GIES2008

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Hydrogen production from water with solar energy

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Hydrogen Production from Water using Solar Energy

$$H_2O \xrightarrow{h\nu} H_2 + \frac{1}{2} O_2 \qquad \Delta G^0 = 238\ kJmol^{-1}$$

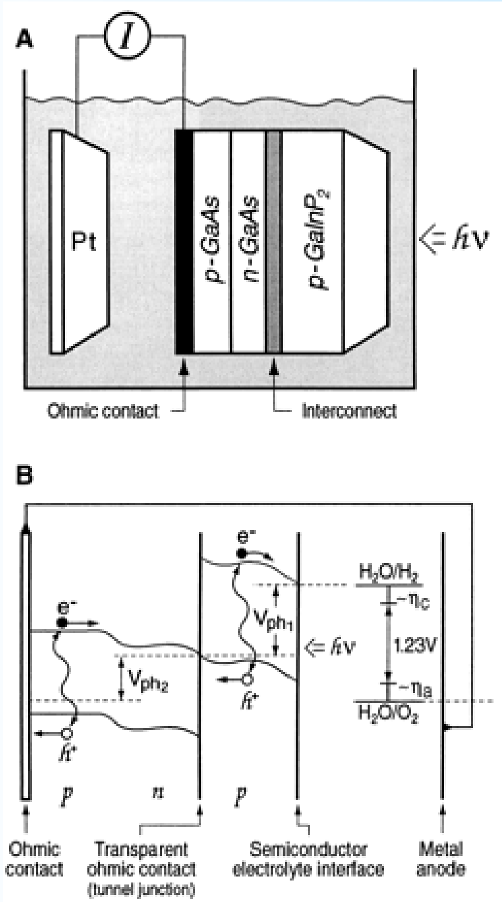
- **Solar cell + Electrolysis**

  : pilot plants

- **Photoelectrochemical Cell**

  : good efficiencies with tandem cells

Two examples of photoelectrochemical cells



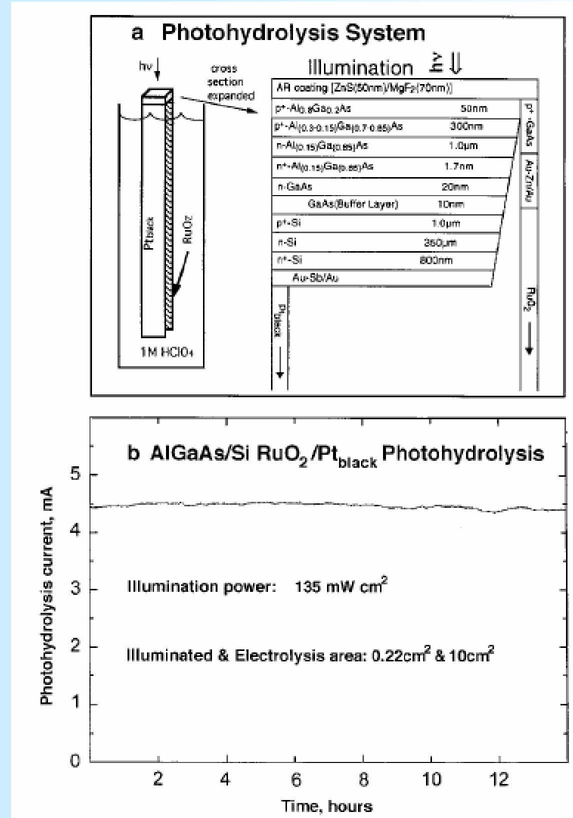
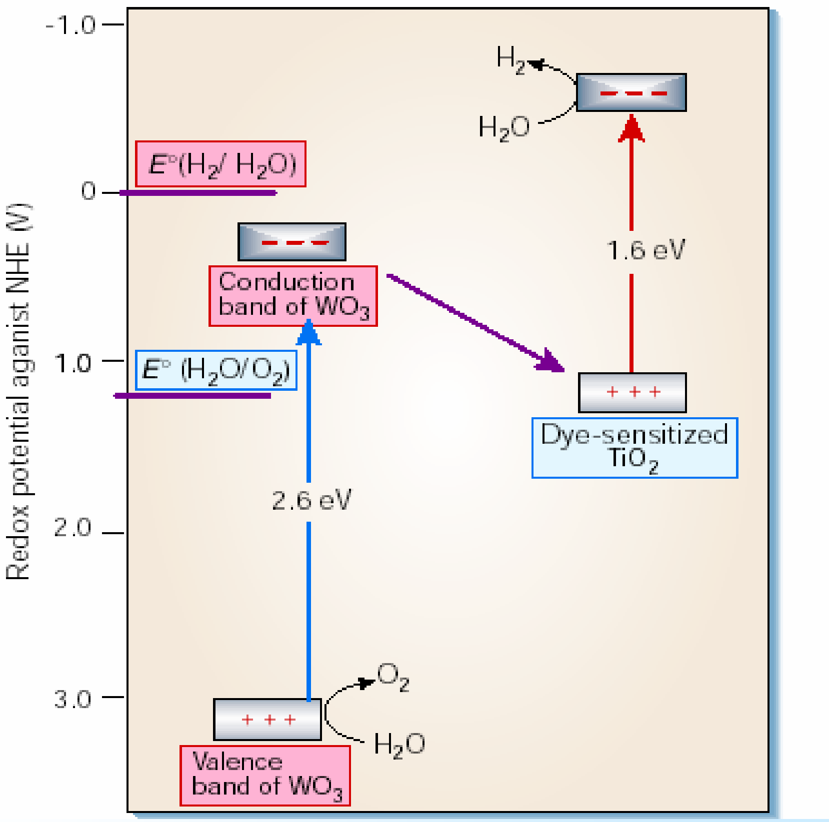


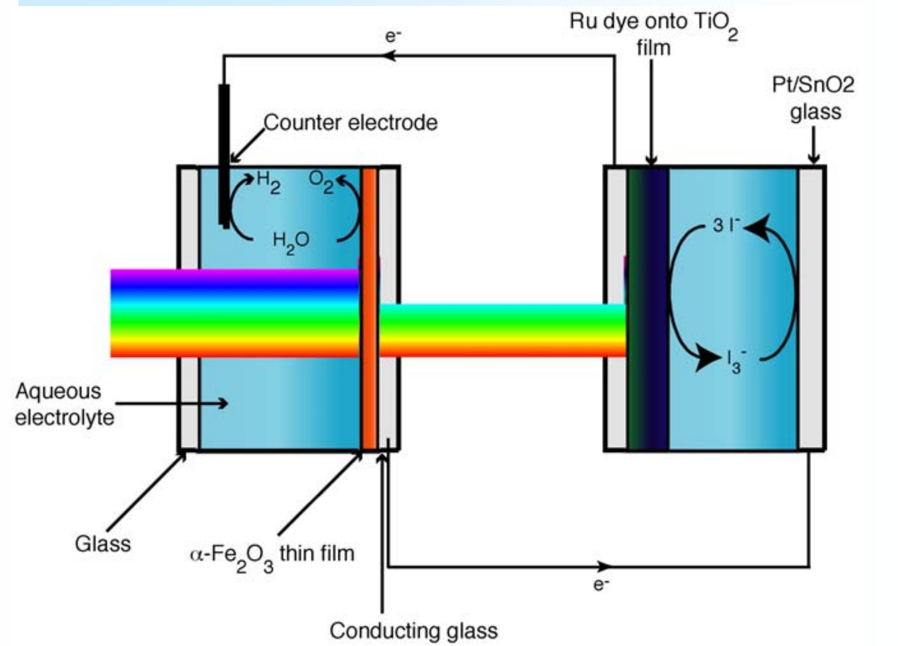
Figure 4. Schematic representation (a) and measured characteristics (b) of the illuminated AlGaAs/Si RuO_2/Pt_{black} photoelectrolysis cell. Further details of the layered AlGaAs/Si structure are given in ref 18.

Efficiency=12.4 %	Efficiency=18.3 %

J. A. Turner et al., *Science* **1998**, S. Licht et al., *J. Phys. Chem. B* **2000**,

Photoelectrochemical cells + PV





M. Grätzel, *Nature* 2001, *414*, 338–344.

solar energy conversion efficiency = 3～4%

$$H_2O \xrightarrow{h\nu} H_2 + \frac{1}{2} O_2 \qquad \Delta G^0 = 238\ kJmol^{-1}$$

- Solar cell + Electrolysis
- Photoelectrochemical Cell
- Artificial Photosynthesis (Photocatalysis)
  - Inorganic solid material
  - metal complex
  - organic material
  - biomaterial
- Photosynthesis

Available photons for water splitting

$$H_2O \rightarrow H_2 + 1/2O_2$$

$$\Delta G^0 = 237 \text{ kJ/mol}$$

$$= n \times F \times E^0$$

$$= 2 \times 96500 \text{ C/mol} \times 1.23 \text{ V}$$

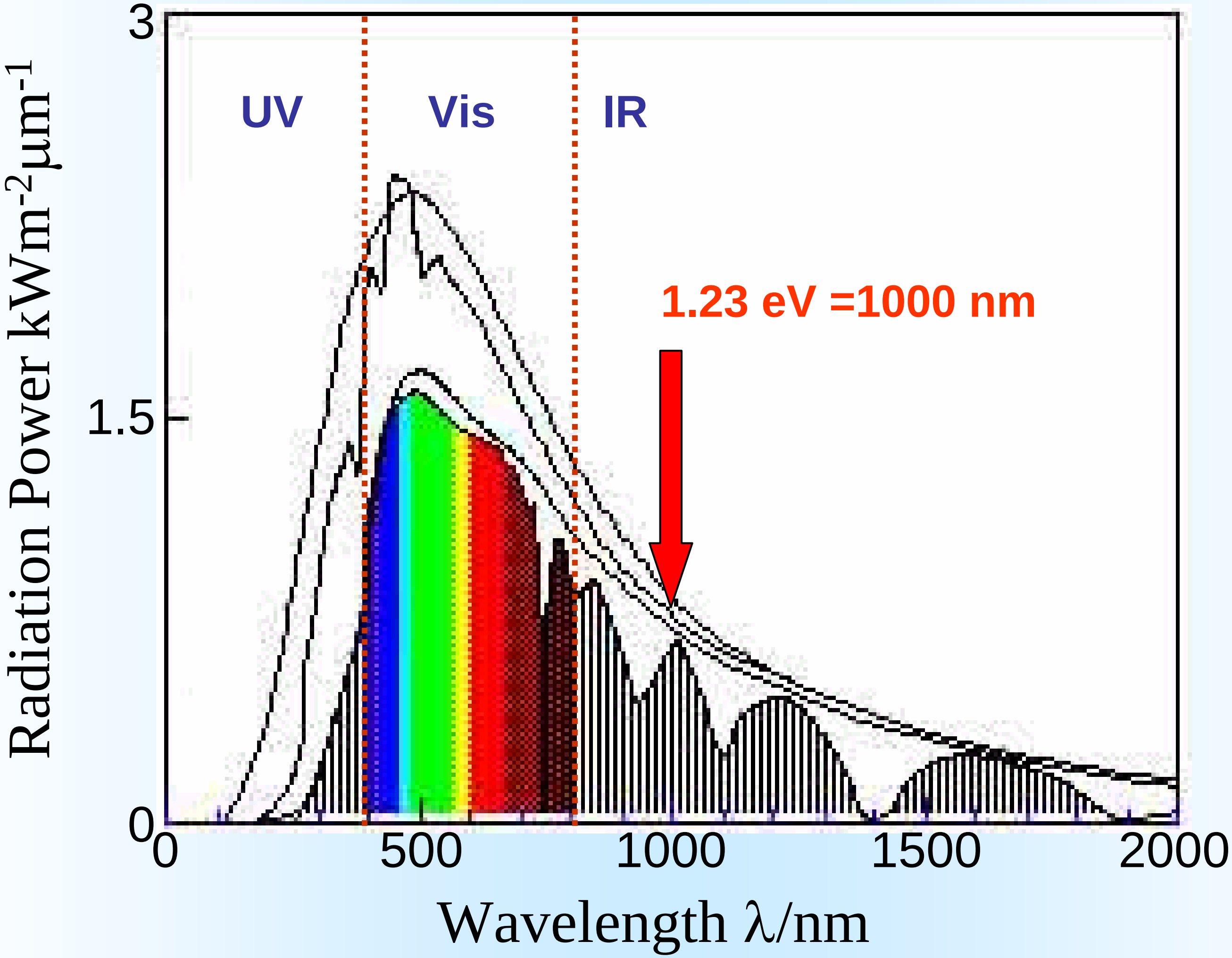
One electron energy = 1.23 eV

Photon energy

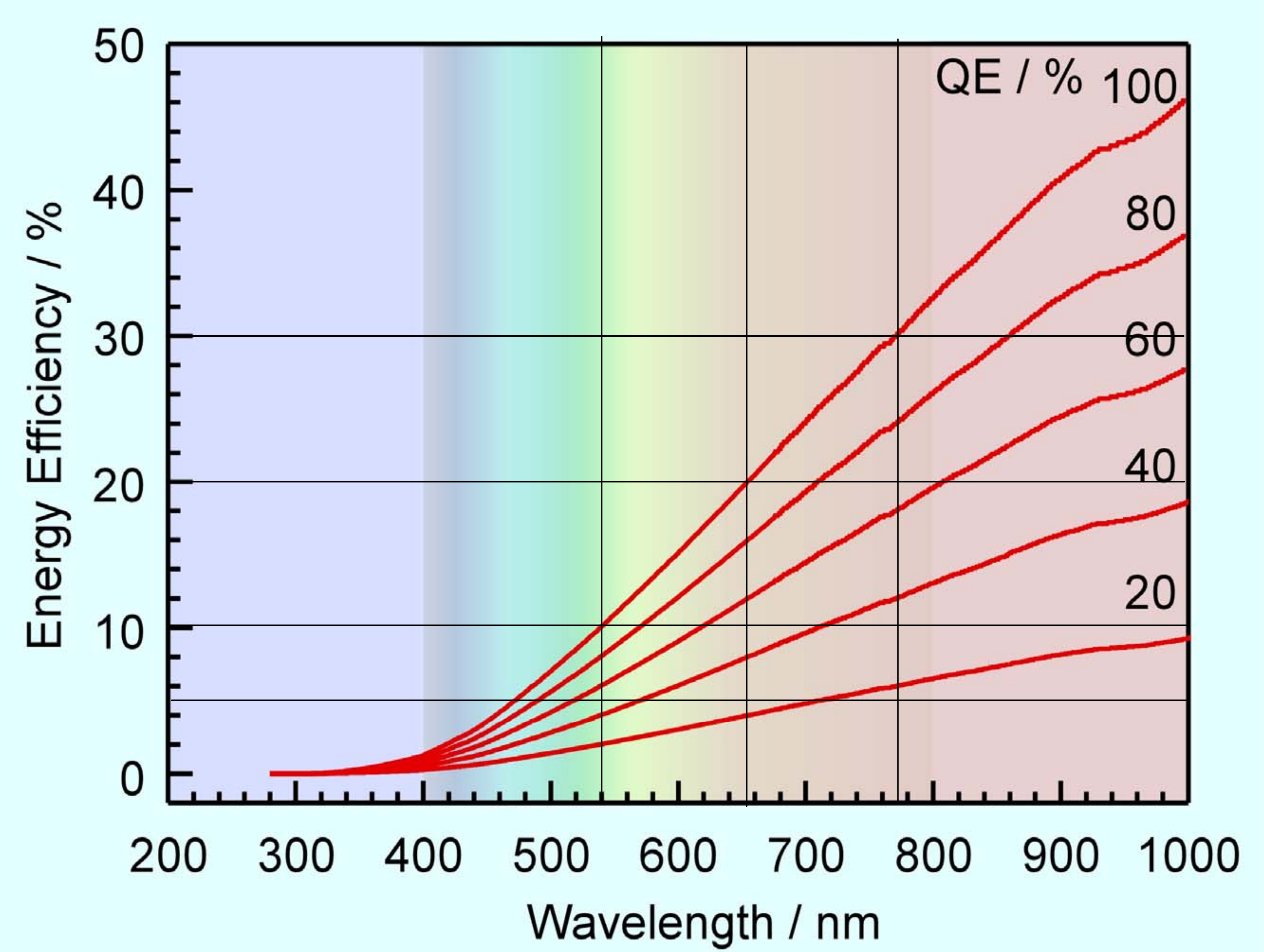
$$E\,(\text{eV}) = h\nu = \frac{1238}{\lambda(nm)}$$

1.23 eV ⇒ λ=1000 nm

Solar Energy Distribution



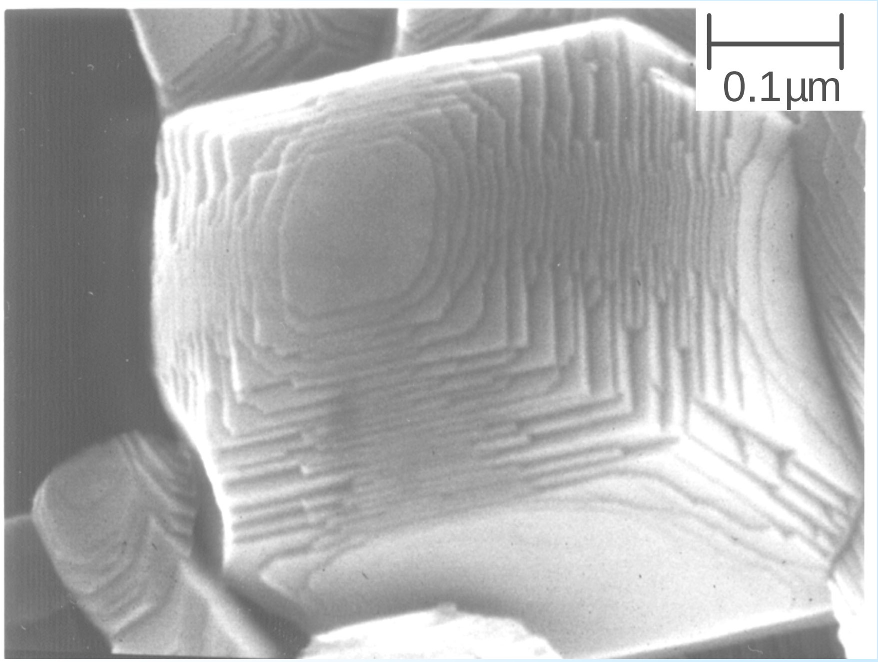
Solar Energy Conversion Efficiency

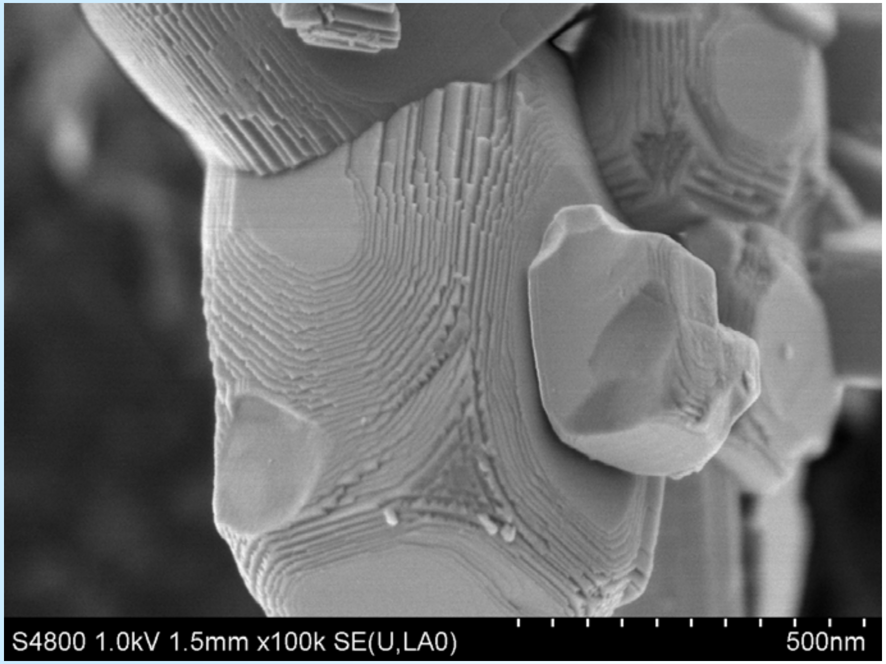


Solar energy conversion efficiency (Q.E.=100 %)

Wavelength / nm	Energy efficiency / %
400	1.67
450	4.29
500	7.95
550	11.9
600	16.2
650	20.6
700	25.1
750	29.4
800	33.5

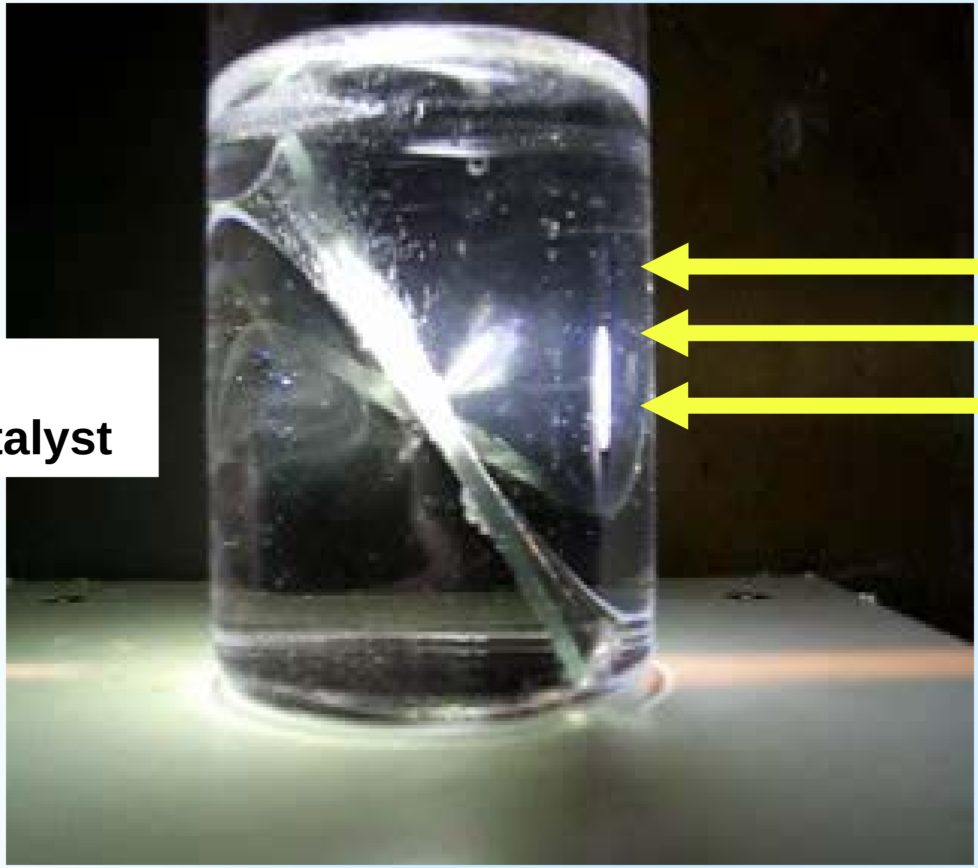
SEM Images of La-doped $NaTaO_3$





Prof. A. Kudo (Tokyo Univ. Sci.)

Overall water splitting on NiO(0.2wt%)/$NaTaO_3$:La



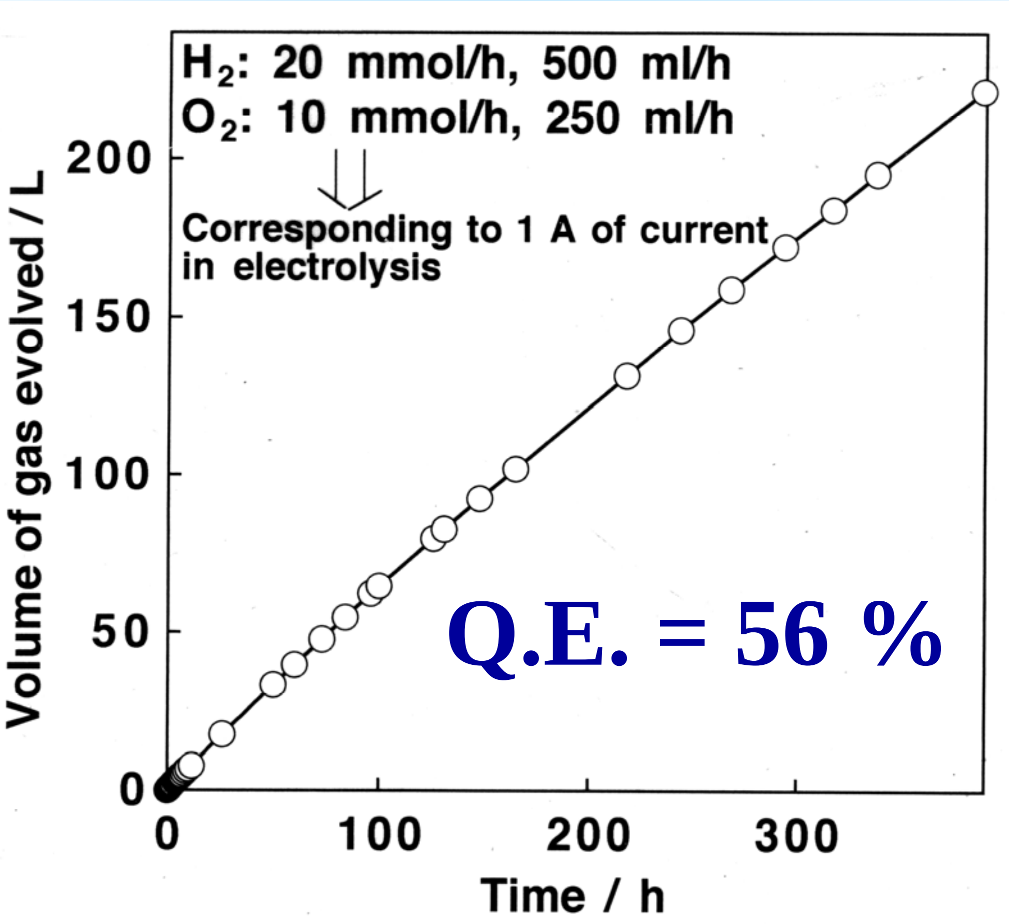
Layered photocatalyst

200W Xe-Hg Lamp

BG:4.1eV
QY:50% (270nm)

Prof. A. Kudo (Tokyo Univ. Sci.)

Time Course of Overall Water Splitting on NiO(0.2wt%)/$NaTaO_3$:La



Challenge with Visible Light

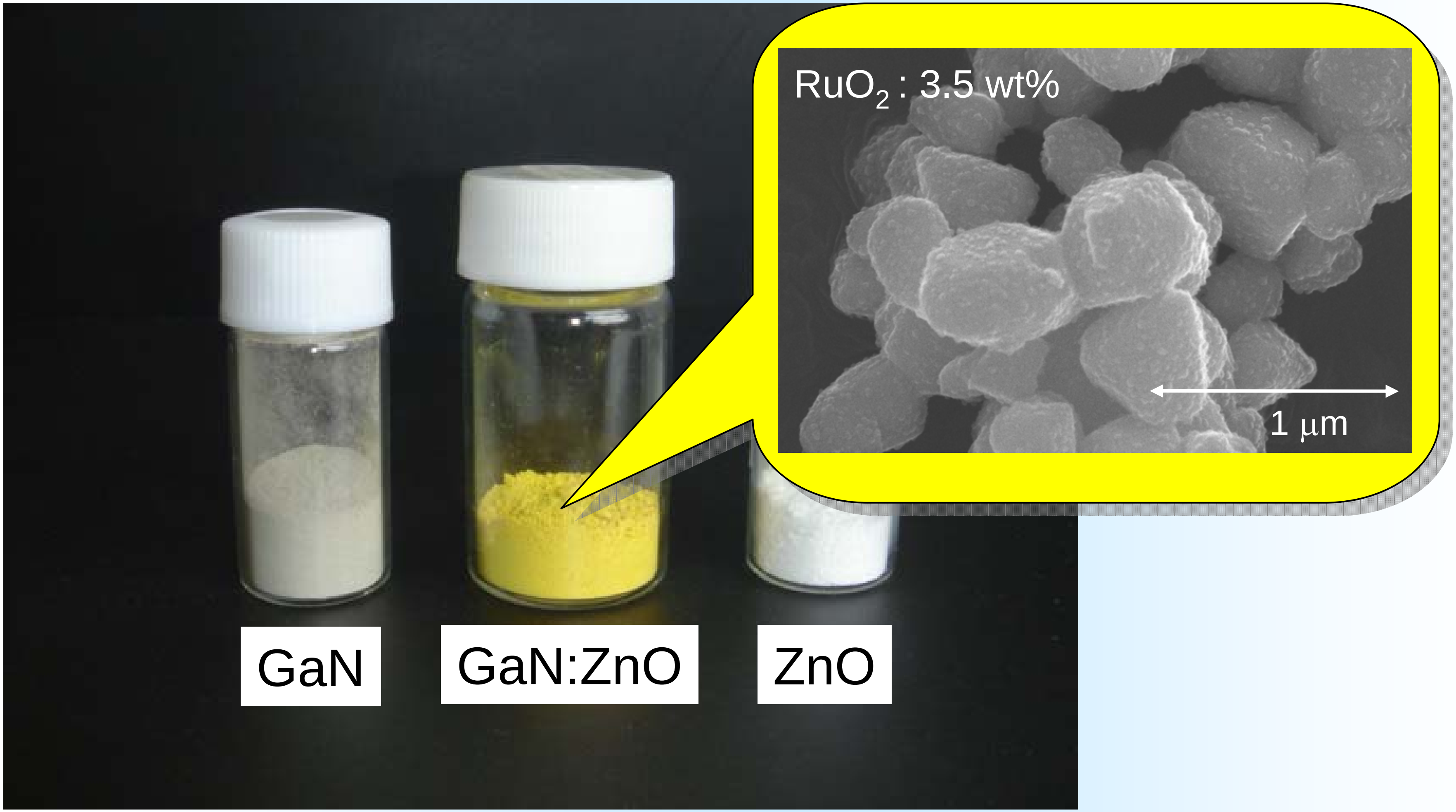
$$H_2O \longrightarrow H_2 + \frac{1}{2} O_2 \qquad \Delta G^0 = 238\ \text{kJmol}^{-1}$$

Photocatalytic Materials ?

with

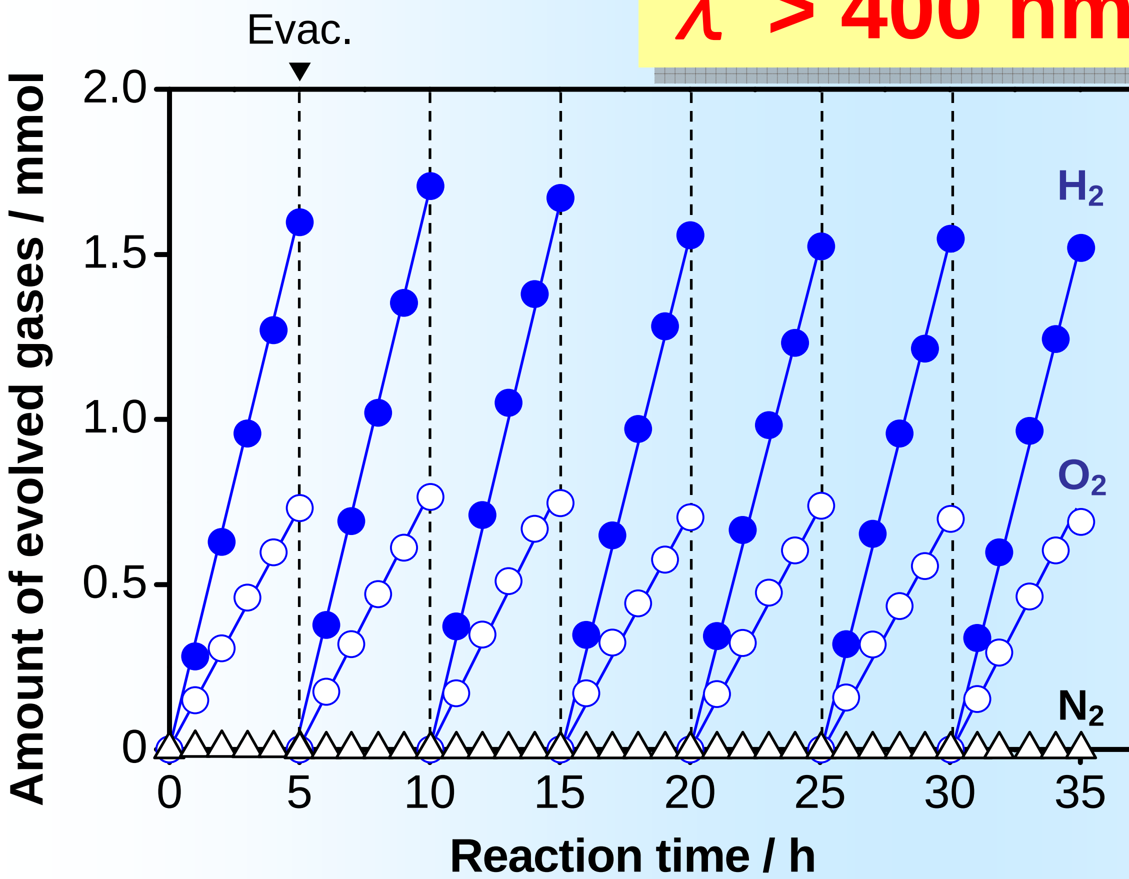
- Sufficient Solar Energy (Visible Light) Absorption
- Potential for Overall Water Splitting
- Enough Stability

GaN:ZnO solid solution

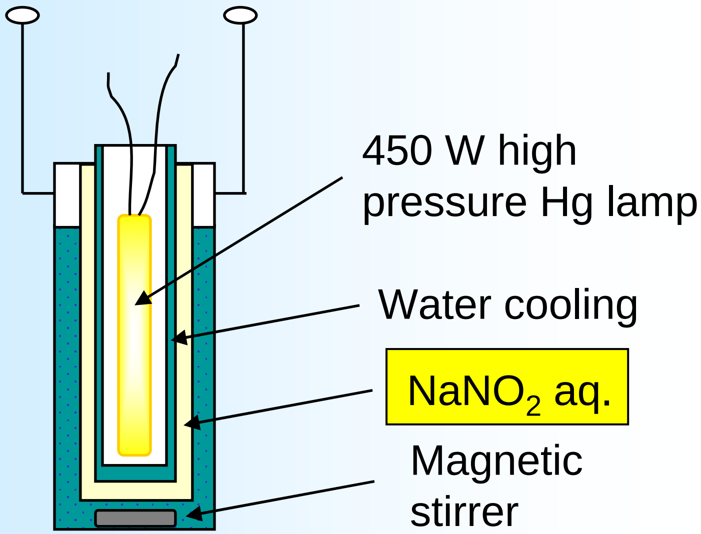


Visible Light-Driven Overall Water Splitting on Rh-Cr oxide / GaN:ZnO

λ > 400 nm



Catalyst: 0.3 g
Cocat.: Rh 1 wt%, Cr 1.5 wt%
Reactant soln.: 370 mL (pH 4.5)
Inner irradiation type cell
with a 2 M $NaNO_2$ aq. filter
450 W Hg lamp



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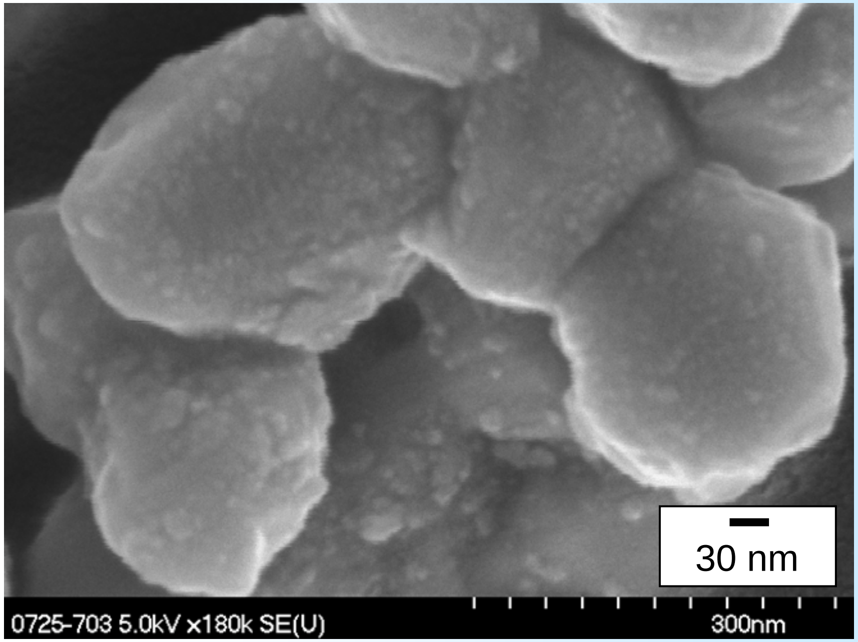
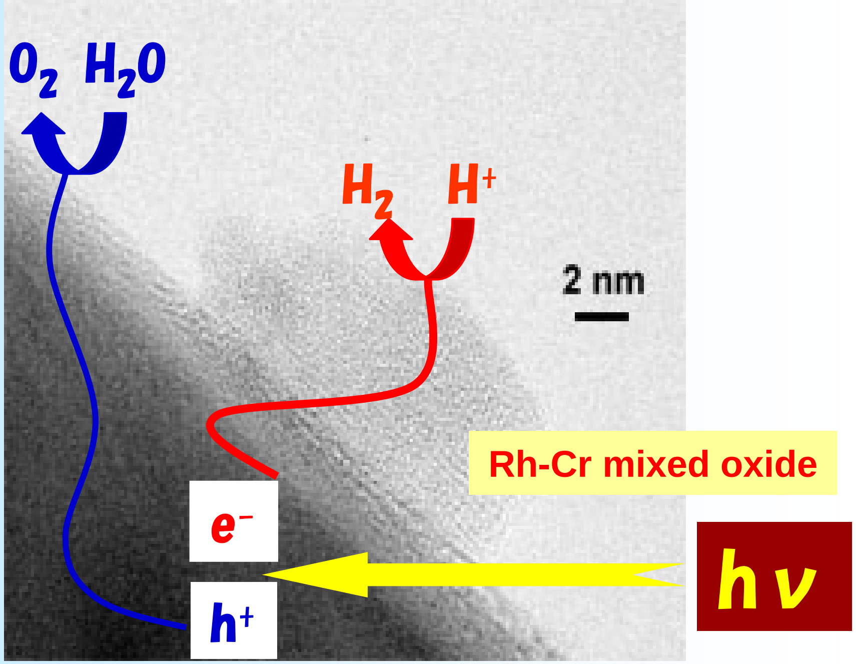
Electron micrographs of Rh-Cr oxide/GaN:ZnO

SEM image



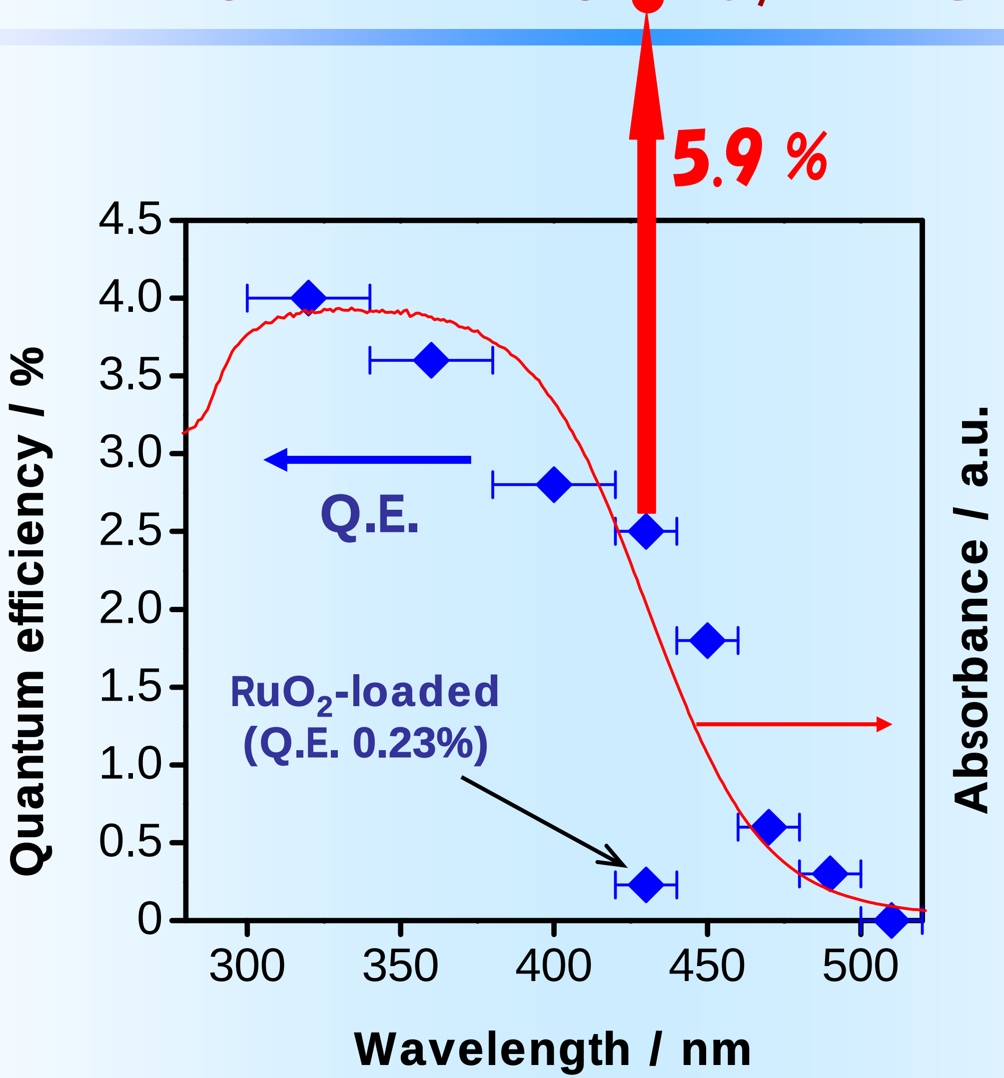
TEM image



Overall water splitting on Rh-Cr oxide/GaN:ZnO

λ > 300 nm

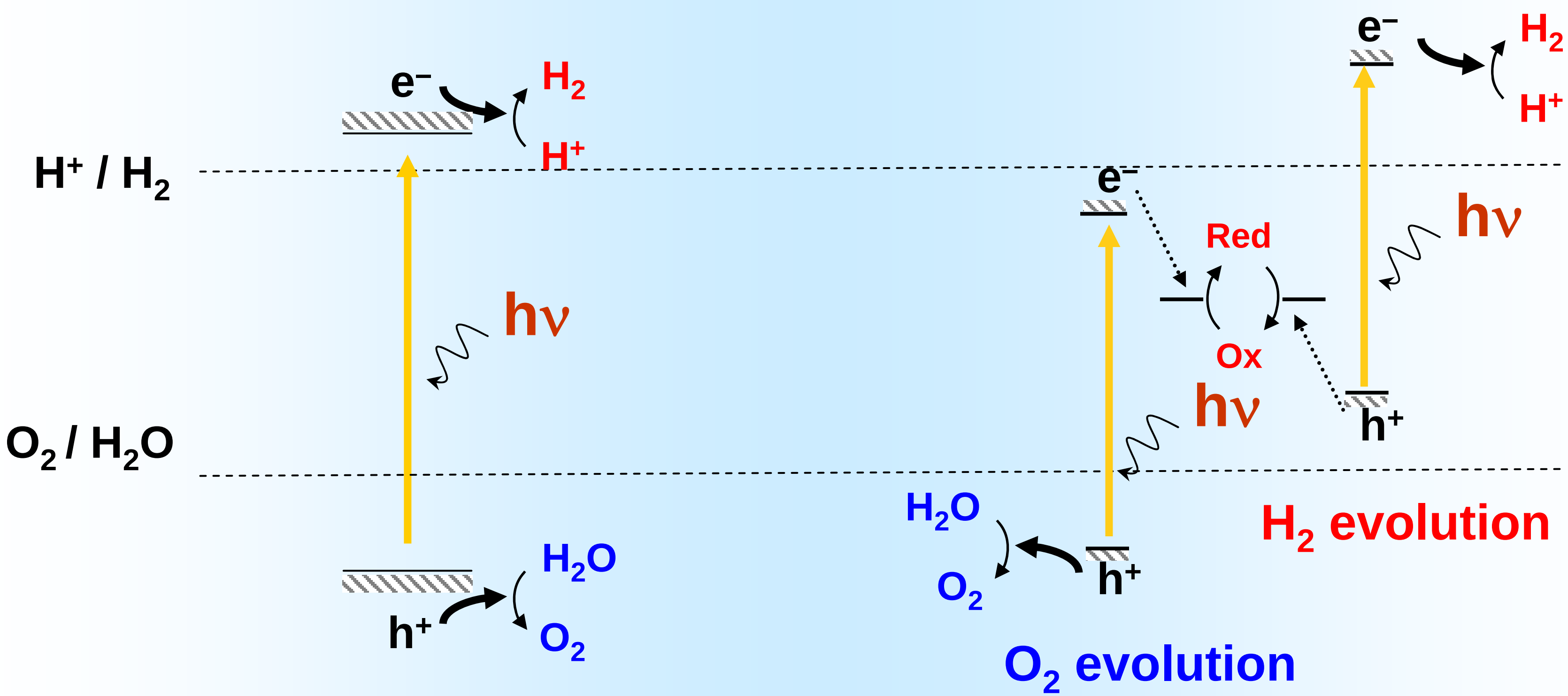
Q.E. of overall water splitting on Rh-Cr oxide/GaN:ZnO



Two approaches for overall water splitting

One-step excitation

Two-step excitation (Z-scheme)



Various Oxynitrides

Oxide

CaLaTiON

$Li_2LaTa_2O_6N$

$CaTaO_2N$

$SrTaO_2N$

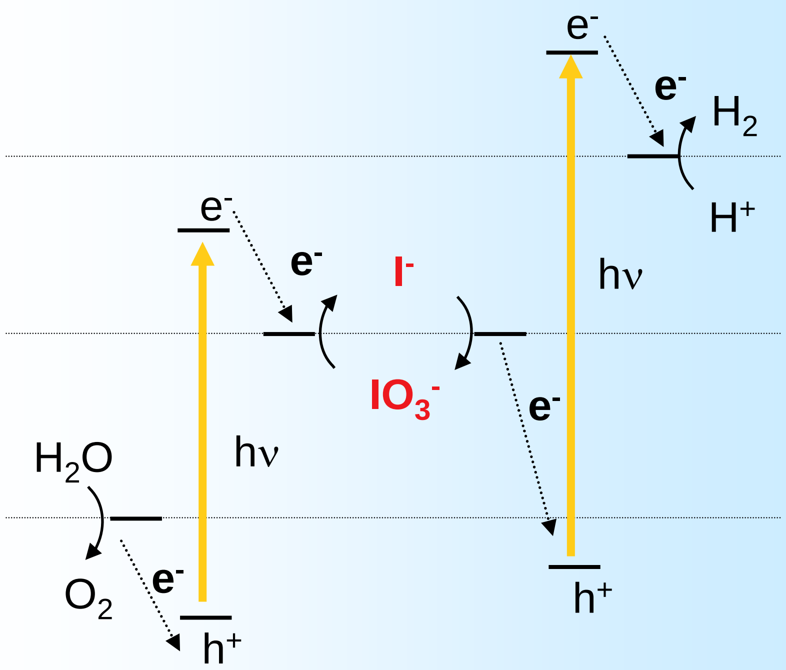
$LaTiO_2N$

$LaTaON_2$

Ta_3N_5

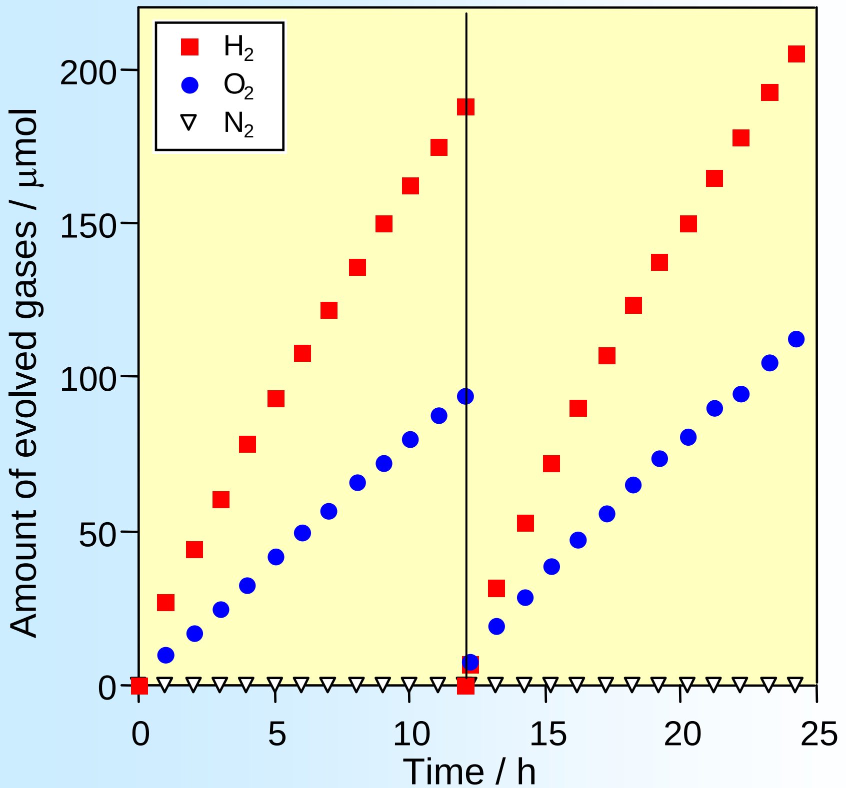
$BaTaO_2N$

Two-step overall water splitting under visible light



Pt/WO$_3$
(λ < 450 nm)

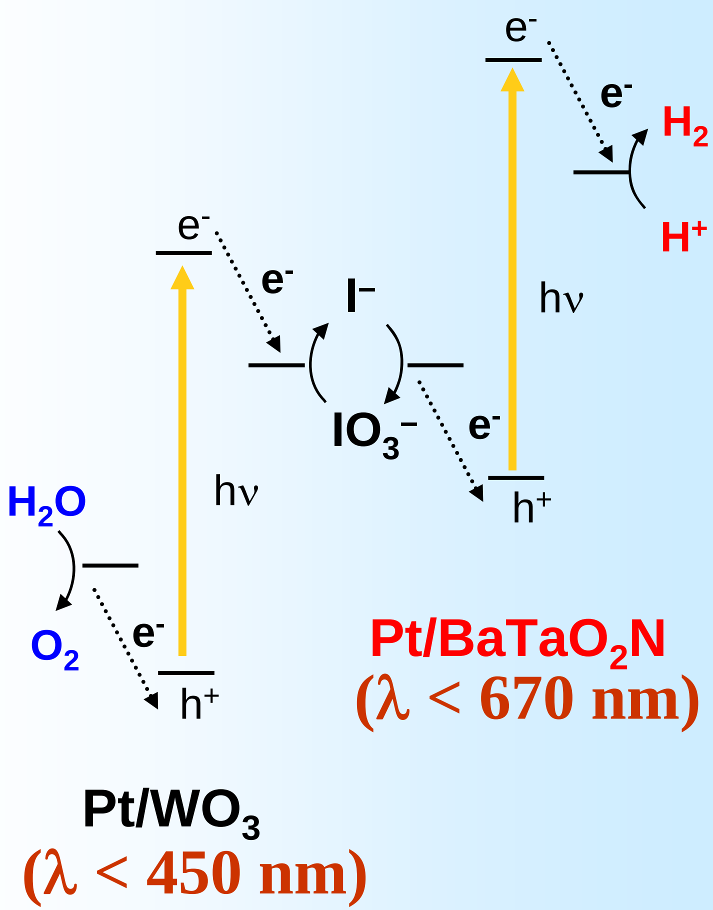
Pt/TaON
(λ < 500 nm)

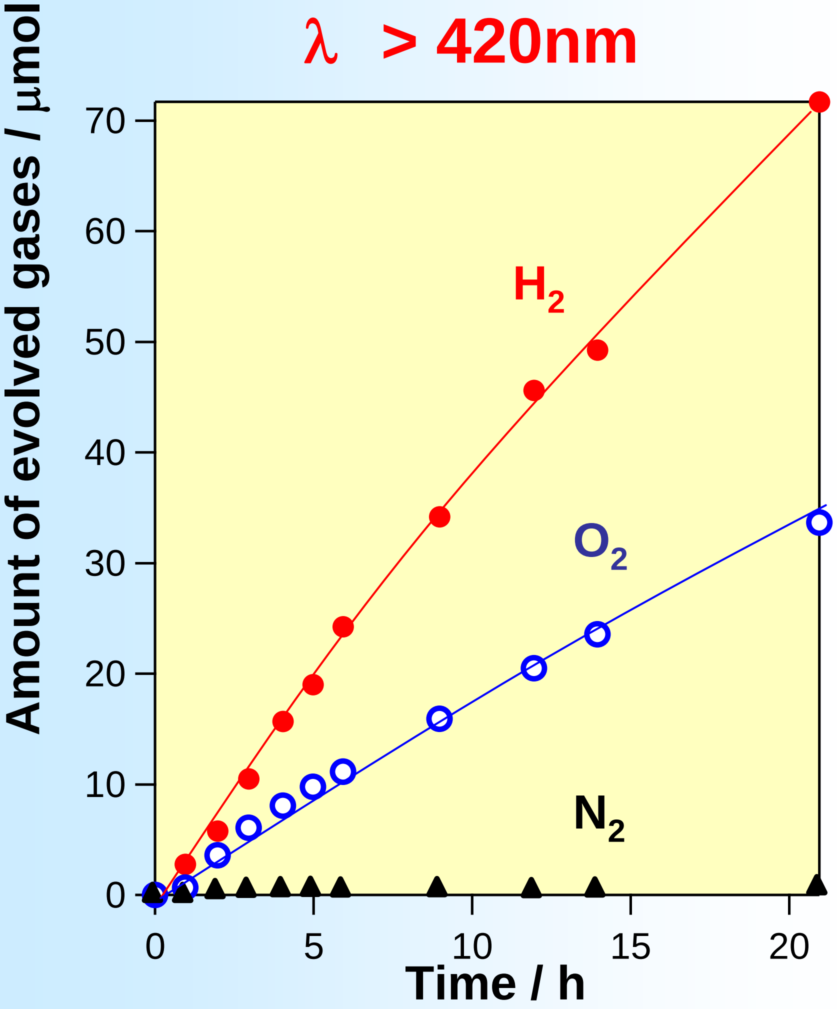


(Reaction conditions)
Pt/TaON: 0.2 g + Pt/WO$_3$: 0.2 g
5 mM-NaI aqueous solution: 250 mL (pH = 6.5)
300 W Xe-lamp, L-42 cut-off filter

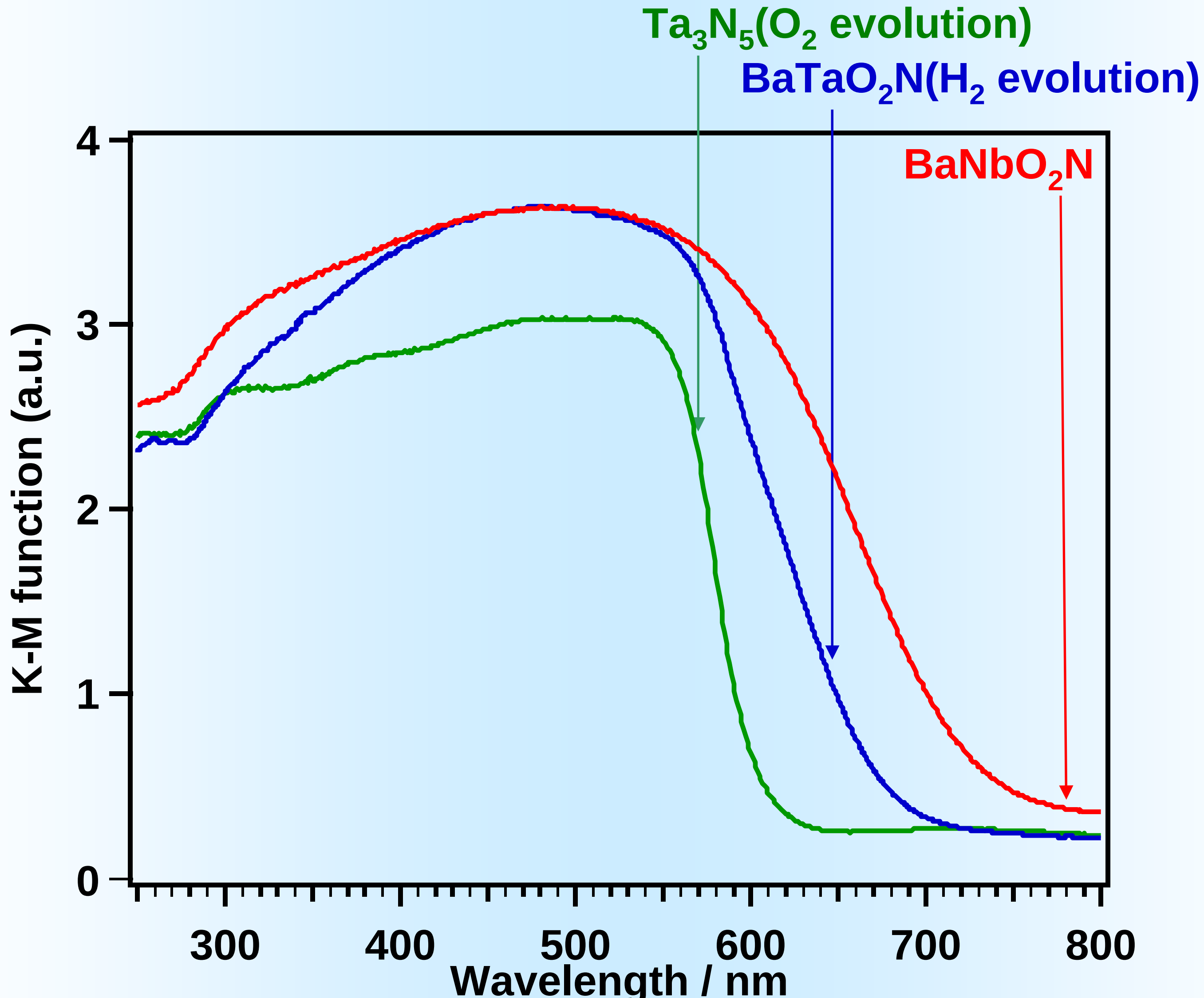
Chem. Commun. **2005**, 3829

Two-step overall water splitting on Pt/WO_3+$Pt/BaTaO_2N$

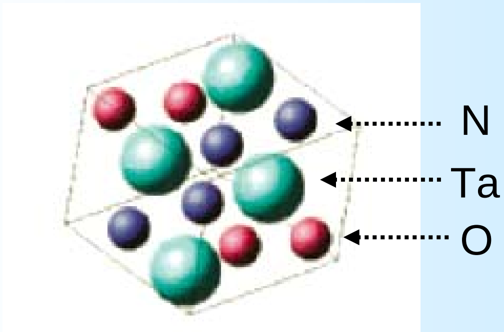




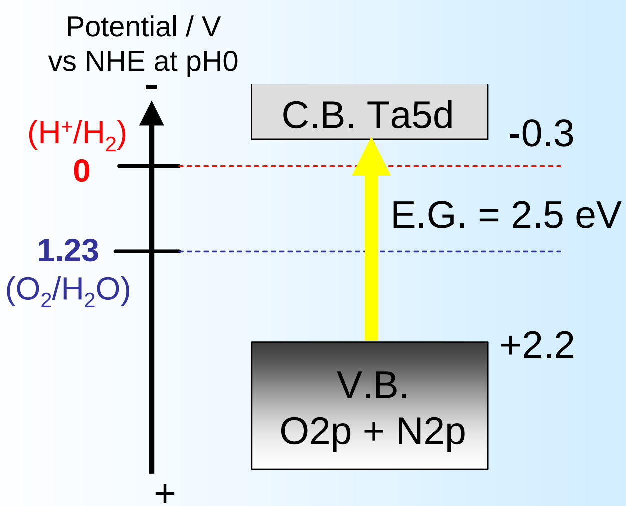
Available materials for two-step overall water splitting



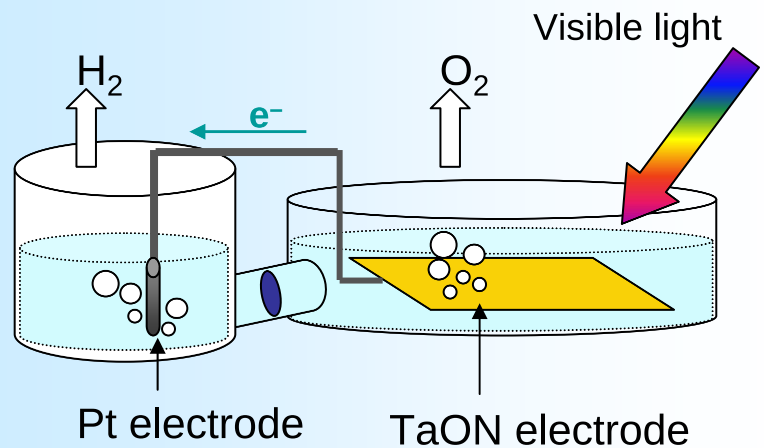
Application of oxynitrides to PEC cell



oxynitride TaON



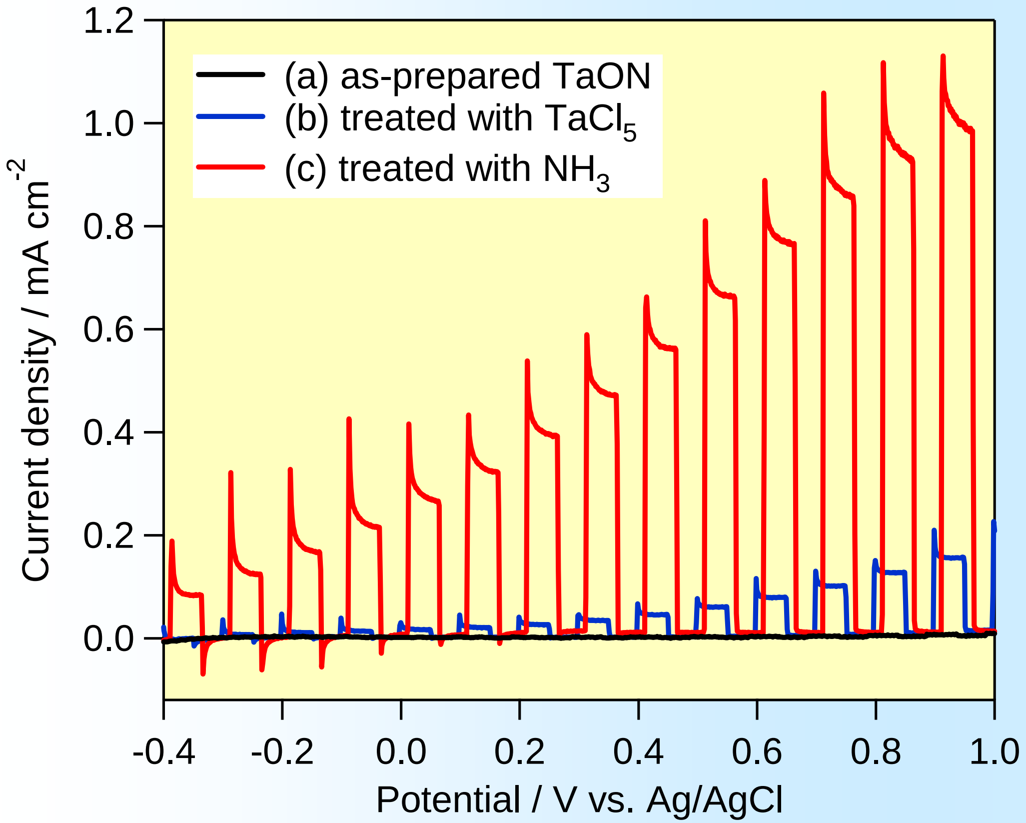
薄膜電極化

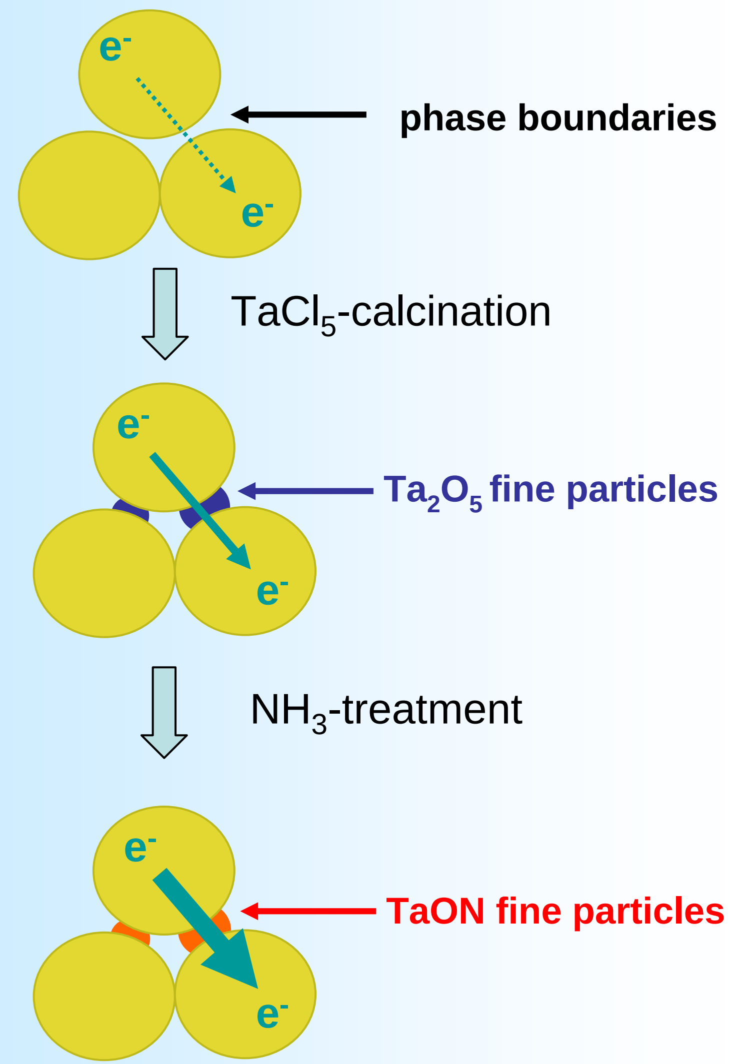


K. Domen et al., *J. Phys. Chem. B*, **2003**, *107*, 1798

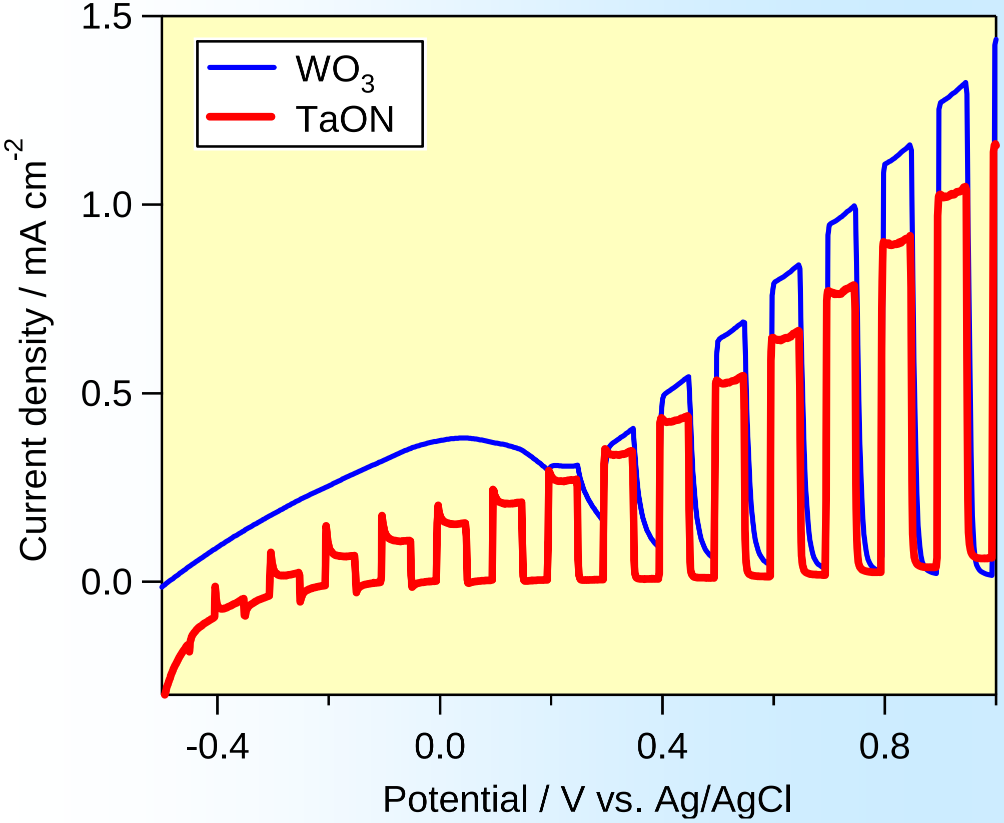
R. Abe et al., *Chem. Commun.*, **2005**, 3829

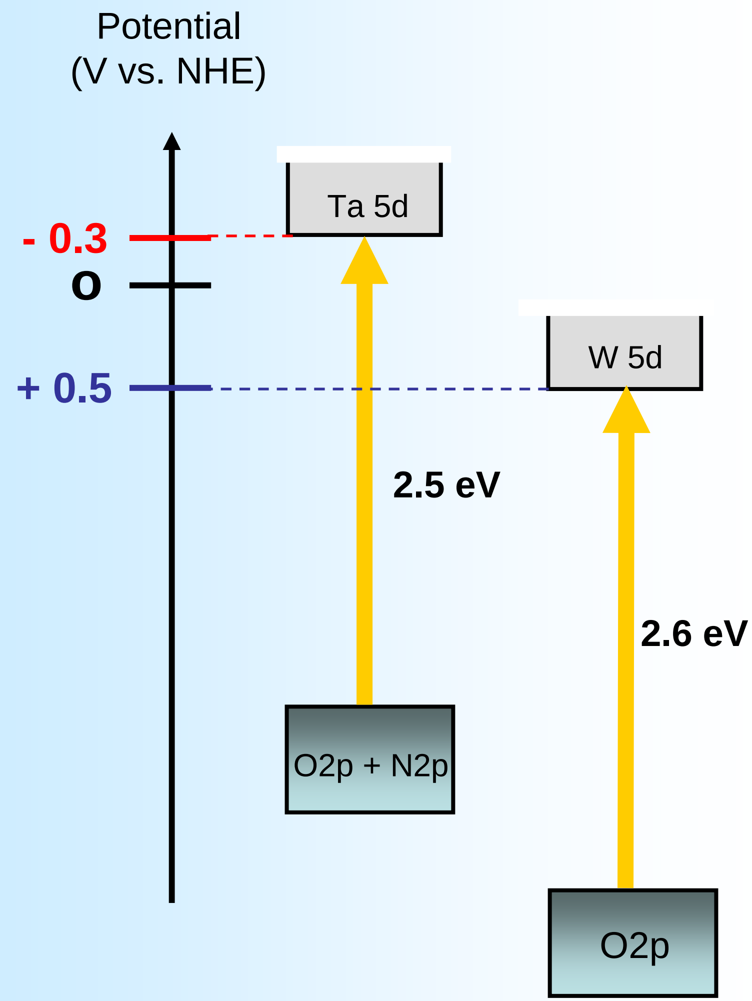
阿部（北海道大学）





[Conditions]
Supporting electrolyte: 0.1 mol-L^{-1} of Na_2SO_4
Potentiostat: PARSTAT 2263
Rate of scan: 50 mV / s
Light source: Xe illuminator (300 W, 300 < λ < 500 nm)





[Conditions]

Supporting electrolyte: 0.1 mol-L^{-1} of Na_2SO_4

Potentiostat: PARSTAT 2263

Rate of scan: 50 mV / s

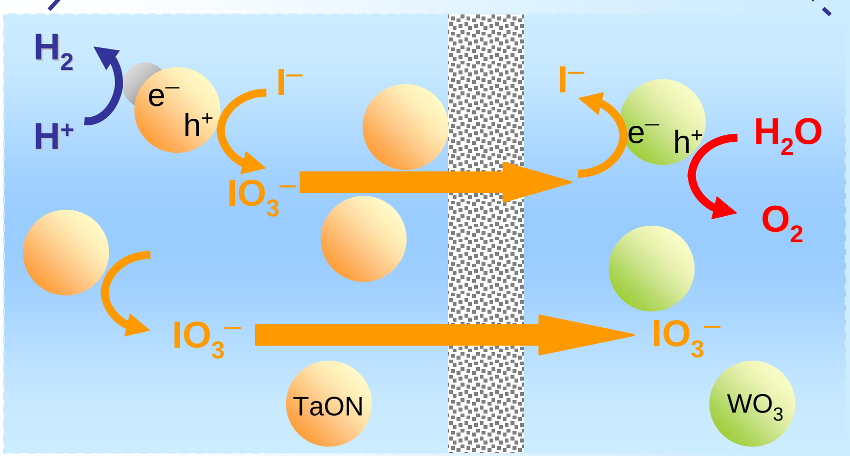
Light source: Xe illuminator (300 W, 300 < λ < 500 nm)

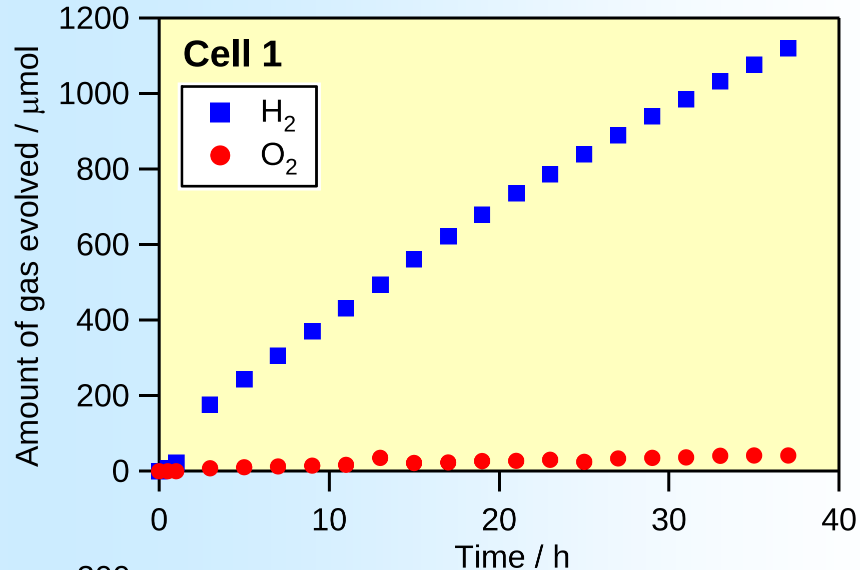
Two-room overall water splitting

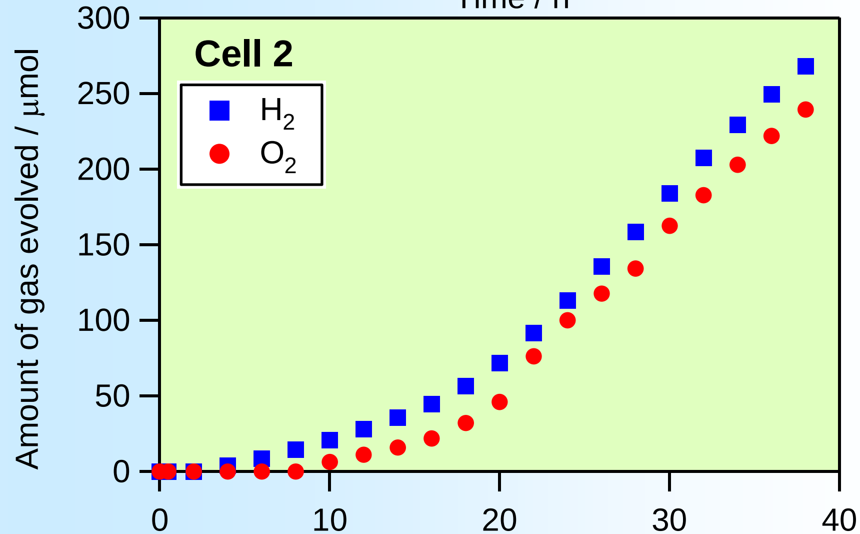
Cell 1
Rh–Cr/GaN:ZnO

Cell 2
Pt/WO_3

20 mmol L^{-1} NaI aq. 500 mL
300 W Xe lamp (λ > 300 nm)







Overall water splitting with sacrificial reagents

$$H_2O \longrightarrow H_2 + 1/2O_2$$

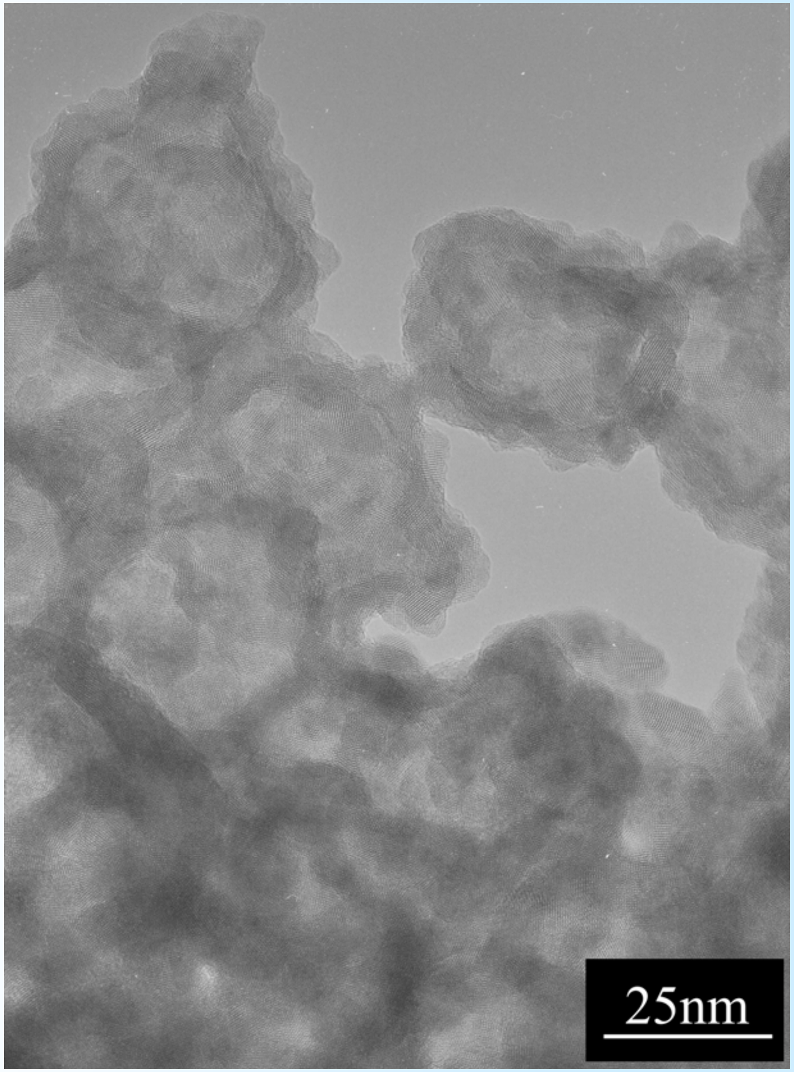
$$\Delta G^0 = 238\ kJmol^{-1}$$

$$2H_2O + Na_2S \longrightarrow H_2 + S + 2NaOH$$

$$H_2O + CH_3OH \longrightarrow 3H_2 + CO_2$$

$$6H_2O + C_6H_{12}O_6 \longrightarrow 12H_2 + 6CO_2$$

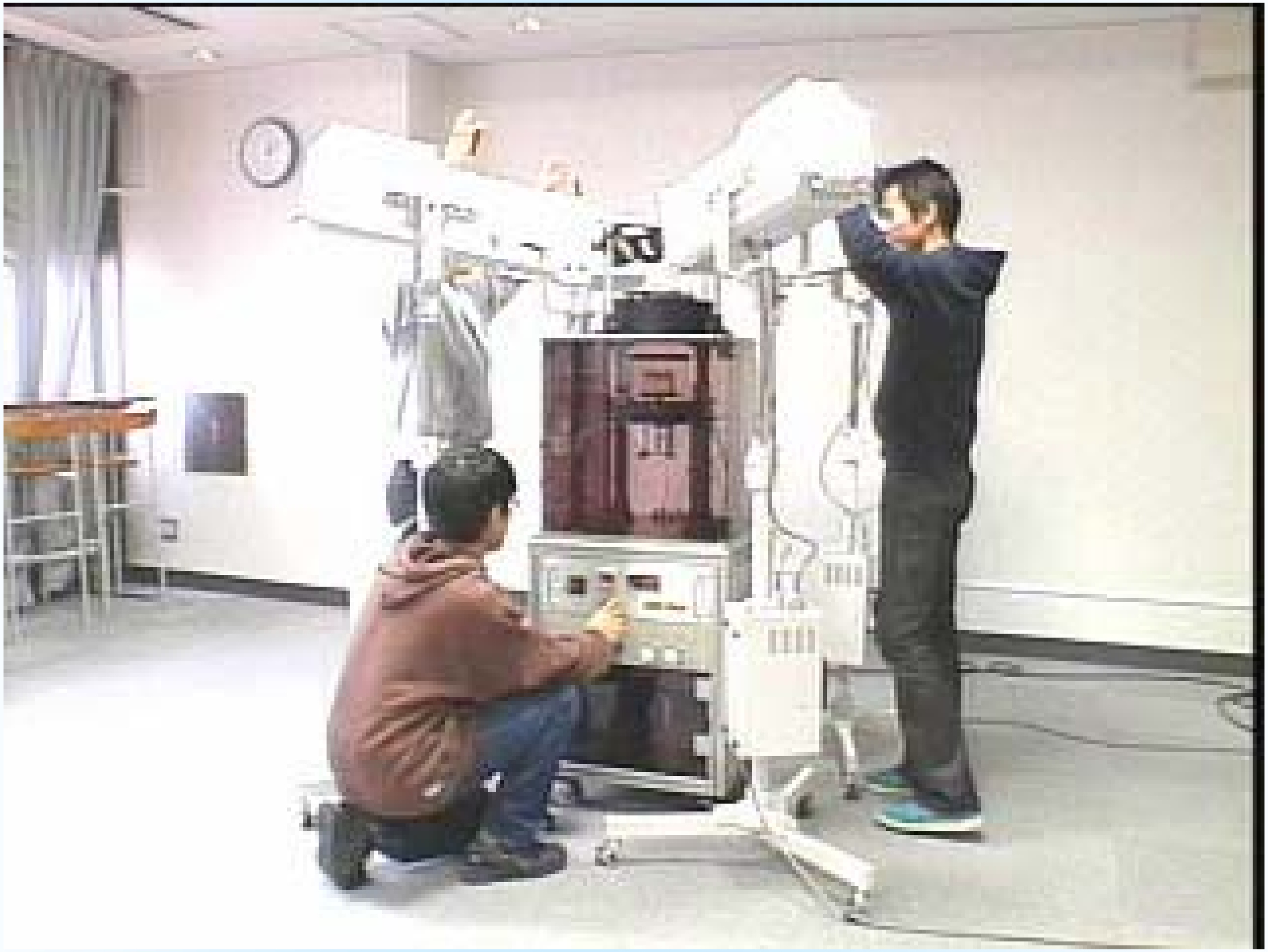
TEM image of stratified CdS



CdS capsules (30 nm) consist of nanoparticles (5nm)

Prof. K. Tohji (Tohoku Univ.)

H_2 production on stratified CdS from Na_2S solution



Prof. K. Tohji (Tohoku Univ.)

Hydrogen Production from Water using Solar Energy

- **Solar cell + Electrolysis**

vs

- **Photoelectrochemical Cell**

materials

- **Artificial Photosynthesis (Photocatalysis)**

Key Issues

New materials

Hybridization; structure

Application to wide area; Reactor design