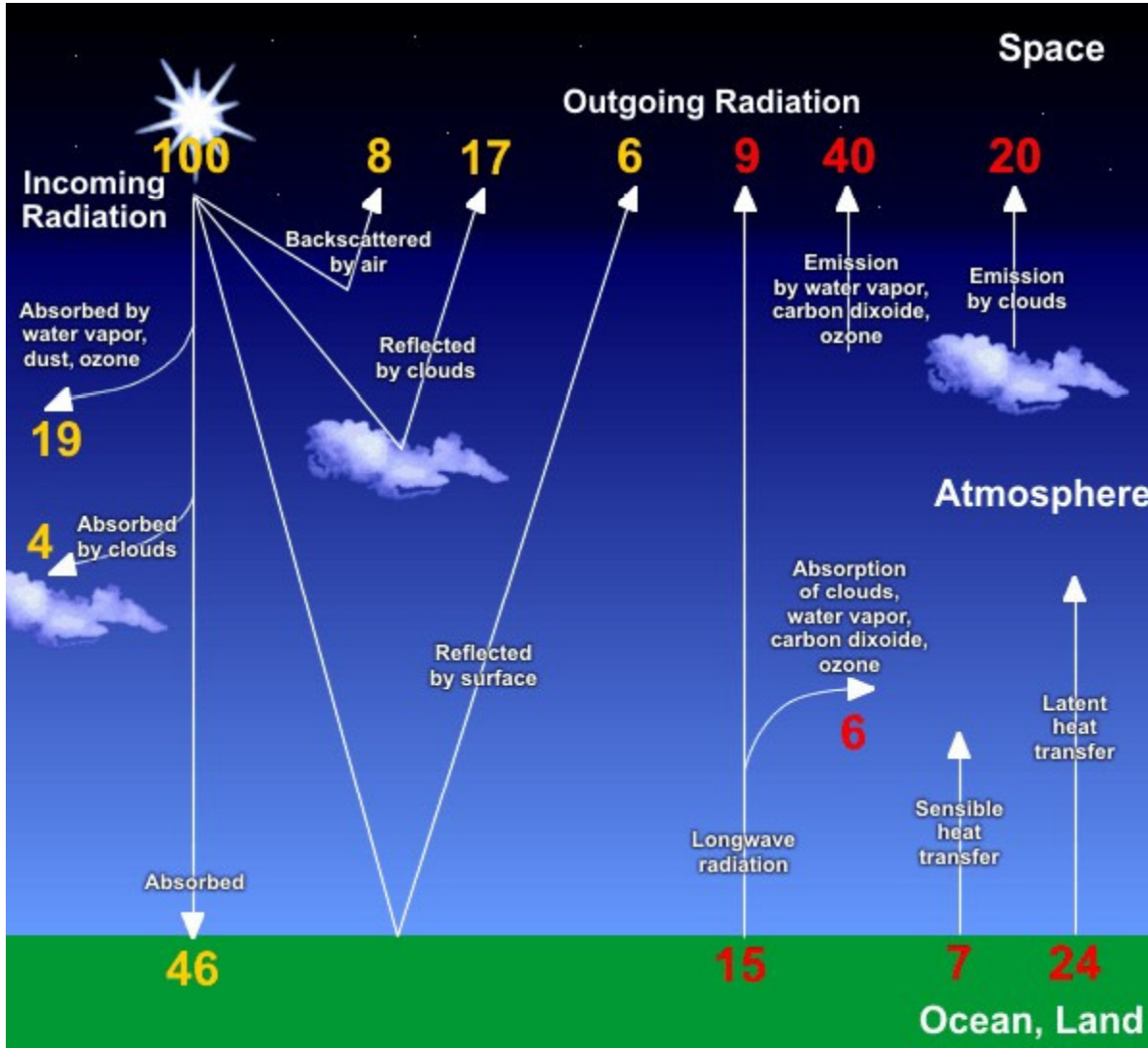


***Photocatalytic Reduction of CO₂
and Water Splitting, I***

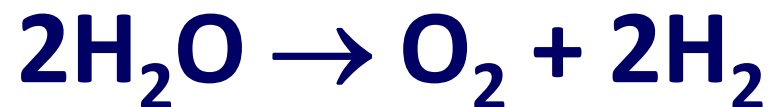
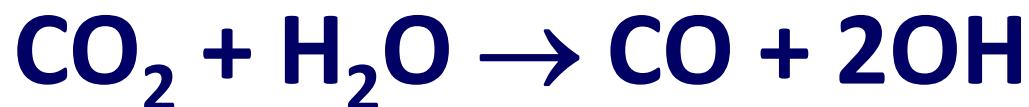
**Nathan I. Hammer
Department of Chemistry & Biochemistry
University of Mississippi**

Solar Radiation



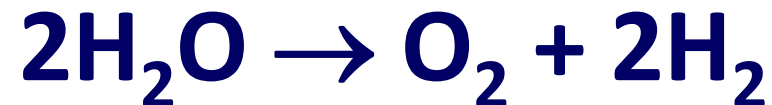
1000 W/m^2

Photocatalytic Reduction of CO₂ and Water Splitting

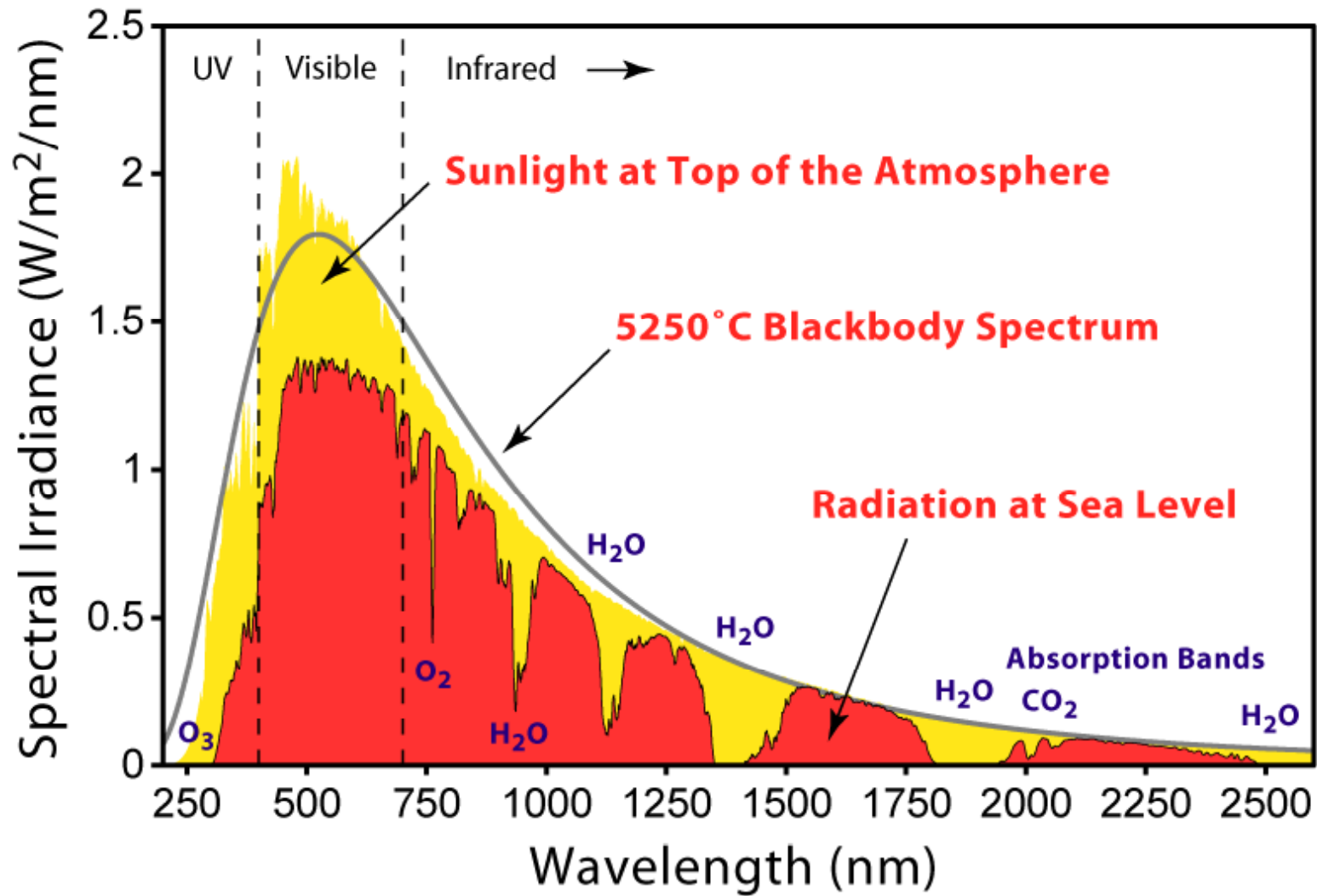


Need for Hydrogen – the Fuel of the Future

- The use of fossil fuels might be partially responsible for climate change.
- Deposits of fossil fuels are limited.
- The price of the fossil fuels is increasing.
- There is a need for a fuel generated from the raw materials which are abundantly available.
- There is a need for a fuel that is environmentally safe.



Solar Spectrum



Energy Levels of Water

TABLE 62 (continued)

State	Point Group	T_0	Vibrational Frequencies			Rotational Constants					Electron Configuration	Observed Transitions	References	Remarks
			ν_1	ν_2	ν_3	A_0	B_0	C_0	r_0 (Å)	α				
PH₂														
\tilde{A}^2A_1	C_{2v}	18276.6		951.3		20.340	5.606	4.311	1.403	123.1°	$\dots(b_2)^2(\alpha_1)(b_1)^2$	$\tilde{A} \leftarrow \tilde{X}$ 8520- ^a 3600 Å	(1042)(452) (286b)	Widely spaced bands with complicated fine structure
\tilde{X}^2B_1	C_{2v}	0		1101.9		9.120	8.087	4.225	1.428	91.5°	$\dots(b_2)^2(\alpha_1)^2(b_1)$		(1571)	
H₂O I.P. = 12.61 ₈ eV; $D(\text{H—OH}) = 5.113_6$ eV (see Fig. 138)														
\tilde{S}												$\tilde{S} \leftarrow \tilde{X}$ 795-750 Å	(494)(836) (494)(1274)	Progressions of diffuse bands
\tilde{R}												$\tilde{R} \leftarrow \tilde{X}$ 857-815 Å		
Ionization continuum starting at 745 Å (134200 cm ⁻¹)														
Two merging strong Rydberg series joining on to \tilde{E} and \tilde{F} ; $\nu = 101780 - R/(n - 0.05)^2$; $n = 3, 4, \dots$														
[interpreted by (631) as the nd and $(n + 1)s$ series]														
Two merging weaker Rydberg series joining on to \tilde{C} and \tilde{D} ; $\nu = 101780 - R/(n - 0.7)^2$; $n = 3, 4, \dots$														
\tilde{F}	C_{2v}	89680									$\dots(3a_1)^2(1b_1)(3d)$	$\tilde{F} \leftarrow \tilde{X}$ 1115 Å	(1015)(631)	Single band
$\tilde{E}(^1B_1)$	C_{2v}	88660									$\dots(3a_1)^2(1b_1)(4sa_1)$	$\tilde{E} \leftarrow \tilde{X}$ 1128 Å	(1015)(631)	Single band
\tilde{D}^1A_1	C_{2v}	82038	3268	1636	(3335)						$\dots(3a_1)^2(1b_1)(3pb_1)$	$\tilde{D} \leftarrow \tilde{X}$ 1219- 1172 Å	(1015)(105a)	Diffuse bands
\tilde{C}^1B_1	C_{2v}	80624.8	3170	(1422) ^a	(3224) ^a	25.6 ₇	12.5 ₅	8.5 ₅	1.01 ₆	106.9°	$\dots(3a_1)^2(1b_1)(3pa_1)$	$\tilde{C} \leftarrow \tilde{X}$ 1241- 1194 Å	(1015)(631) (1278)(105a)	See Fig. 112. Lines of higher J are diffuse
$\tilde{B}(^1A_1)$	$(D_{\infty h})$	70870 ^b		(800)							$\dots(3a_1)(1b_1)^2(3sa_1)$	$\tilde{B} \leftarrow \tilde{X}$ 1411- 1256 Å	(1278)	Progression of very diffuse bands ^c
$\tilde{A}(^1B_1)$	C_{2v}	(53800)	continuous absorption with broad maximum at 1655 Å ^d								$\dots(1b_2)^2(3a_1)^2(1b_1)(3sa_1)$	$\tilde{A} \leftarrow \tilde{X}$ 1860- 1450 Å	(1302) (1278)	$k_{\text{max}} = 124\text{cm}^{-1}$
\tilde{X}^1A_1	C_{2v}	0	3657.0 ₅	1594.7 ₈	3755.7 ₉	27.877°	14.512°	9.285°	0.956 ^f	105.2 ^g	$\dots(1b_2)^2(3a_1)^2(1b_1)^2$	infrared sp.	(107)(265)	
H₂S I.P. = 10.47 ₂ eV ^a ; $D(\text{H—SH}) = 3.26$ eV ^b More recent work on Rydberg series (1575)-(1577)														
			Rydberg series joining on to \tilde{A} : $\nu = 84420 - R/(n - 1.04)^2$; $n = 4, 5, \dots, 13$										(1015)(1024) (1015) (1015)(1024)	No vibrational structure
			Rydberg series of three members joining on to \tilde{F} and \tilde{G} for which no formula is given											
			Rydberg series joining on to \tilde{D} : $\nu = 84520 - R/(n - 1.57)^2$; $n = 4, 5, \dots, 10$											

585

^aIn absorption 5500-3600 Å, in emission 8520-4540 Å. Improved constants in (1571)(1572).

^bEstimated from $\nu_2 = 1038.4$ for D₂O assuming valence force system (631). (105a) gives $\nu_1 = 3179$, $\nu_2 = 1407$, $\nu_3 = (3238)_{\text{calc}}$.

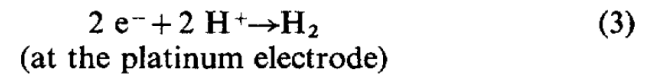
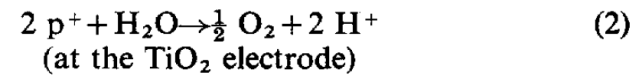
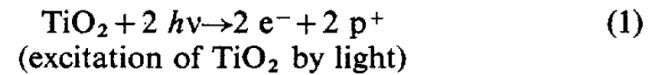
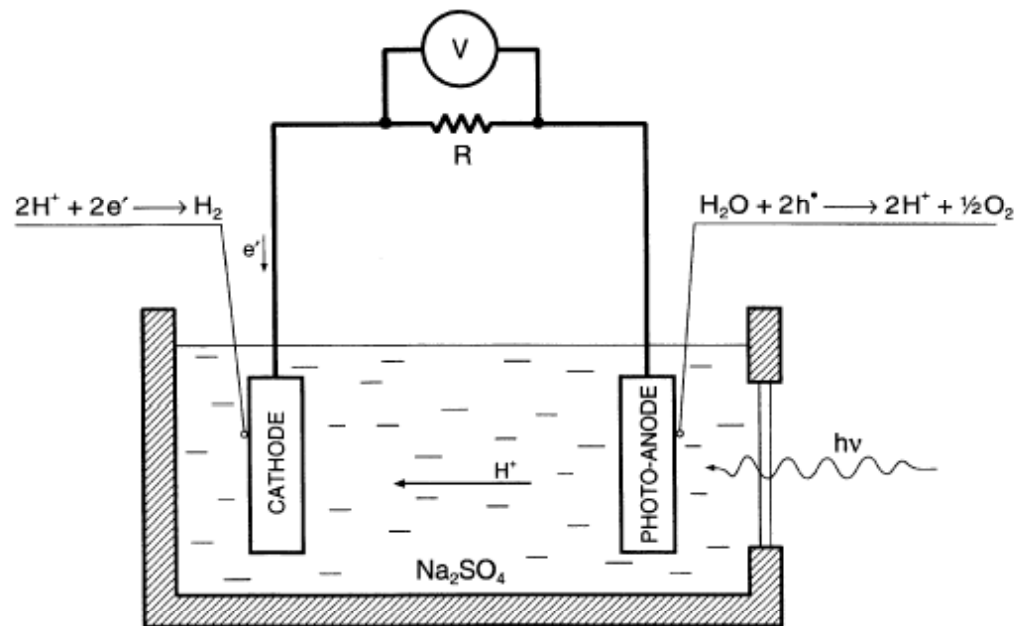
^cWave number of first diffuse band; origin of band system may be much lower. ^dOverlapped by continuum.

^e(1302) give three maxima at 1718, 1648 and 1608 Å, but these are not observed in the photoelectric work of (1278) [see also (629)].

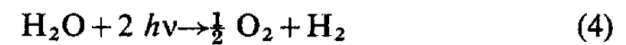
^f $\alpha_1^A = 0.747$, $\alpha_2^A = -3.32_3$, $\alpha_3^A = 1.241$; $\alpha_1^B = 0.22_2$, $\alpha_2^B = -0.16_7$, $\alpha_3^B = 0.11_2$; $\alpha_1^C = 0.18_0$, $\alpha_2^C = 0.13_5$, $\alpha_3^C = 0.12_9$ cm⁻¹. Slightly different A_0 , B_0 , C_0 and α values are given by (106a). See also (1573)

^gThese are r_0 and α values. The equilibrium values, given by (106a), are 0.957₂ Å and 104.5₂°.

Water Splitting



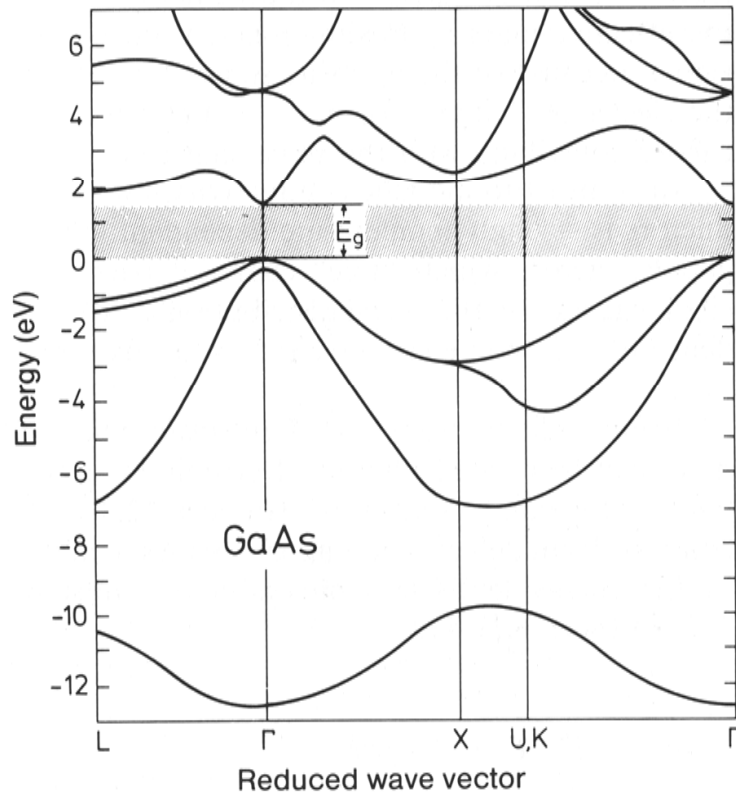
The overall reaction is



Water Splitting

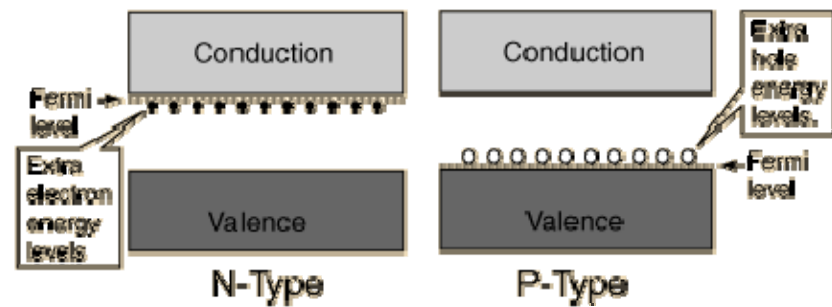
- Photogeneration of charge carriers (electron and hole pairs) in some material occurs.
- In TiO_2 , light with energy larger than the band gap is absorbed and electrons and holes are generated in the conduction and valence bands, respectively.
- Charge separation occurs.
- Holes migrate to the interface between the semiconductor and the electrolyte and electrons migrate to the counter electrode through the external circuit.
- The photogenerated electrons and holes cause redox reactions.
- Water molecules are reduced by the electrons to form H_2 and oxidized by the holes to form O_2 , leading to overall water splitting. Actually, oxidation of water forms H^+ and O_2 at the anode and reduction of H^+ ions to H_2 by electrons occurs at the cathode.

Band Gaps of Materials



Conduction Band

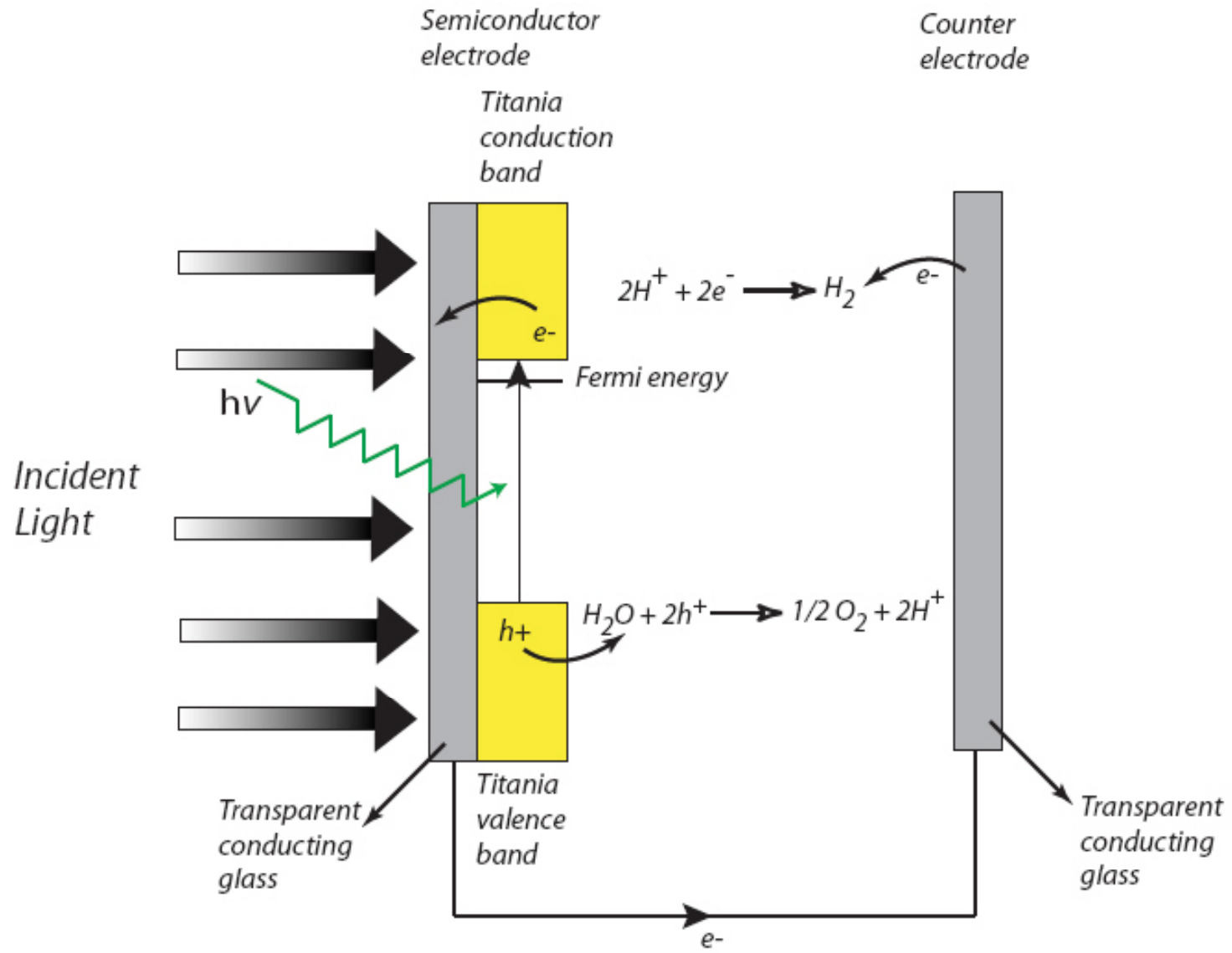
Valence Band



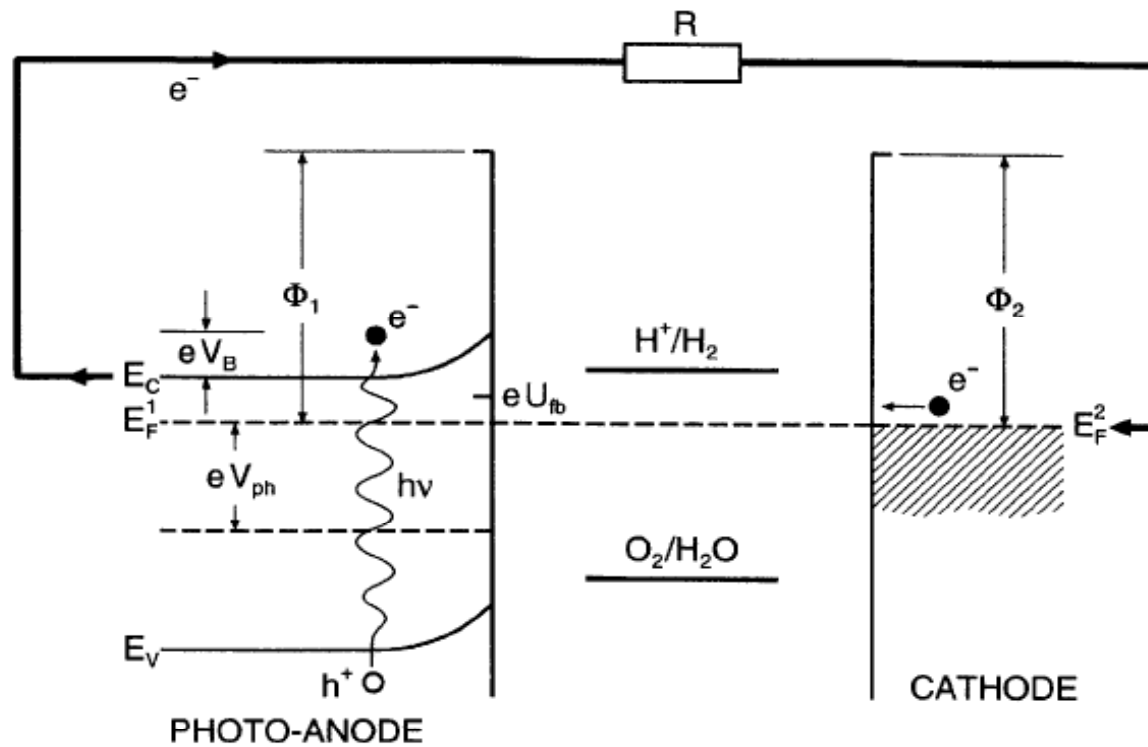
H. Ibach and H. Lüth, "Solid-State Physics. An Introduction to Principles of Materials Science", Springer, 2003.

<http://hyperphysics.phy-astr.gsu.edu/hbase/solids/dope.html>

Water Splitting



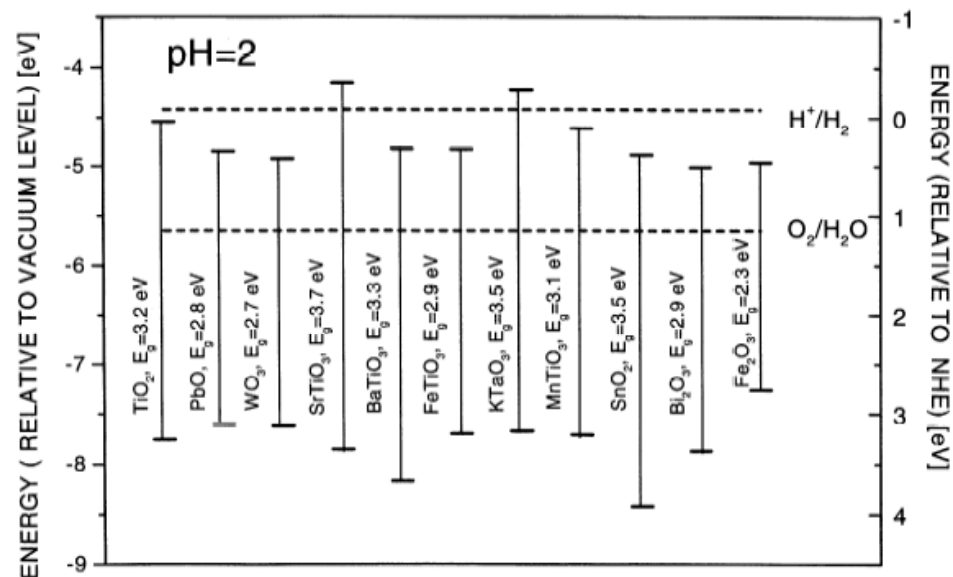
Water Splitting



T. Bak, J. Nowotny, M. Rekas, and C. C. Sorrell, "Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects," *International Journal of Hydrogen Energy* **2002**, 27, 991-1022

Water Splitting – Photocatalyst Properties

- The width of the band gap and the potentials of the conduction and valence bands are important.
- The conduction and valence band positions should satisfy the energy requirements set by the reduction and oxidation potentials for H₂O.
- The bottom level of the conduction band has to be more negative than the reduction potential of H⁺/H₂ (0 V vs NHE), while the top level of the valence band has to be more positive than the oxidation potential of O₂/H₂O (1.23 V).
- Band gap of a visible-light-driven photocatalyst should be narrower than 3.0 eV (> 420 nm).



A. Kudo, H. Kato and I. Tsuji, "Strategies for the Development of Visible-light-driven Photocatalysts for Water Splitting," *Chemistry Letters* **2004**, 33, 1534-1539.

T. Bak, J. Nowotny, M. Rekas, and C. C. Sorrell, "Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects," *International Journal of Hydrogen Energy* **2002**, 27, 991-1022

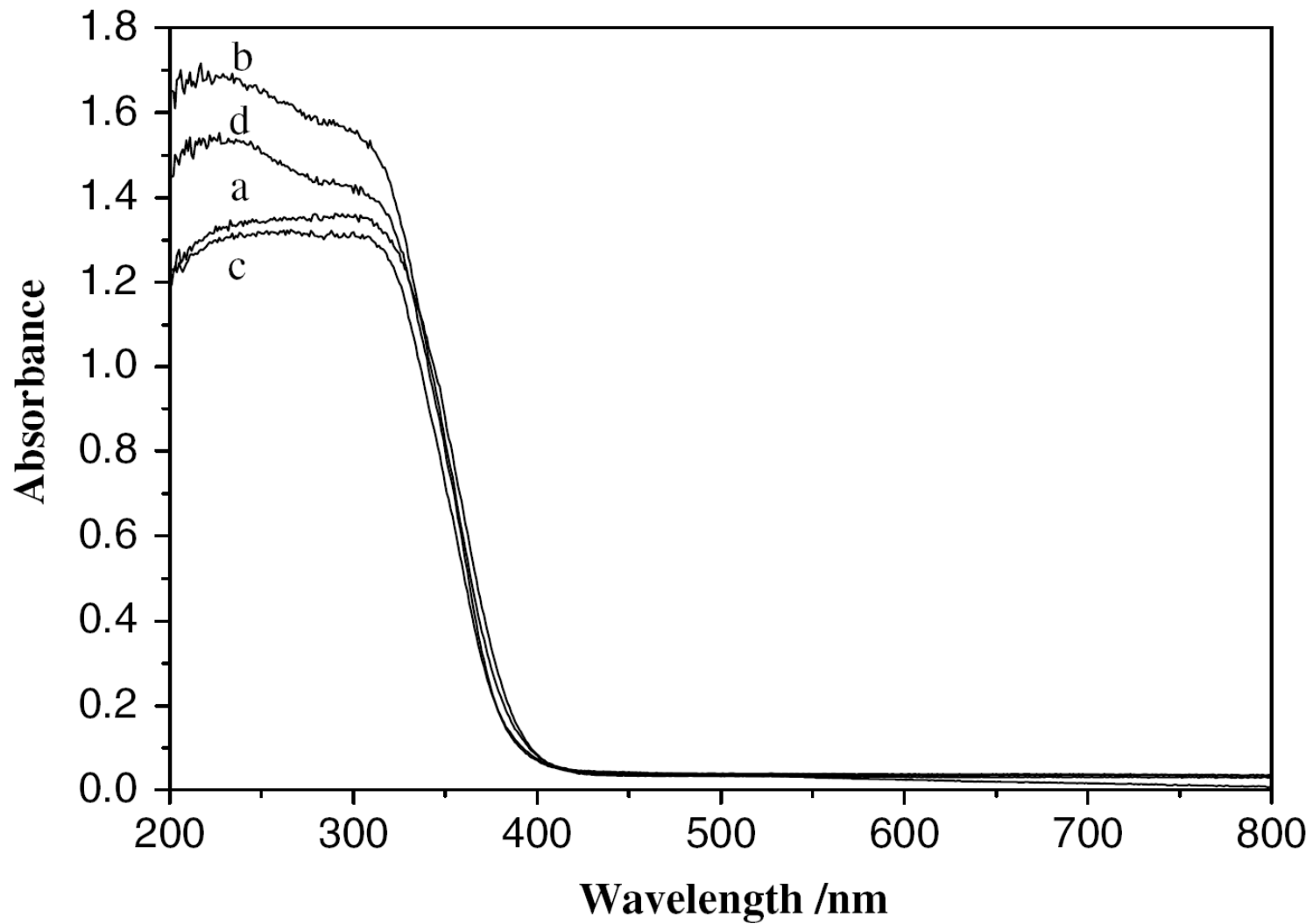
Water Splitting – Photocatalyst Properties

- Charge carrier separation, migration, and lifetimes of photogenerated carriers are affected by the crystal structure and the crystallinity of the photocatalyst.
- The higher the crystalline quality, the smaller is the amount of defects. The defects operate as trapping and recombination centers between photogenerated electrons and holes, resulting in a decrease in the activity.
- Surface chemical reactions and surface properties such as surface states, surface chemical groups, surface area, and active reaction sites are also important.
- The water-splitting process affects the local pH environment and surface structures of the electrode.
- Most contain titanium oxides.
- Cocatalysts such as Pt and NiO and/or additives in the water such as NaOH and Na₂CO₃ are indispensable for the water splitting on many photocatalysts. Such cocatalysts introduce active sites for H₂ evolution.
- Most models require UV radiation.
- Materials need to absorb visible light to overlap with solar spectrum.

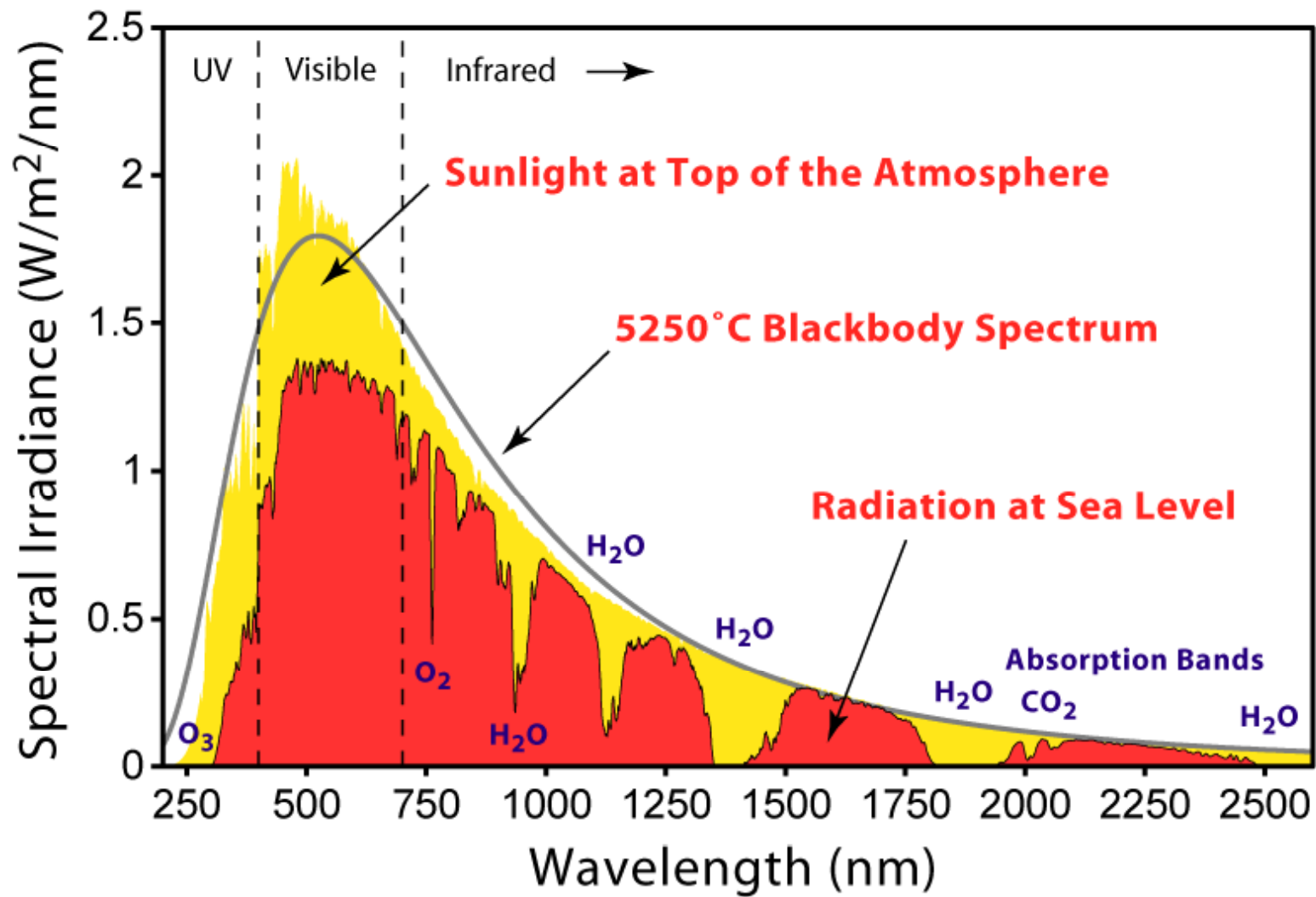
X. Chen and S. S. Mao, "Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications," *Chemical Reviews* **2007**, *107*, 2891-2959.

A. Kudo, H. Kato and I. Tsuji, "Strategies for the Development of Visible-light-driven Photocatalysts for Water Splitting," *Chemistry Letters* **2004**, *33*, 1534-1539.

Water Splitting



Water Splitting



Water Splitting – Other Photocatalysts

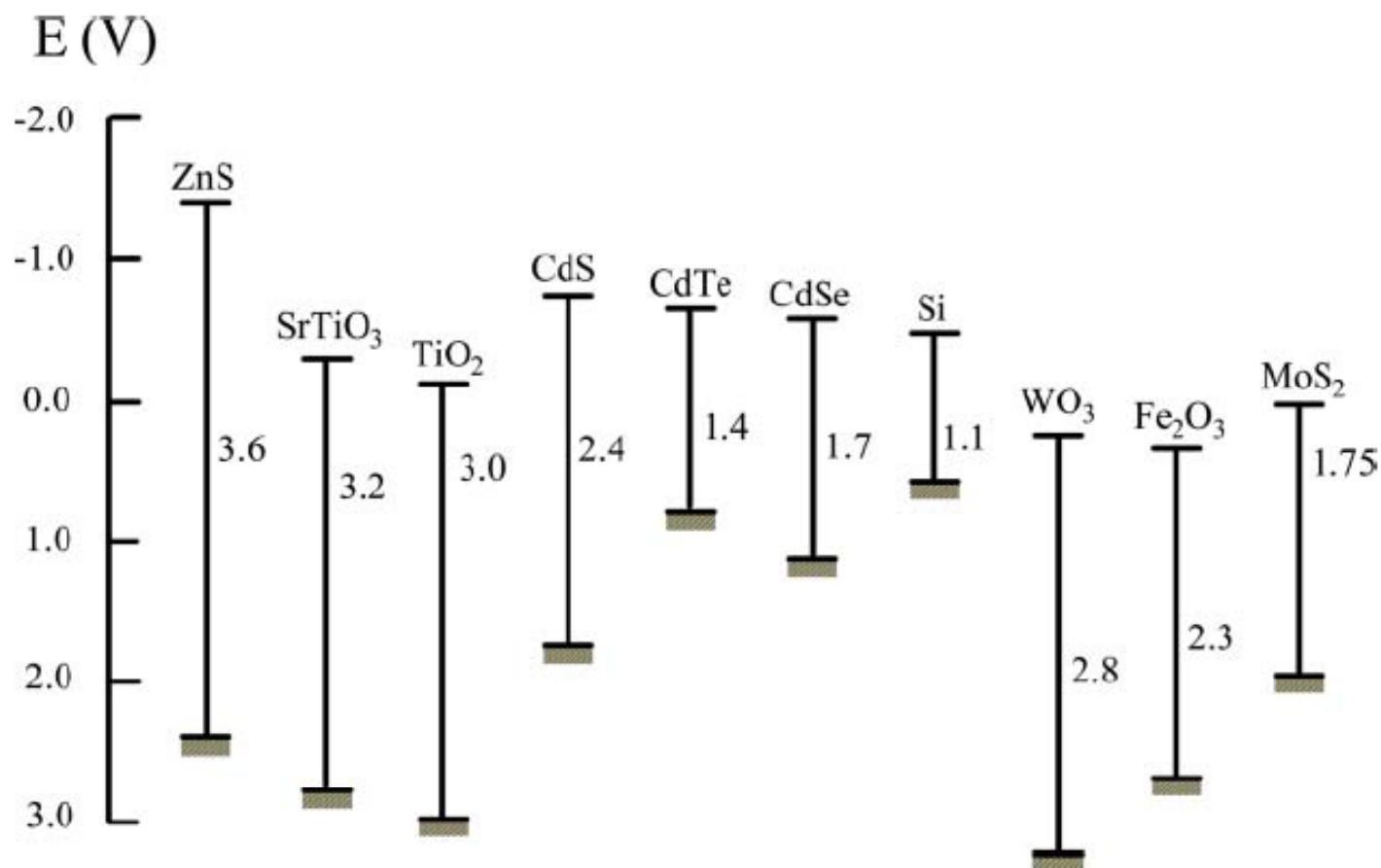


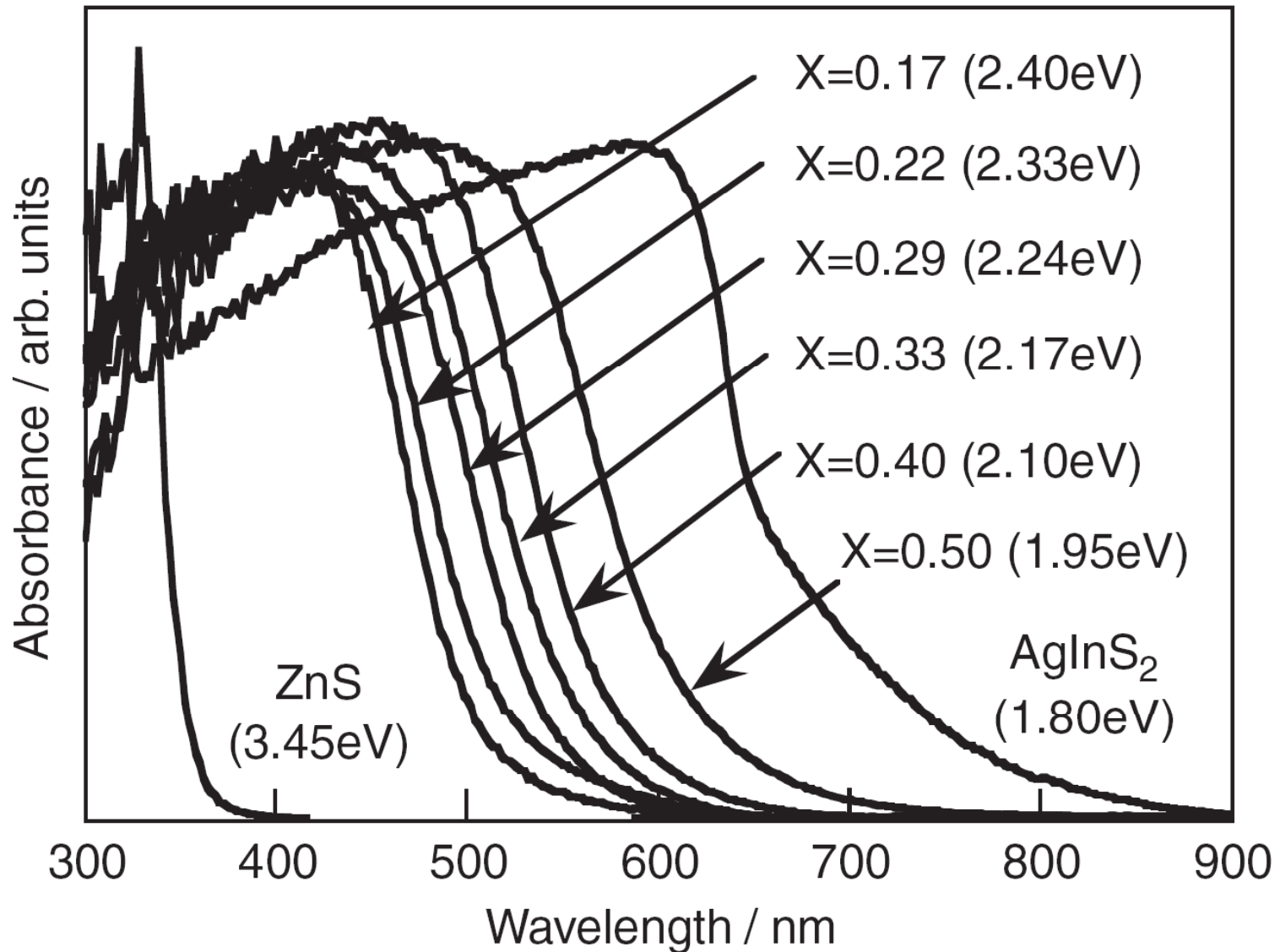
Fig. 2 Band gaps and redox potentials (vs. NHE) at pH = 1.

Water Splitting – Other Photocatalysts

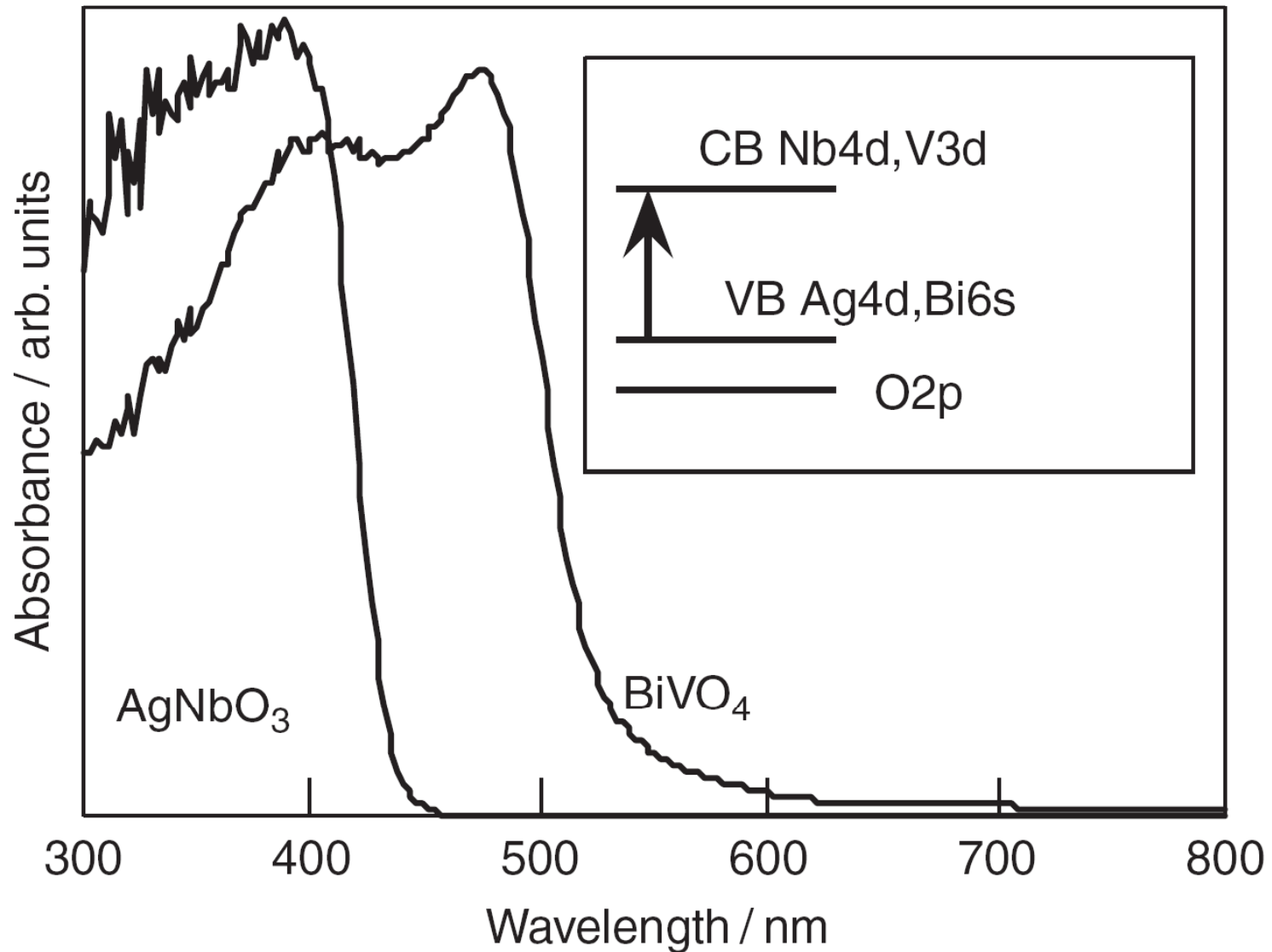
Table 1. Continued

no.	material	cocatalyst	irradiation conditions	reaction details and refs
124d	CdS	variable	variable	micelles, ^{223–225} CdS composites with (TiO ₂ , ²²⁶ ZnS, ^{228,229} CdSe ²³⁰) different cocats. (Pt, Pd, Rh, Ru, Ir, Fe, Ni, Co), ^{231,232} hollow CdS microparticles, ²³³ Cu-doped CdS, ^{234,235} effect of preparation ^{236,237}
125a	ZnS		125 W Hg at > 290 nm	0.5 mL of H ₂ /h (22 μmol) per 12 mg of cat. from THF(aq) ²³⁸
125b	ZnS	Pt	200 W Hg at > 300 nm	295 mL/h (13 mmol/h) of H ₂ from 0.4 g of cat., QE = 90%; ¹³ from aqueous S ²⁻ , SO ₃ ²⁻ , S ²⁻ /HPO ₂ ⁻ , or S ₂ O ₃ ²⁻ solution
125c	M:ZnS (M = Ni, Pb, Cu)		300 W Xe at >420 nm	M = Ni, 280 μmol/h/g (QE = 1.3%) of H ₂ from aqueous K ₂ SO ₃ and Na ₂ S; ²⁴⁰ M = Pb, 15 μmol/h/g from aqueous SO ₃ ²⁻ ; ²⁴¹ M = Cu, 450 μmol/h/g of H ₂ were evolved (QE = 3.7%) from Na ₂ SO ₃ (aq) ²³⁹
125d	ZnS, doped with AgInS ₂ or CuInS ₂	Pt or Ru	300 W Xe at >420 nm	for Ru-modified (CuAg) _{0.15} In _{0.3} Zn _{1.4} S ₂ , H ₂ at up to 2.3 mmol/h/0.3 g from aqueous Na ₂ S and K ₂ SO ₃ with QE = 7.5%; ²⁴³ Pt-loaded (AgIn) _{0.22} Zn _{1.56} S ₂ has QE = 20%. ²⁴⁵
126–128	Na ₁₄ In ₁₇ Cu ₃ S ₃₅ , (AEP) ₆ In ₁₀ S ₁₈ , Na ₅ In ₇ S ₁₃		300 W Xe at >420 nm	9 μmol/h/0.5 g of H ₂ from Na ₂ S(aq) with QE = 3.7% (QE = 0.37% for SO ₃ ²⁻ (aq)); (AEP) ₆ In ₁₀ S ₁₈ evolved 20 μmol/h/0.5 g; ²⁴⁷ AEP = protonated 1-(2-aminoethyl)piperazine; Na ₅ In ₇ S ₁₃ produced 2.4 μmol/h/0.25 g from Na ₂ SO ₃ (aq) ²⁴⁶
129a/b	[In(OH) _y S _z] with or without Zn doping		300 W Xe at >420 nm	0.9–1.8 μmol/h/0.3 g from aqueous Na ₂ S/Na ₂ SO ₃ ; for Pt/In(OH) _y S _z :Zn, activity up to 67 μmol/h/0.3 g (QE = 0.59%) under similar conditions ²⁴⁸
130–132	MInS ₂ (M = Cu, Na, CuIn ₅ S ₈)		UV, 400 W Xe	CuInS ₂ (0.006 mL/h/0.5 g of cat.) and CuIn ₅ S ₈ (0.04 mL/h/0.5 g of cat.) from Na ₂ SO ₃ (aq); ²⁴⁹ NaInS ₂ –Pt produces H ₂ (470 μmol/h/0.7 g) from K ₂ SO ₃ (aq); ²⁵⁰ under vis light (>420 nm, 300 W Xe).
133	WS ₂		1000 W Xe at >435 nm	0.05 mL of H ₂ /h/10 mg of cat. from EDTA(aq) with fluoresceine as the sensitizer and SiO ₂ as the support ²⁵¹
134	Bi ₂ S ₃		500 W halogen lamp, vis	H ₂ at 0.011 mL/h/0.001 g from aqueous sulfide; platinization improves the activity by 25%. ²⁵²

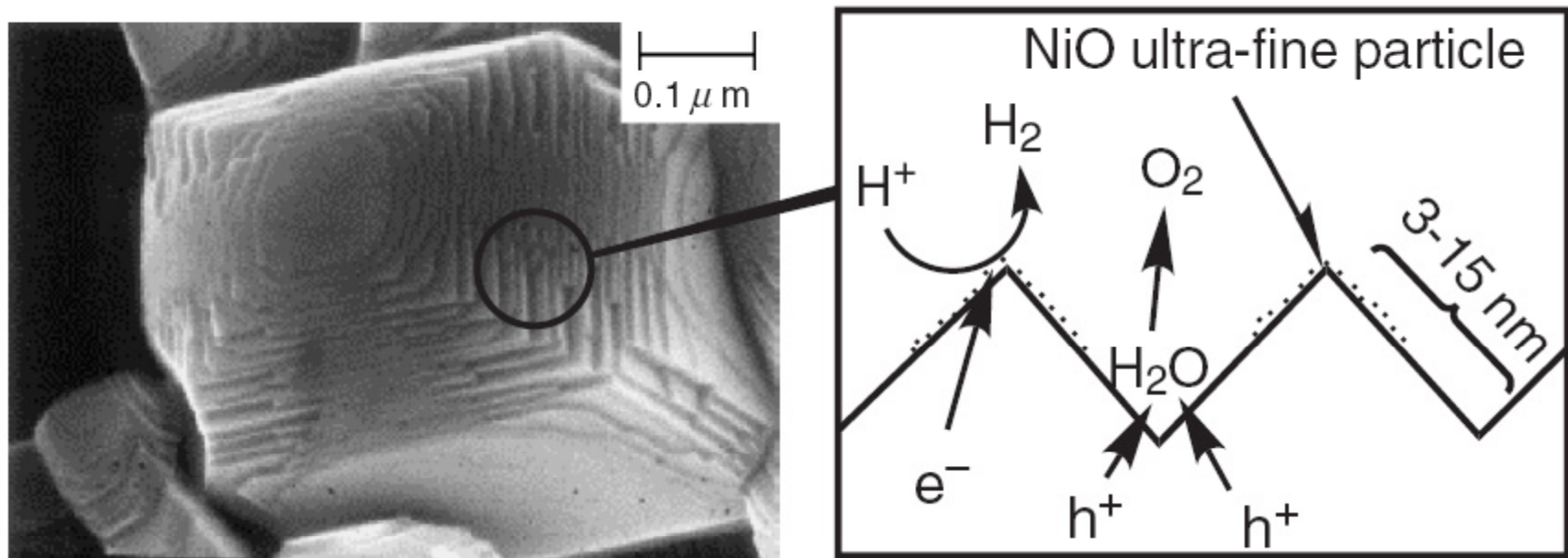
Water Splitting – Other Photocatalysts



Water Splitting – Other Photocatalysts



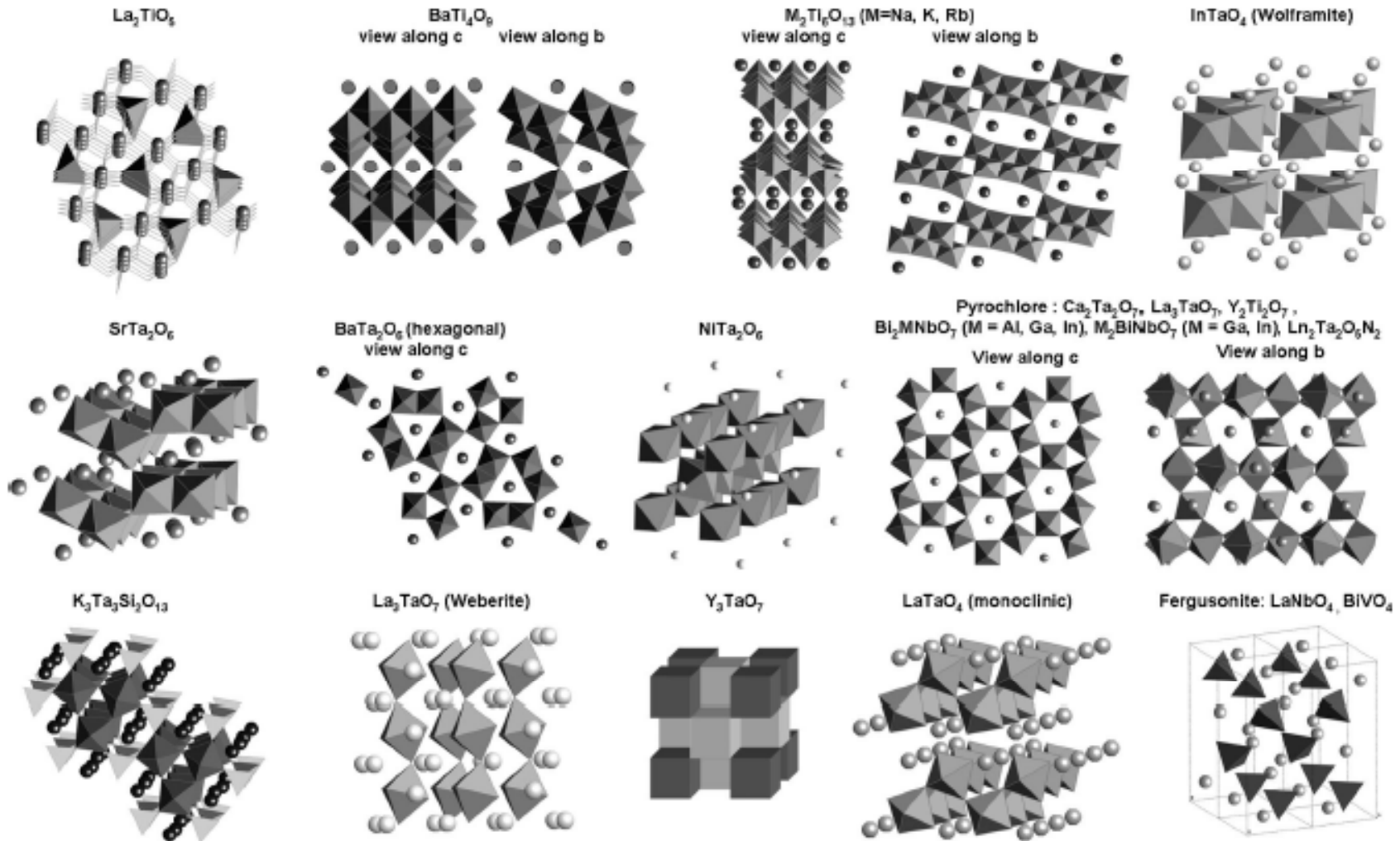
Water Splitting – Photocatalytic



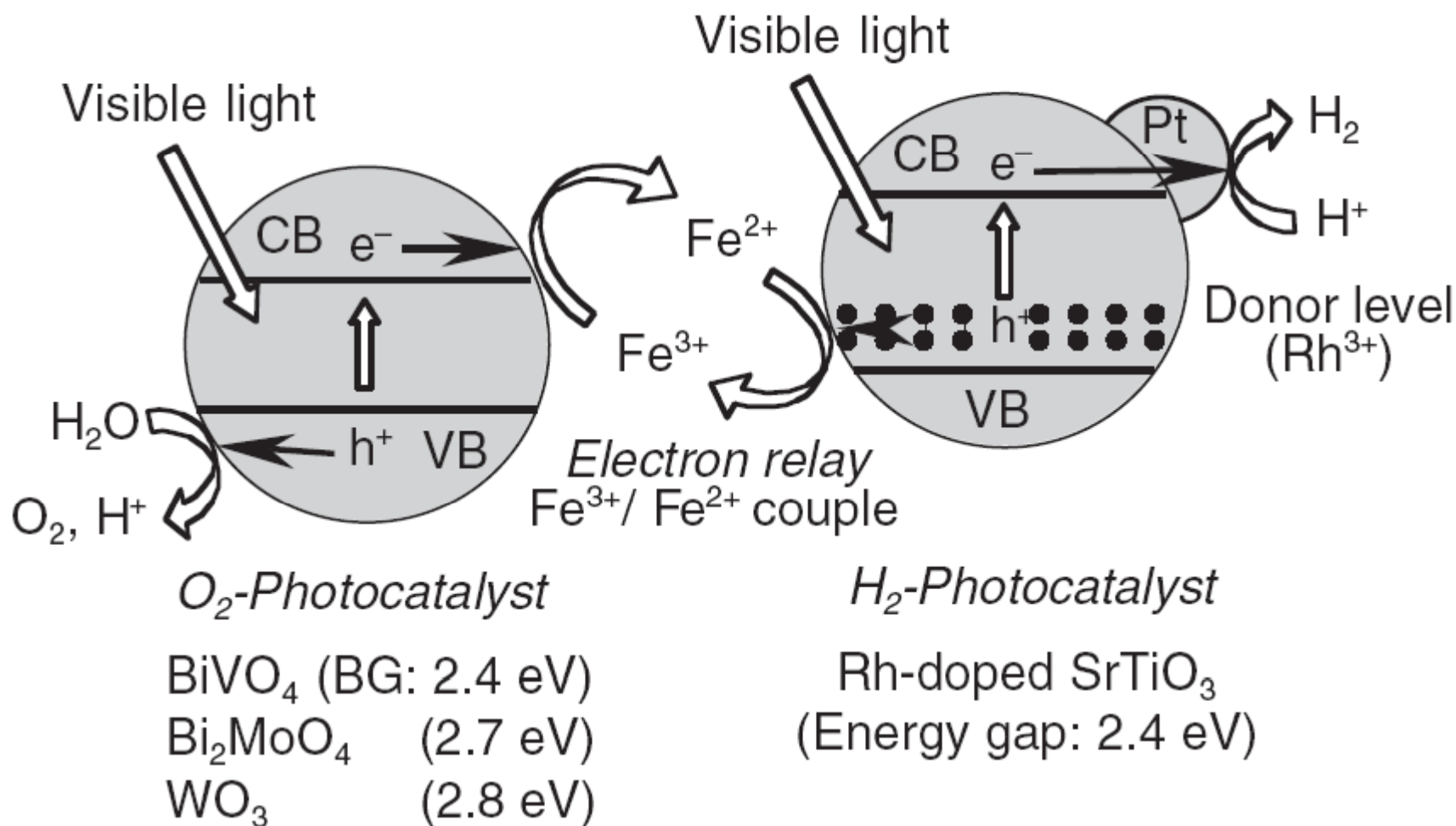
- UV Radiation required...
- Need to Develop Visible-Light-Driven Photocatalysts
- Band Engineering
- Two Photon Processes

A. Kudo, H. Kato and I. Tsuji, "Strategies for the Development of Visible-light-driven Photocatalysts for Water Splitting," *Chemistry Letters* **2004**, 33, 1534 – 1539.

Water Splitting – Photocatalytic



Water Splitting – Visible Light



A. Kudo, H. Kato and I. Tsuji, "Strategies for the Development of Visible-light-driven Photocatalysts for Water Splitting," *Chemistry Letters* **2004**, 33, 1534 – 1539.

Water Splitting – Visible Light

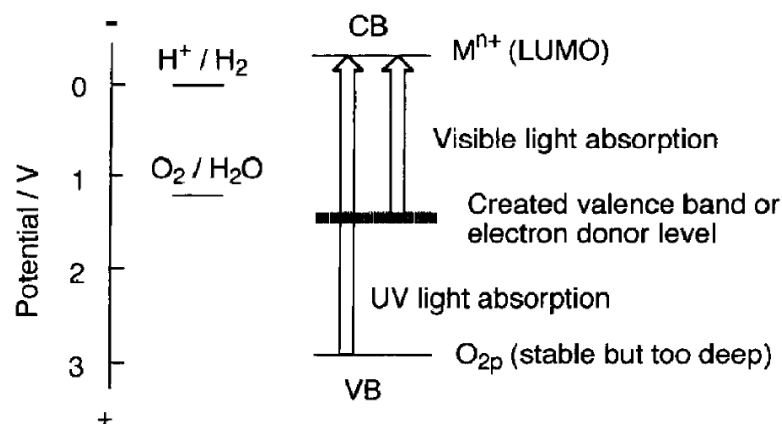


Figure 81. Strategy of the development of photocatalysts with a visible light response. Reprinted Figure 6 from Kudo, A. *Catal. Surv. Asia* **2003**, 7, 31, Copyright 2003, with kind permission of Springer Science and Business Media.

- Forming a donor level above a valence band by doping some element into conventional photocatalysts with wide band gaps such as TiO_2 .
- Creating a new valence band employing some element.
- Controlling the band structure by making a solid solution.

Carbon Dioxide Reduction

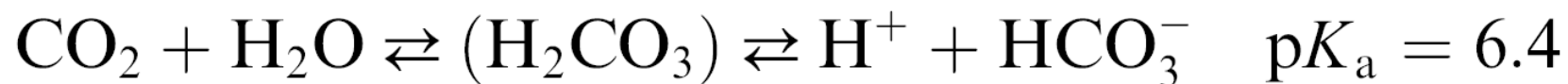
- Solution for shortage of fossil fuels – Fix CO₂ into useful chemicals.
- May help prevent global warming.
- But... low energy conversion efficiencies so far.
- The shape and size of the photocatalyst are very important.
- The products depend upon the photocatalyst and environment.



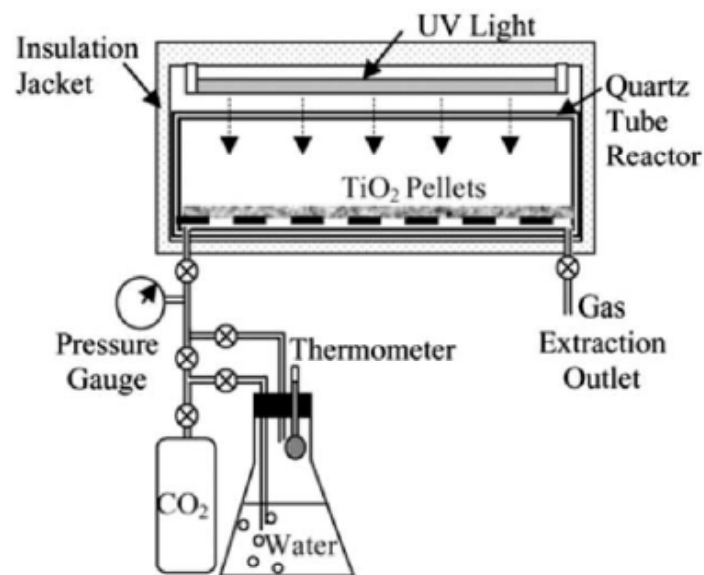
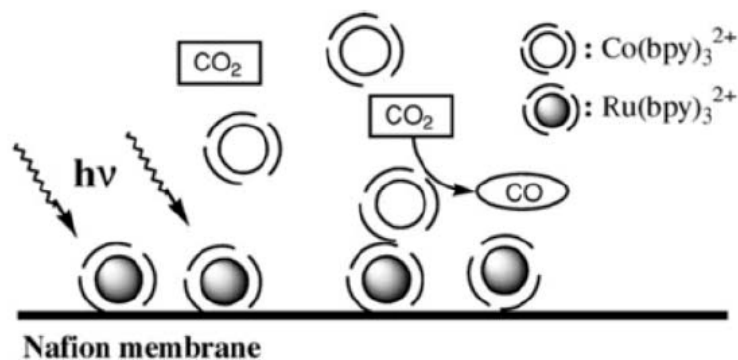
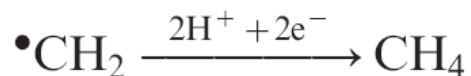
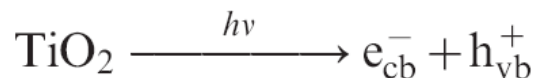
Carbon Dioxide Reduction

- TiO₂ suspensions including metals such as Pd, Rh, Pt, Au, Cu, or Ru.
- Reduction can also take place with other metals such as Hg, Cd, Pb, Tl, In, Sn, Pt, Ni, Fe, Ti, Au, Ag, and Zn.
- Other catalysts such as ZnS and CdS work well.
- Researchers have also used zeolites and solid-gas systems.
- More recently, transition metal complexes such as ruthenium(II) polypyridine carbonyl complex, cobalt(II) trisbipyridine, cobalt(III) macrocycles, and rhenium-(I) bipyridine (bpy) complexes have been employed with much success.

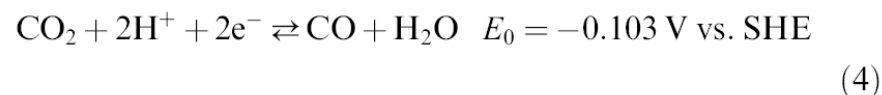
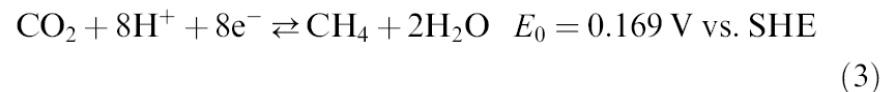
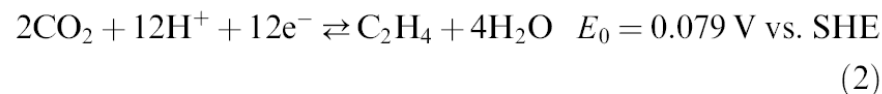
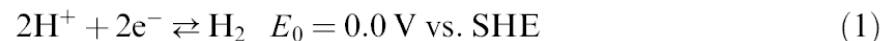
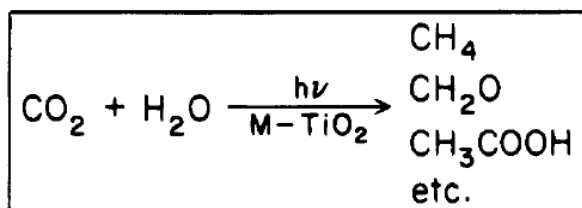
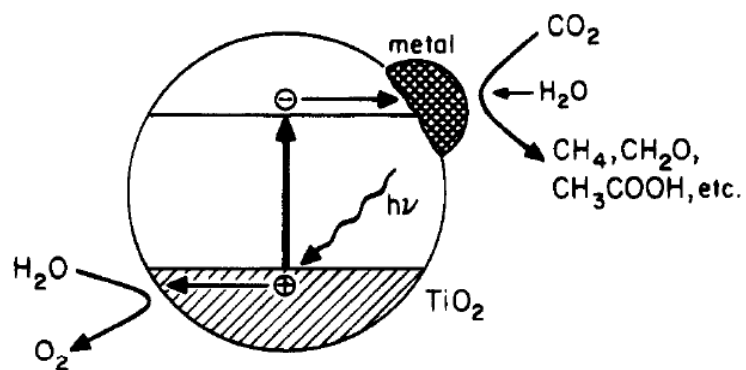
Carbon Dioxide Equilibria



Carbon Dioxide Reduction



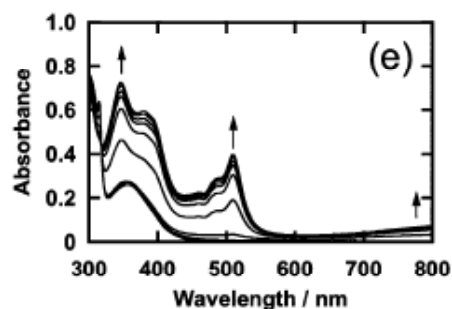
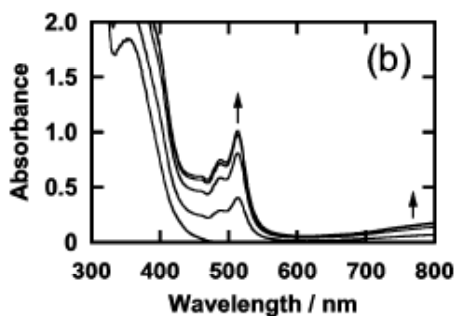
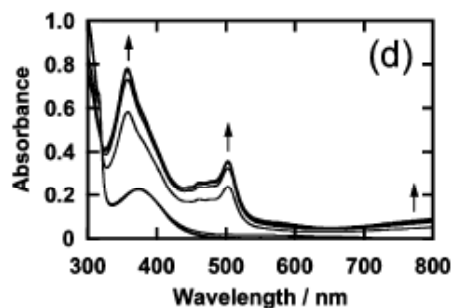
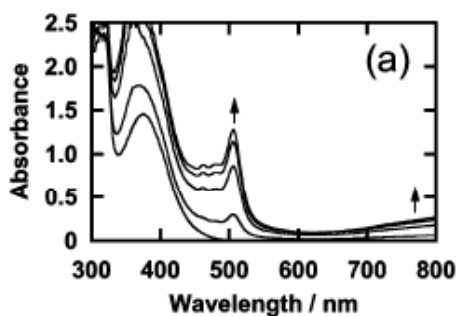
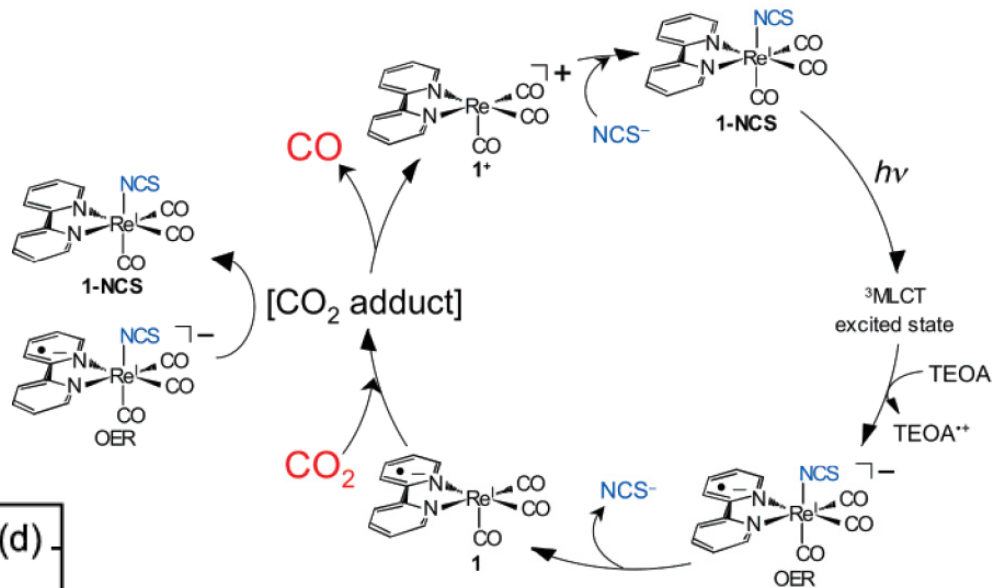
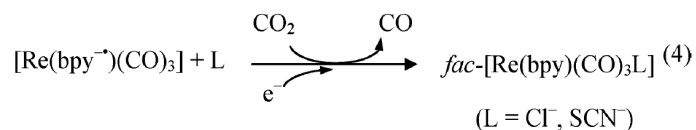
Carbon Dioxide Reduction



A. Linsebigler, G. Lu, and J. T. Yates, Jr., "Photocatalysis on TiO_n Surfaces: Principles, Mechanisms, and Selected Results," *Chemical Reviews* **1995**, 95, 735-758.

H. Takeda, K. Koike, H. Inoue, and O. Ishitani, "Development of an Efficient Photocatalytic System for CO_2 Reduction Using Rhenium(I) Complexes Based on Mechanistic Studies," *Journal of the American Chemical Society* **2008**, 130, 2023-2031.

Carbon Dioxide Reduction – Transition Metal Complexes

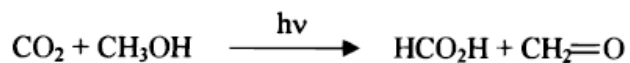


H. Takeda, K. Koike, H. Inoue, and O. Ishitani, "Development of an Efficient Photocatalytic System for CO₂ Reduction Using Rhenium(I) Complexes Based on Mechanistic Studies," *Journal of the American Chemical Society* **2008**, *130*, 2023-2031.

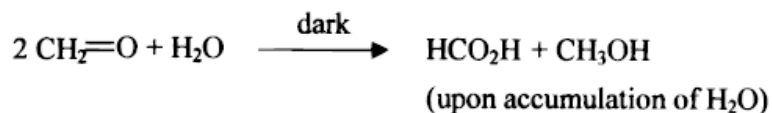
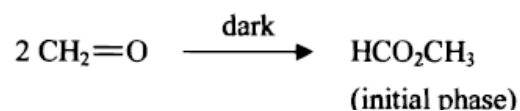
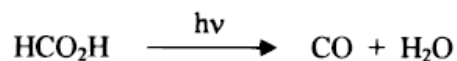
Carbon Dioxide Reduction – Competing Processes

SCHEME 1

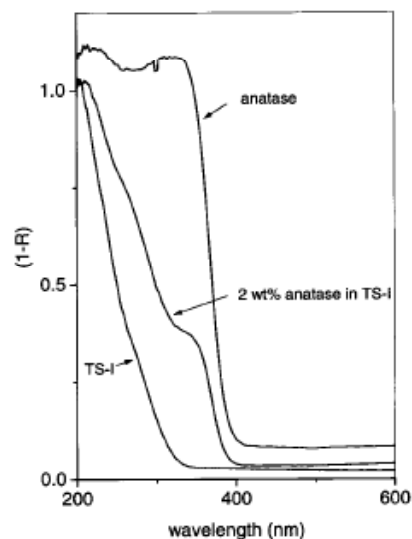
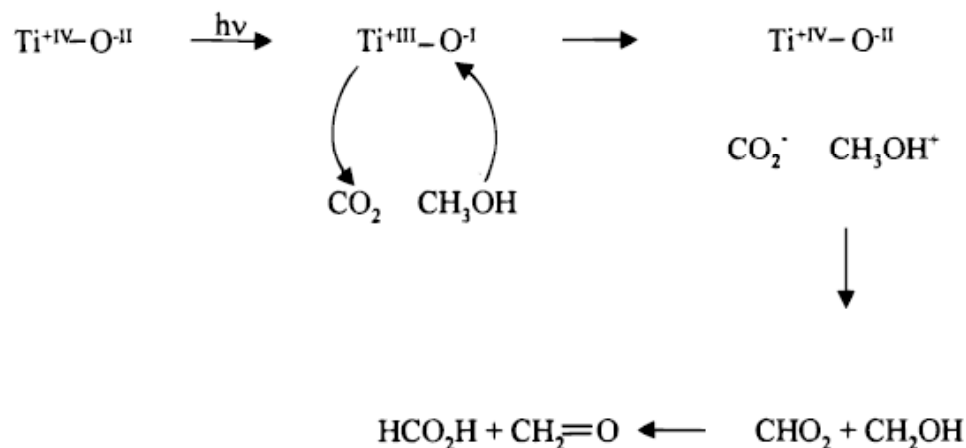
Primary Photochemistry



Secondary Reactions



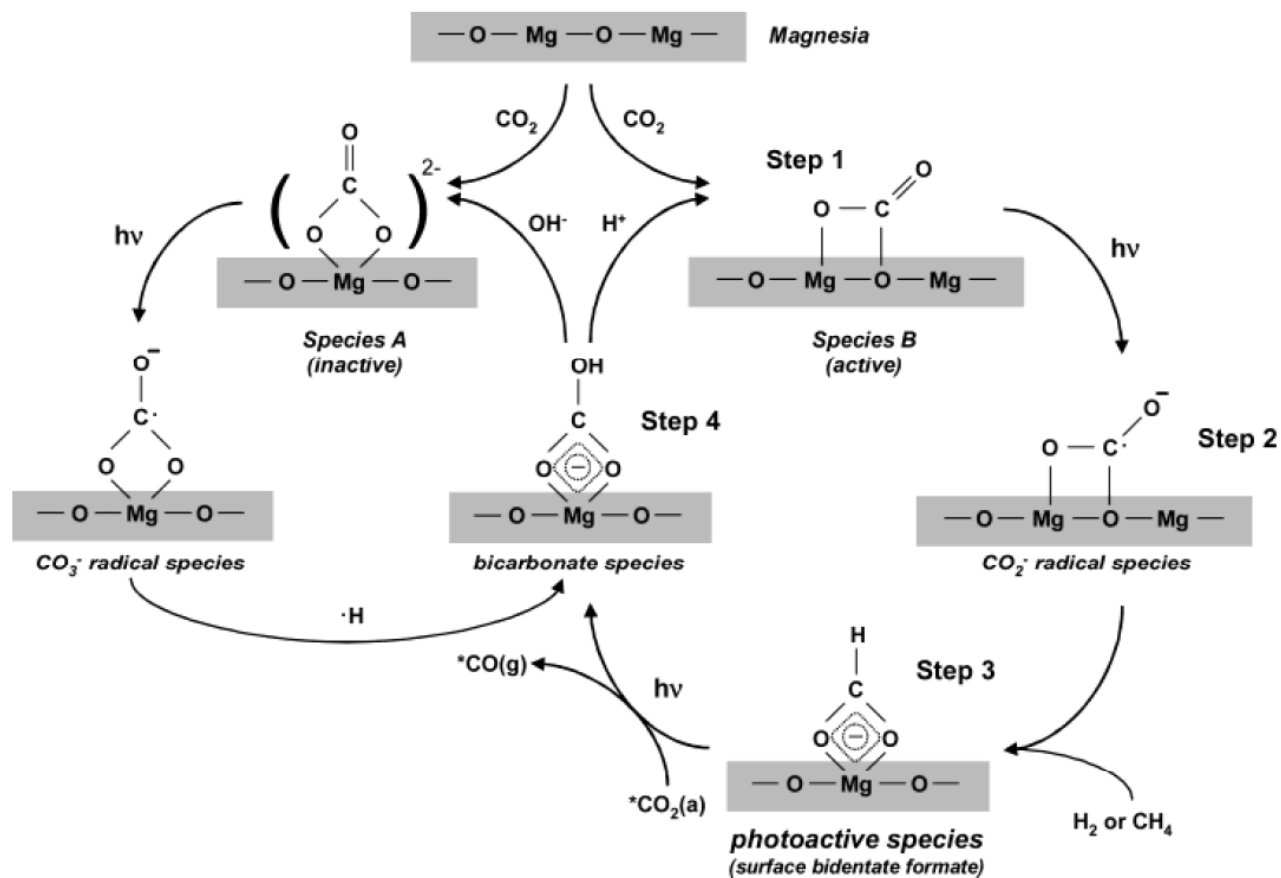
SCHEME 2



N. Ulagappan and H. Frei, "Mechanistic Study of CO₂ Photoreduction in Ti Silicalite Molecular Sieve by FT-IR Spectroscopy" *Journal of Physical Chemistry A* **2000**, 104, 7834-7839.

Carbon Dioxide Reduction – MgO

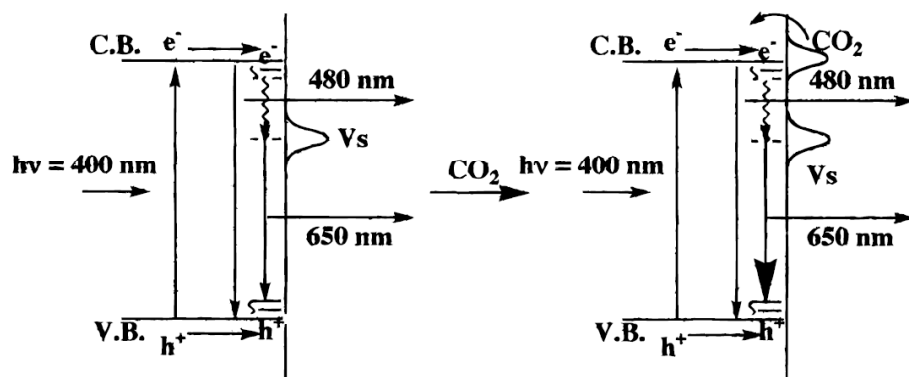
SCHEME 1. Mechanism of Photocatalytic Reduction of CO₂ in the Presence of H₂ or CH₄



K. Teramura, T. Tanaka, H. Ishikawa, Y. Kohno, and T. Funabiki, "Photocatalytic Reduction of CO₂ to CO in the Presence of H₂ or CH₄ as a Reductant over MgO," *Journal of Physical Chemistry B* **2004**, *108*, 346-354.

Carbon Dioxide Reduction – CdS

SCHEME 2



SCHEME 3

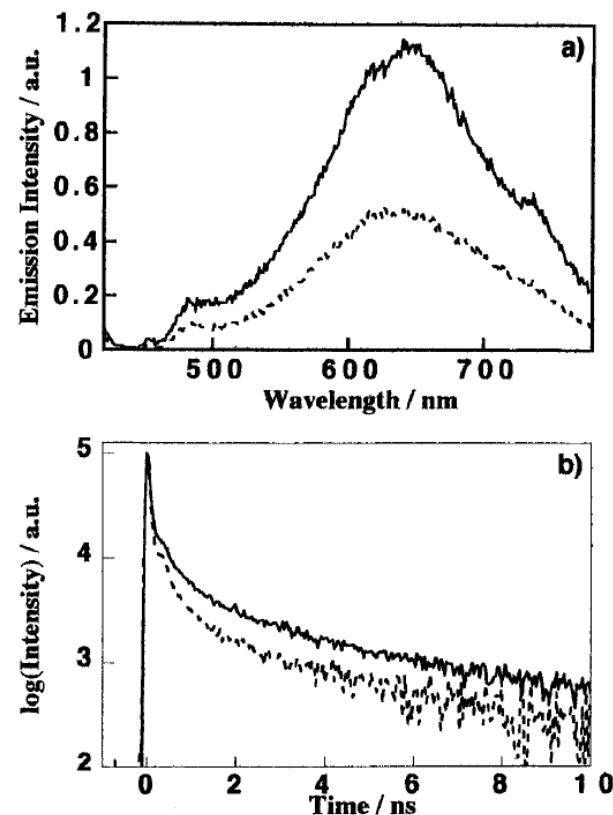
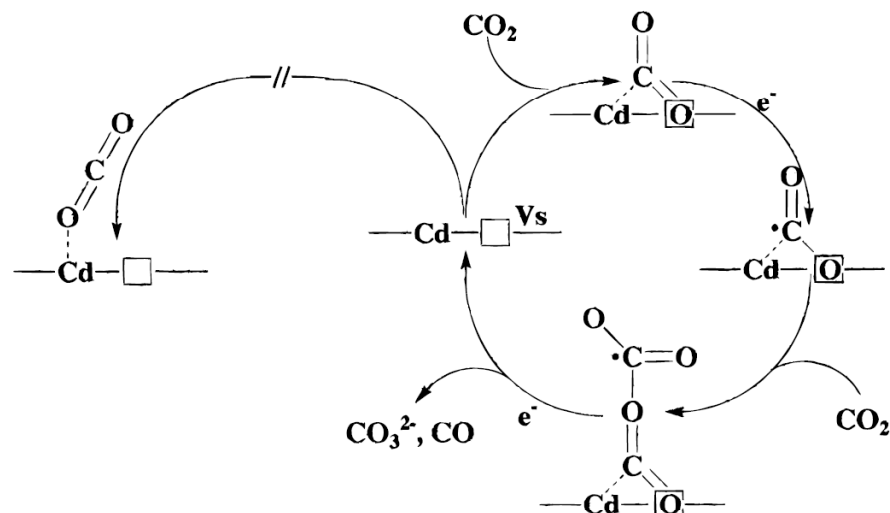


Figure 6. Effect of CO₂ addition on emission properties in the presence of TEA: (a) emission and (b) emission lifetime monitored at $\lambda = 480$ nm.; in the absence (---) and the presence (—) of CO₂.

H. Fujiwara, H. Hosokawa, K. Murakoshi, Y. Wada, S. Yanagida, T. Okada, and H. Kobayashi, "Effect of Surface Structures on Photocatalytic CO₂ Reduction Using Quantized CdS Nanocrystallites," *Journal of Physical Chemistry B* **1997**, *101*, 8270-8278.