March 12, 2021:霞が関プラザホール・オンライン

CCUS・水素に関する国際シンポジウム（環境省）

大規模展開を目指した光触媒水分解を用いる水素製造
“Solar hydrogen production using photocatalytic water splitting for large scale application”

Kazunari Domen

Shinshu University & The University of Tokyo

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Outline

[1] Introduction

[2] Particulate photocatalysts for water splitting

- *Al-doped $SrTiO_3$*
- *$Y_2Ti_2O_5S_2$*

[3] Photocatalyst sheets & water splitting panel

- *La, Rh-doped $SrTiO_3$ & Mo-doped $BiVO_4$*
- *Al-doped $SrTiO_3$*

[4] Construction of a prototype solar hydrogen production system

[5] Summary

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[5] Summary

Comparison of Energies (J/y)

- Solar energy on the Earth 3.0×10^{24}
- Consumption by human beings 5.5×10^{20}
- Photosynthesis on the Earth 3.0×10^{21}

About 0.02 % of solar energy is enough to support our life.

If solar energy will be one of the major energy resources in future・・・

- **Technology available for ~10^5 km^2**

  Assuming to provide 1/3 of total energy in 2050,
  10 % solar energy conversion efficiency
  with a scale of 5 km x 5 km = 25 km^2,

  10,000 plants have to be constructed.

  Scalability is the most important factor!

- **Storable and transportable Energy**

  Chemical Energy

  H_2, CH_3OH, CH_4, NH_3 etc.

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

- Solar cell (PV) + Electrolysis

- Artificial Photosynthesis :Photocatalysis
  - Inorganic solid state materials
  - metal complexes
  - organic materials
  - biomaterials

Target Reaction

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

using solar energy
on heterogeneous photocatalysts

- H_2 produced from solar energy and H_2O is clean & sustainable energy carrier and chemical resource.

- Production of solar fuels on a large scale at a low cost in a near future

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Photocatalytic & Photoelectrochemical water splitting

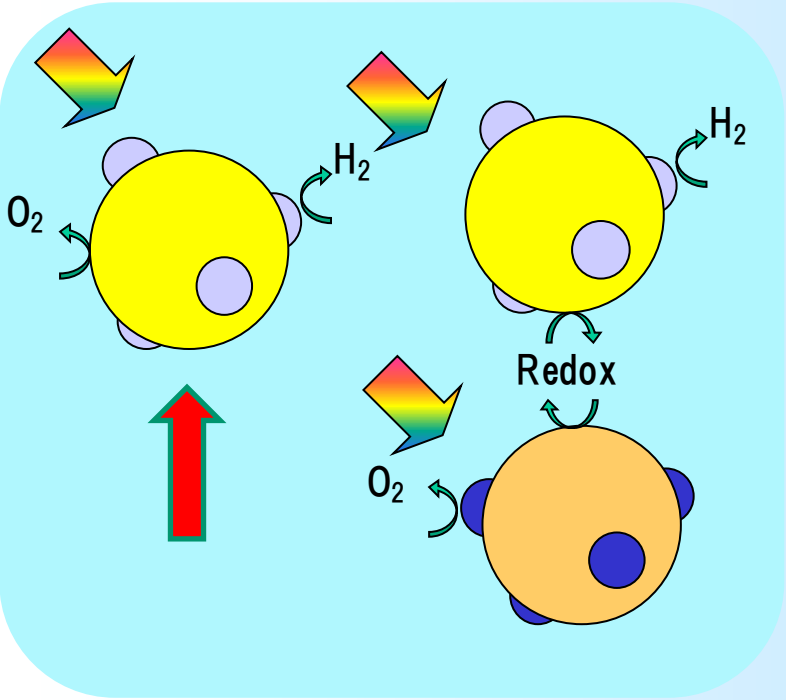
Photocatalysts → **Photocatalyst sheet**

Photoelectrodes

Water splitting panel

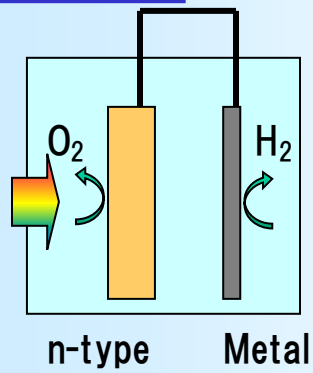
1-step

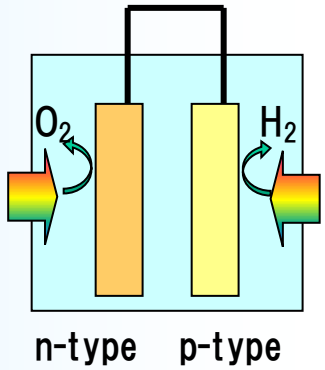
2-step

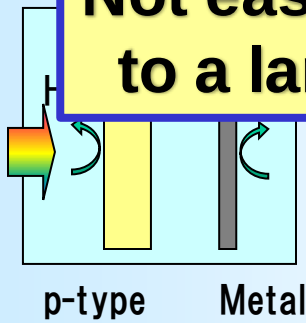


tep

2-step







Not easy to scale up to a large area!

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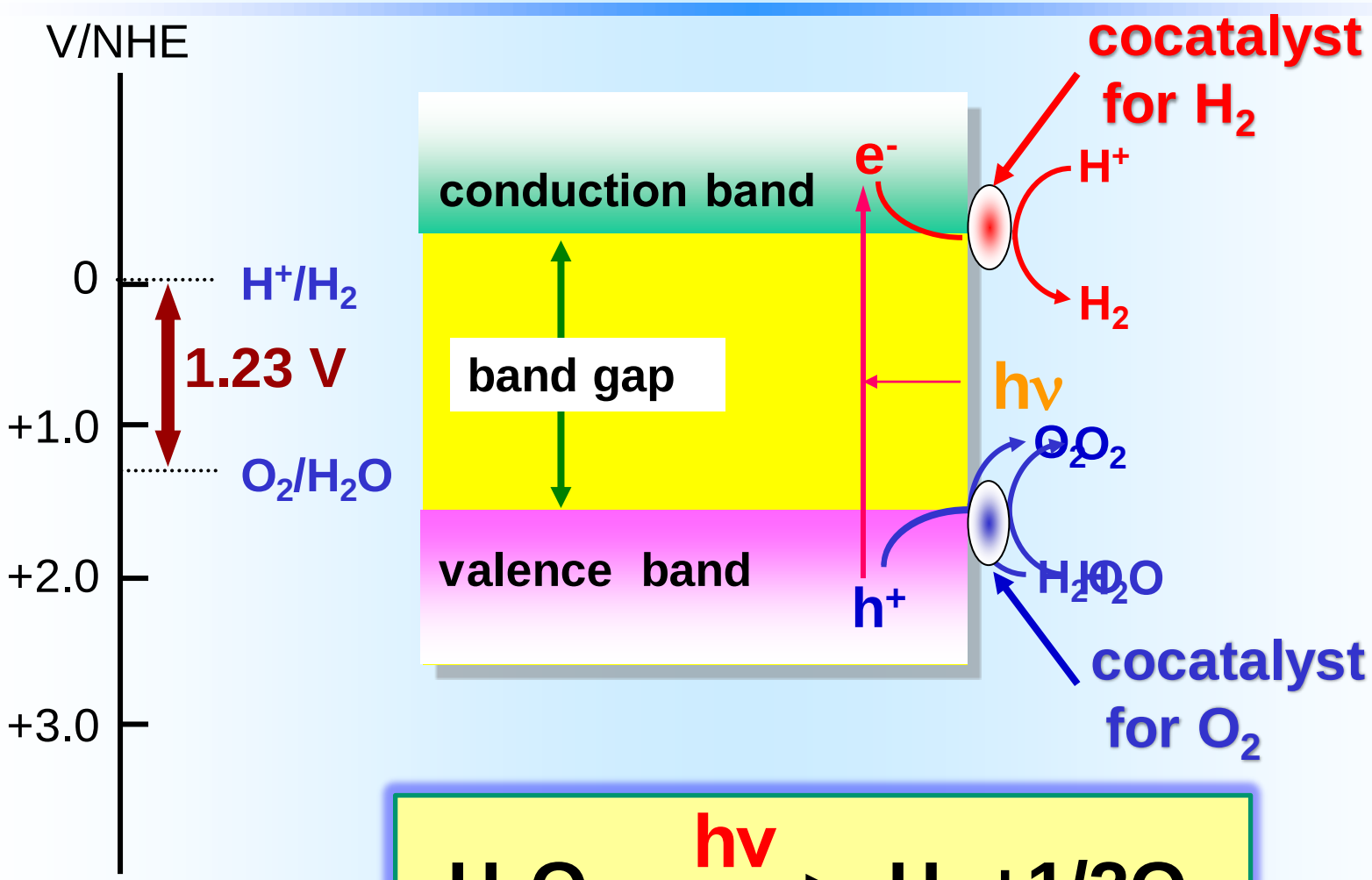
Basic principles of overall water splitting



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

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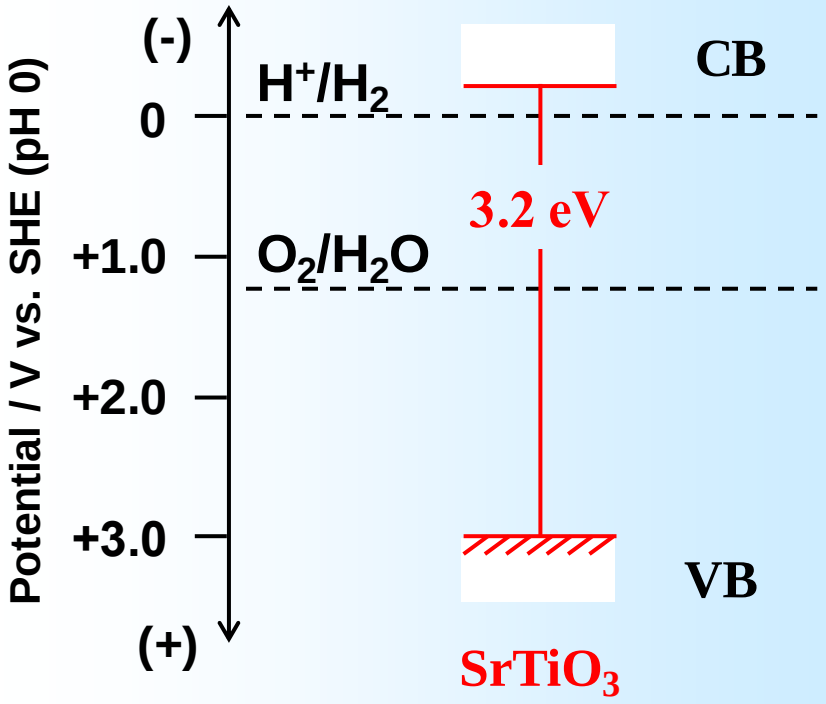
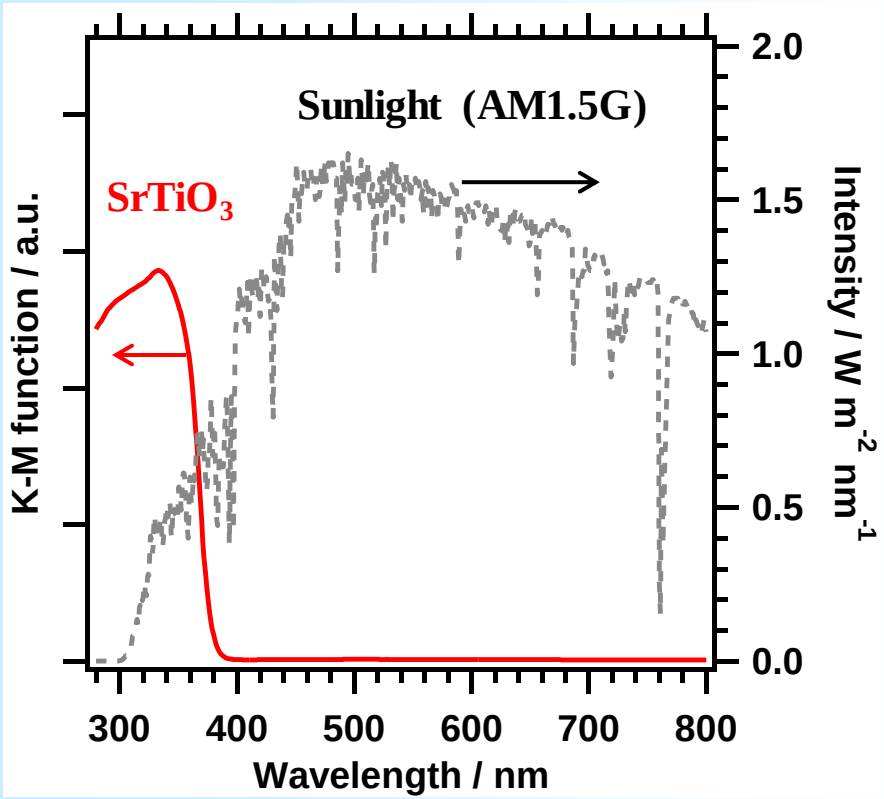
Potential of $SrTiO_3$ as photocatalyst





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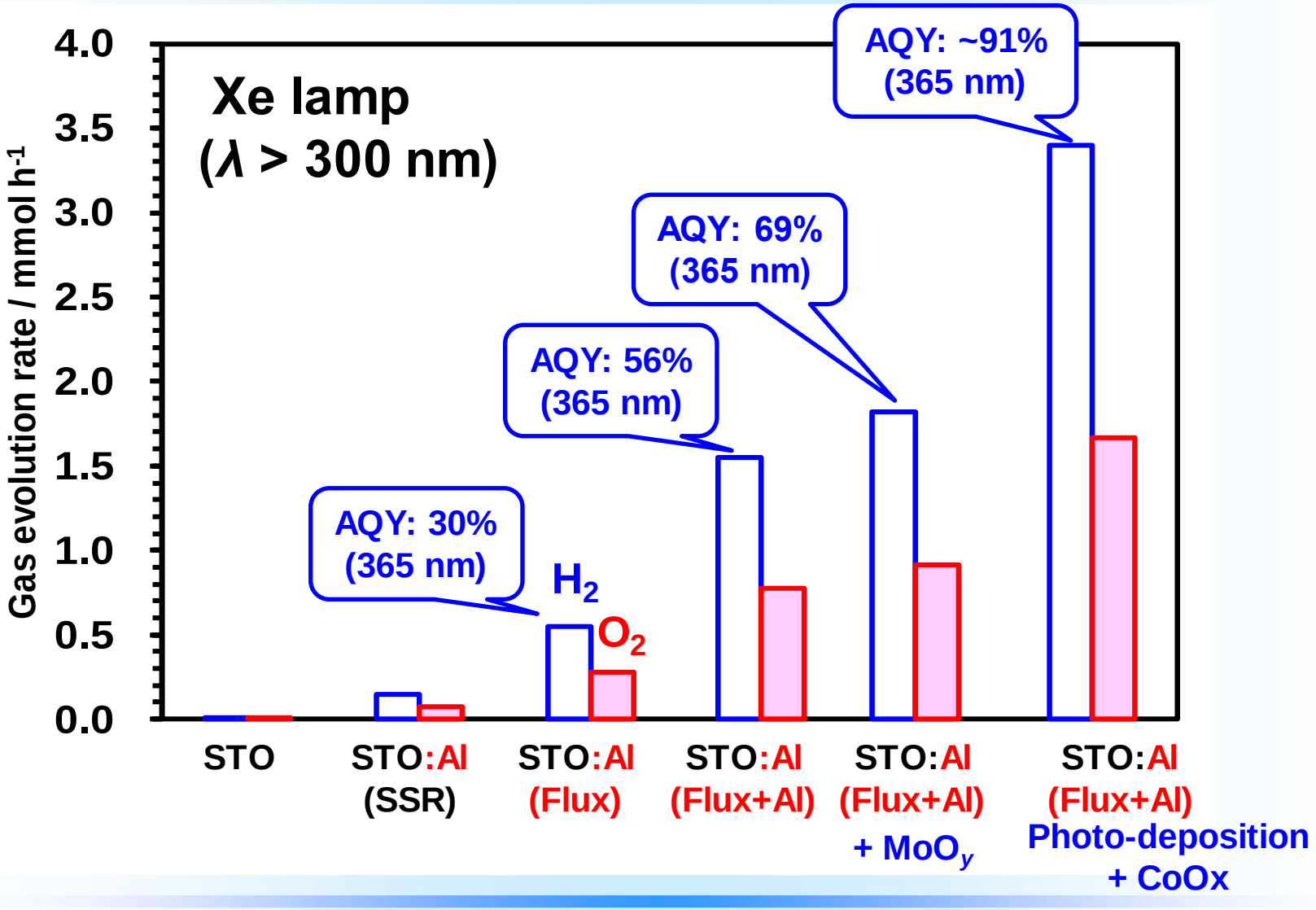
Activities of various $RhCrOx/SrTiO_3$:Al



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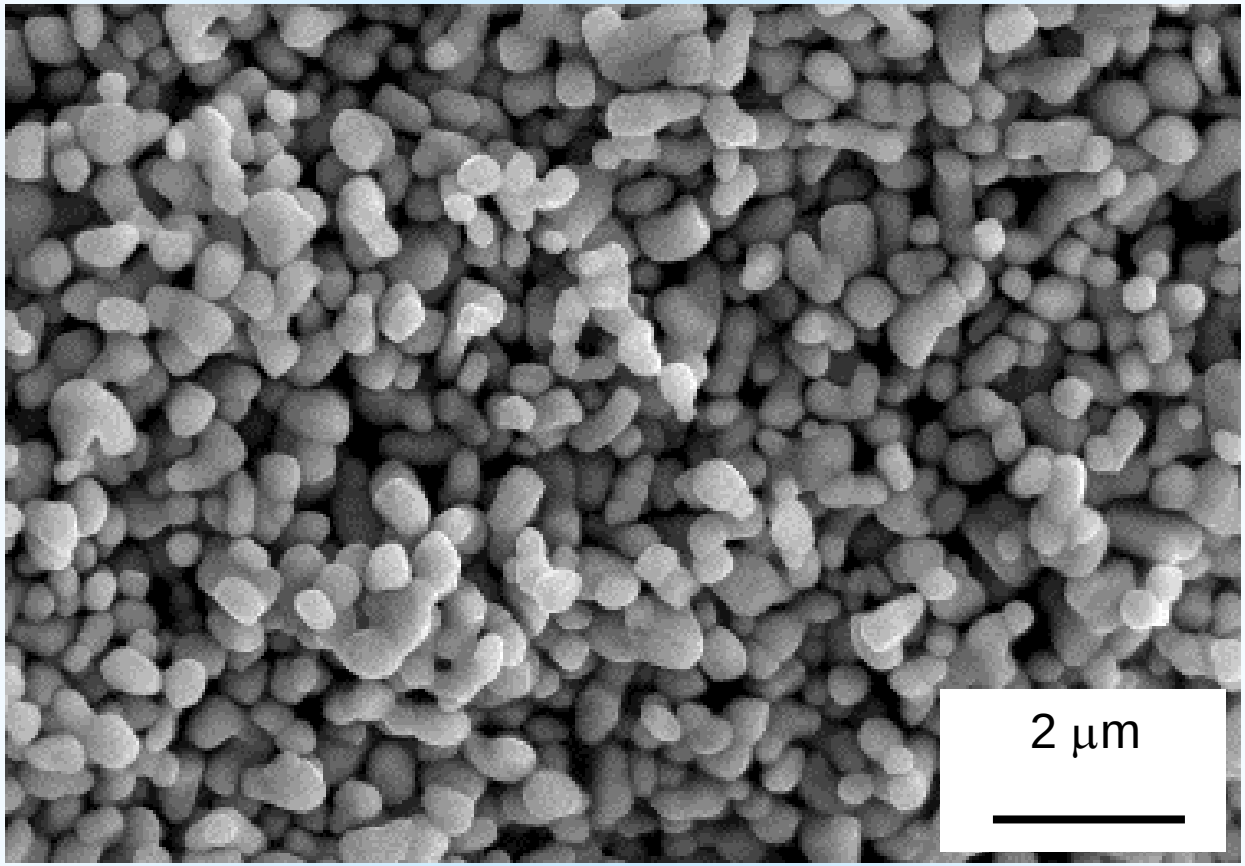
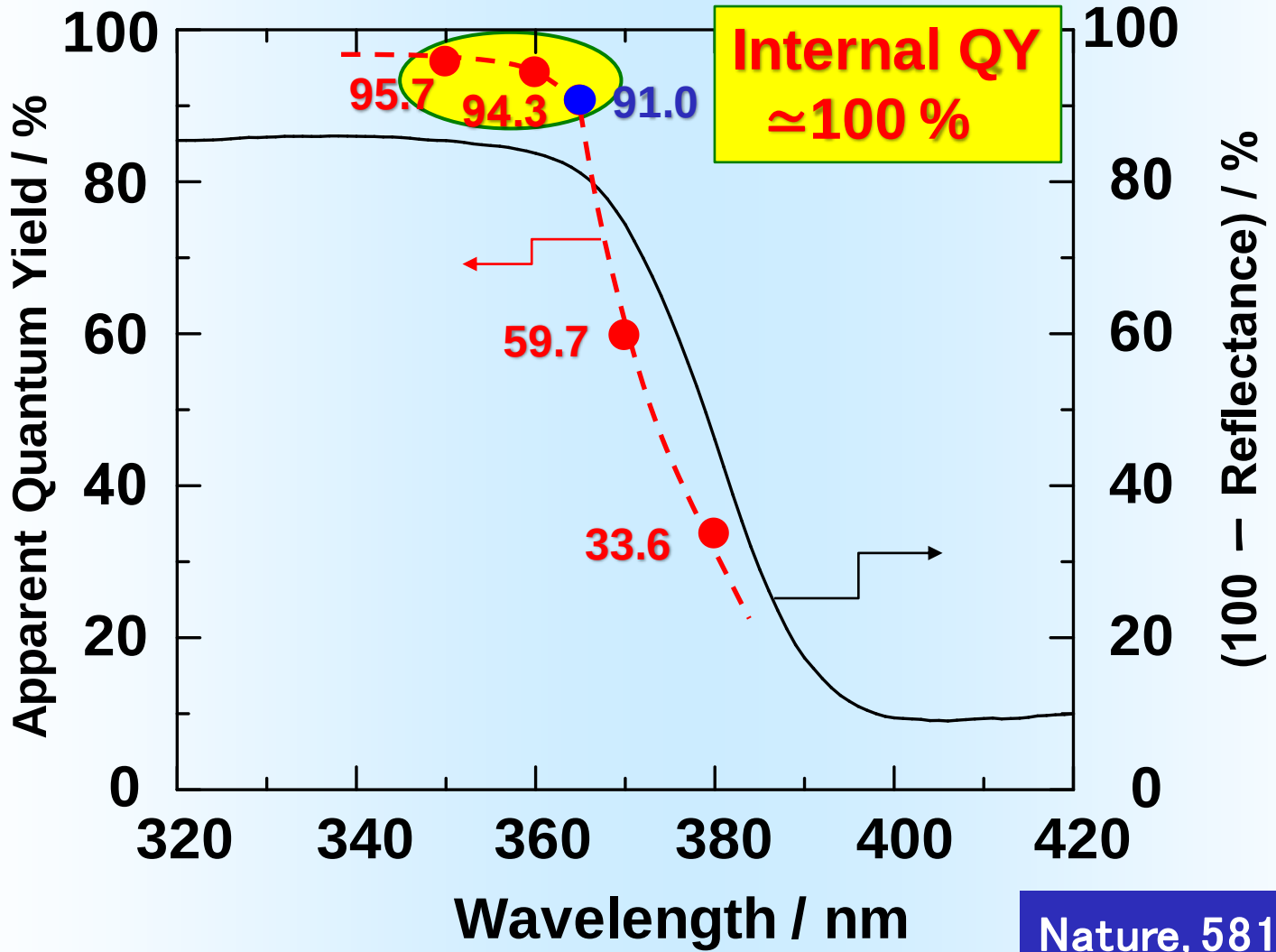
SEM image of Al doped $SrTiO_3$ prepared by flux method

$SrCl_2$(flux) : $SrTiO_3$: Al_2O_3(dopant) = 10 : 1 : 0.1

Amount of doped Al = ~0.1 at%



Wavelength dependence of AQY



Nature, 581, 411 (2020)

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Preparation procedure of CrO_x-Rh / $SrTiO_3$:Al / CoO_x

Photodeposition method in H_2O

- H_2 evolution cocatalyst: CrO_x-Rh

$Rh^{3+} + 3e^- \longrightarrow Rh^0$ (metal)

$Cr^{6+} + 3e^- \longrightarrow Cr^{3+}$ (oxide)

"photoreduction"

Core-shell

- O_2 evolution cocatalyst: CoO_x

$Co^{2+} + h^+ \longrightarrow Co^{3+}$ (oxide)

"photooxidation"

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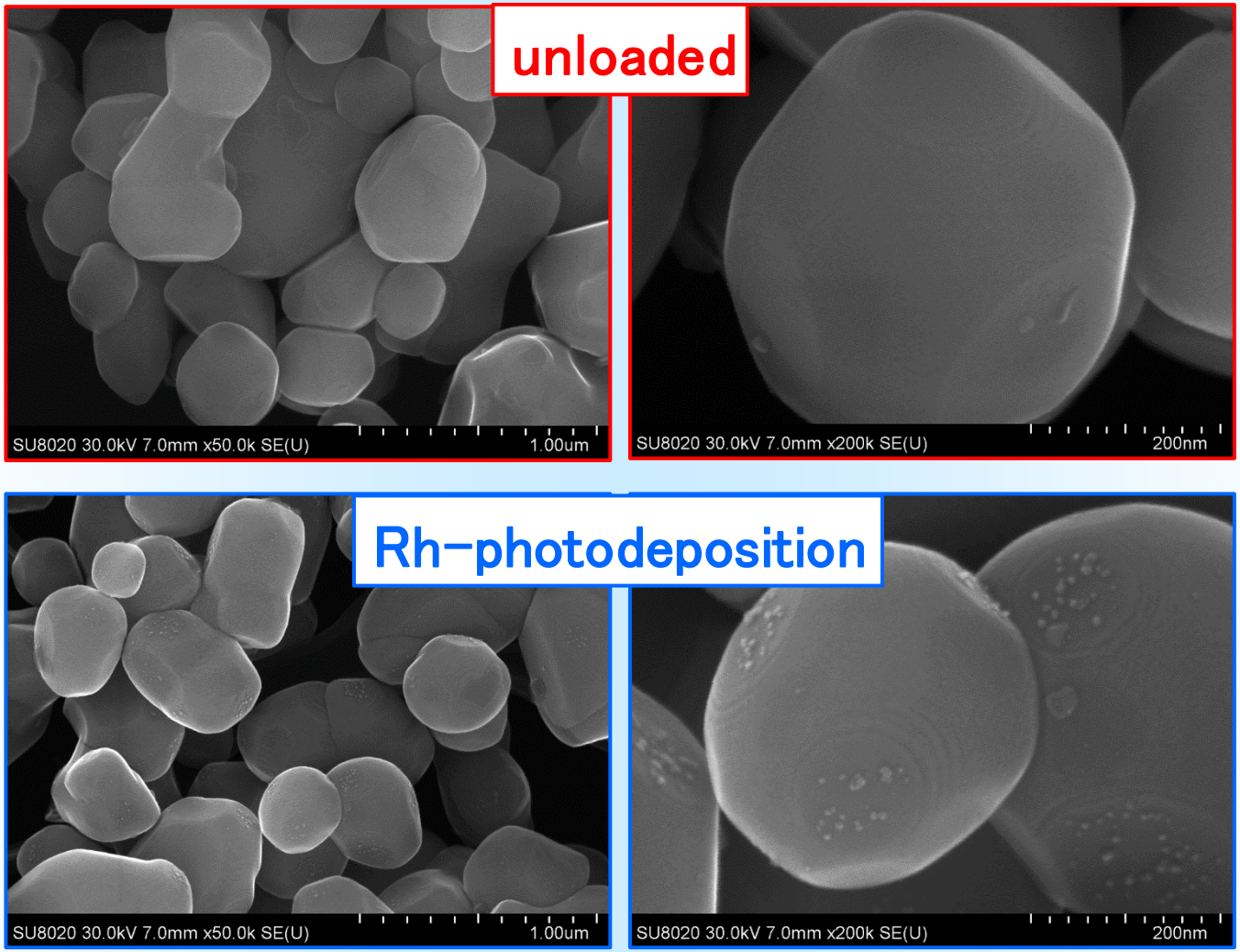
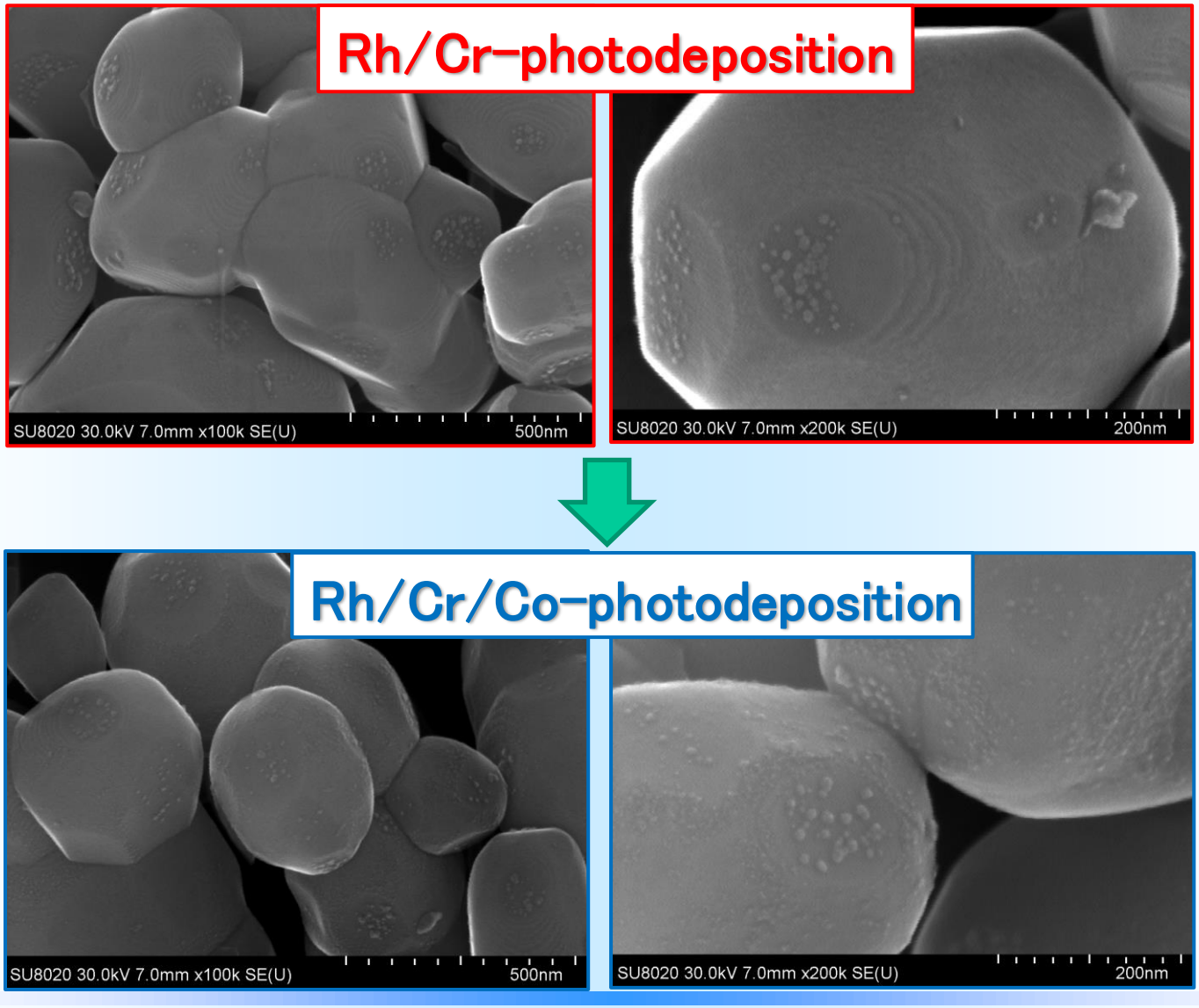
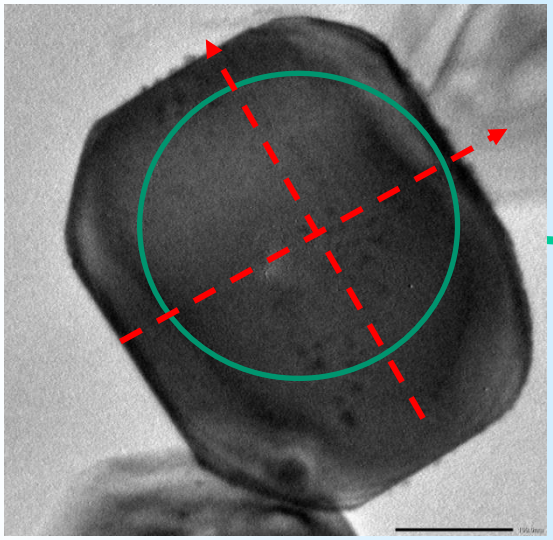
SEM images after deposition of cocatalysts

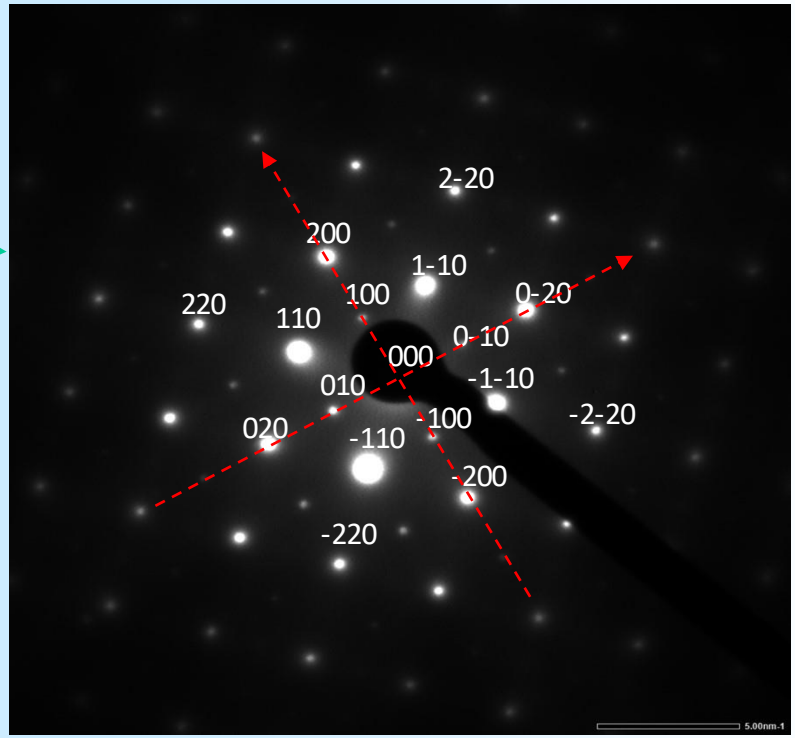


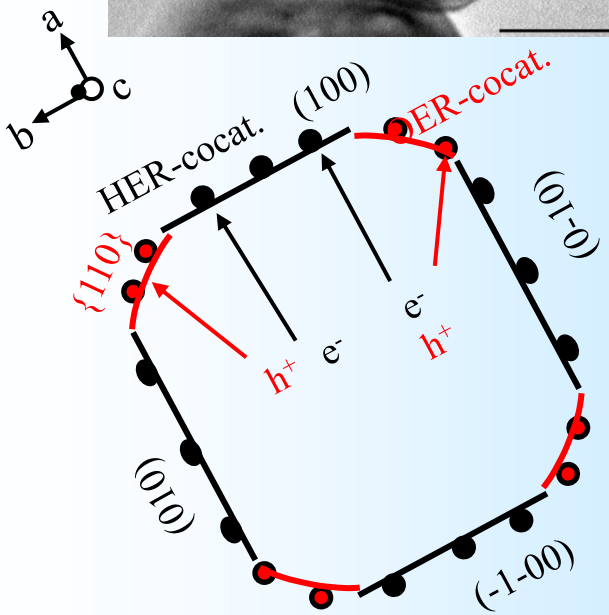
SEM images after deposition of cocatalysts



STEM image & ED after deposition of cocatalysts







e^- & h^+ are transported to different facets with almost 100% efficiency

What is the driving force?

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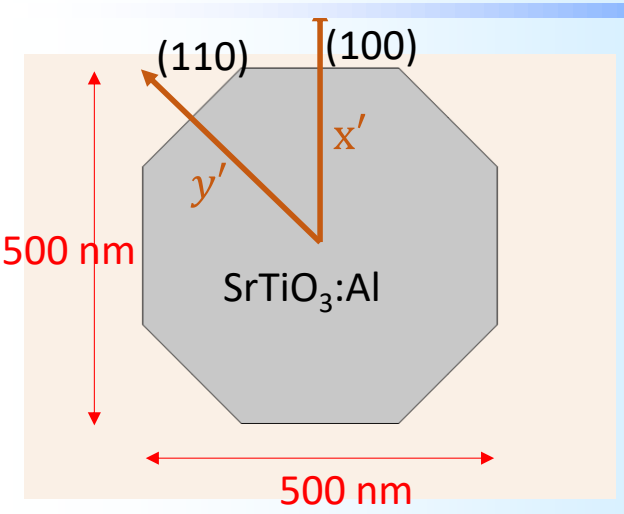
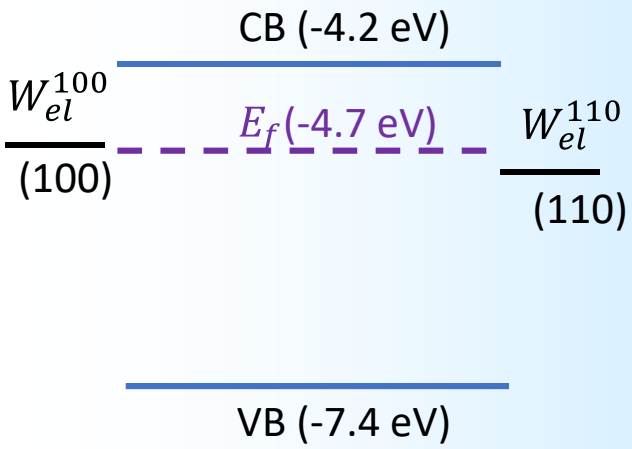
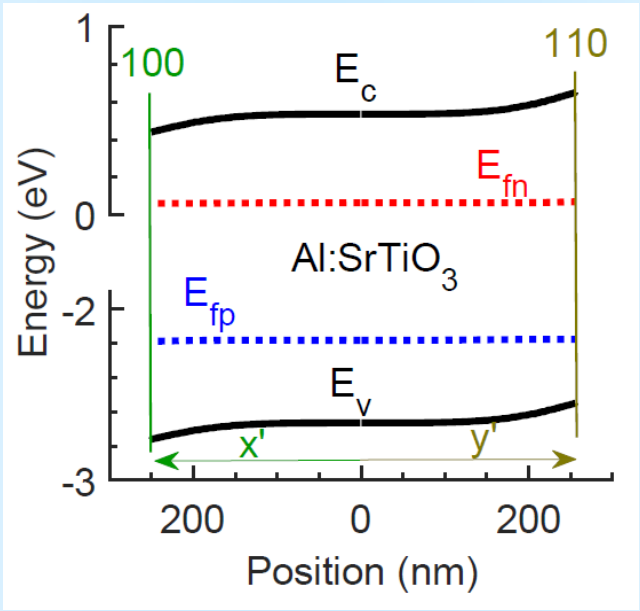
Simulation of internal electric field (ΔW=0.2 eV)

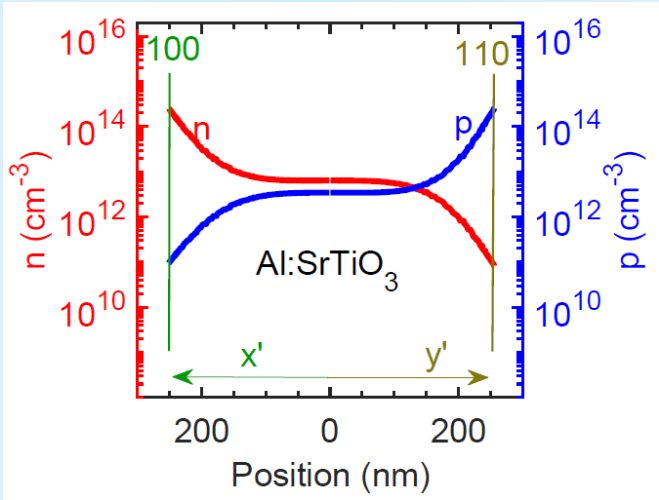


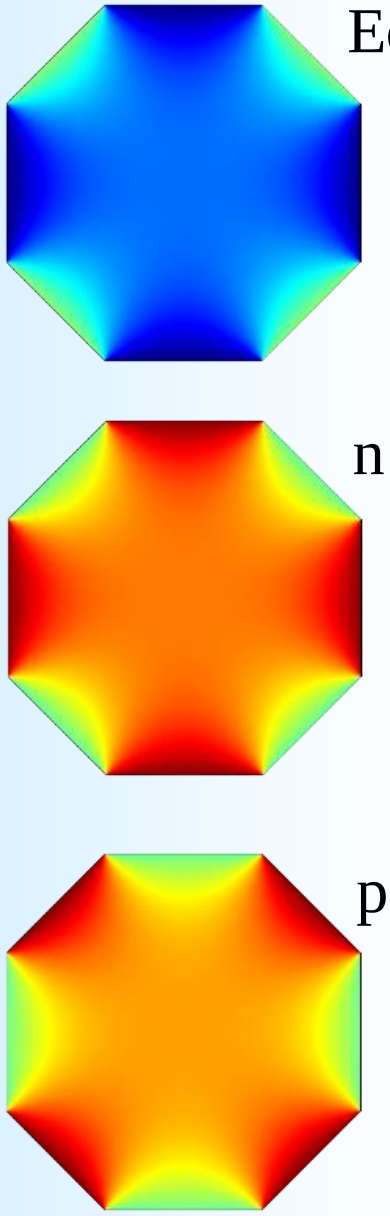
Model Schematic



Energy level alignment







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[4] Is safety operation of water splitting panel & system possible?

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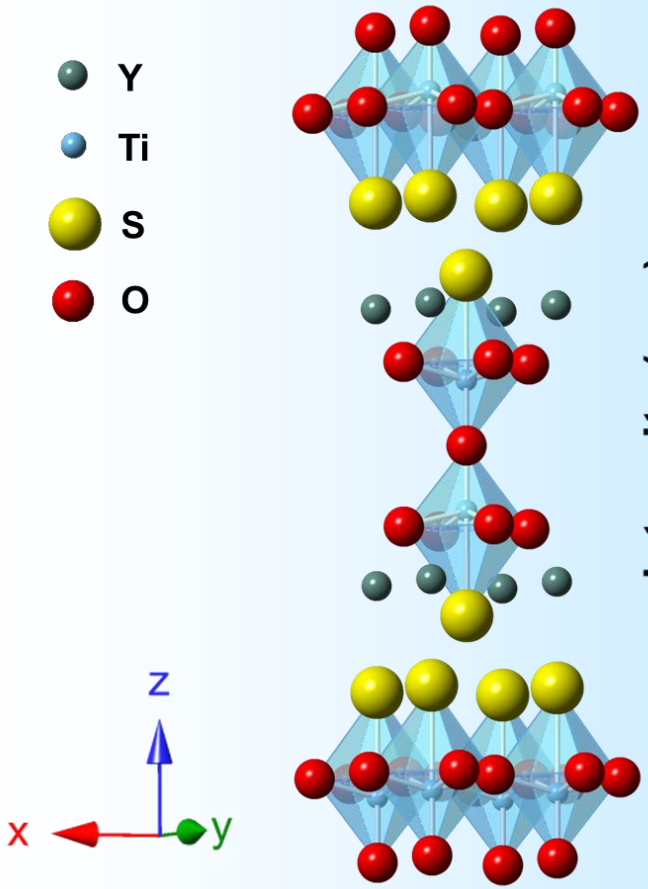
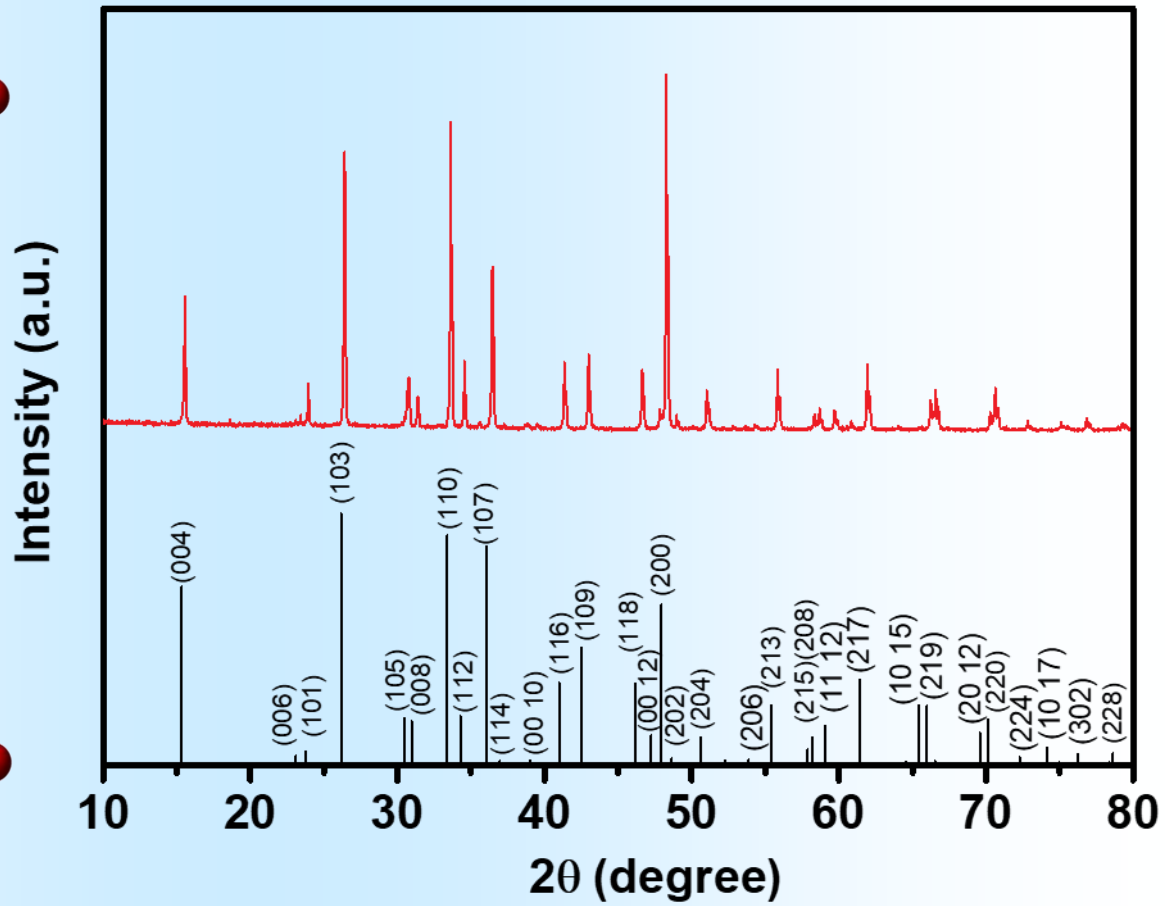
Structure of $Y_2Ti_2O_5S_2$





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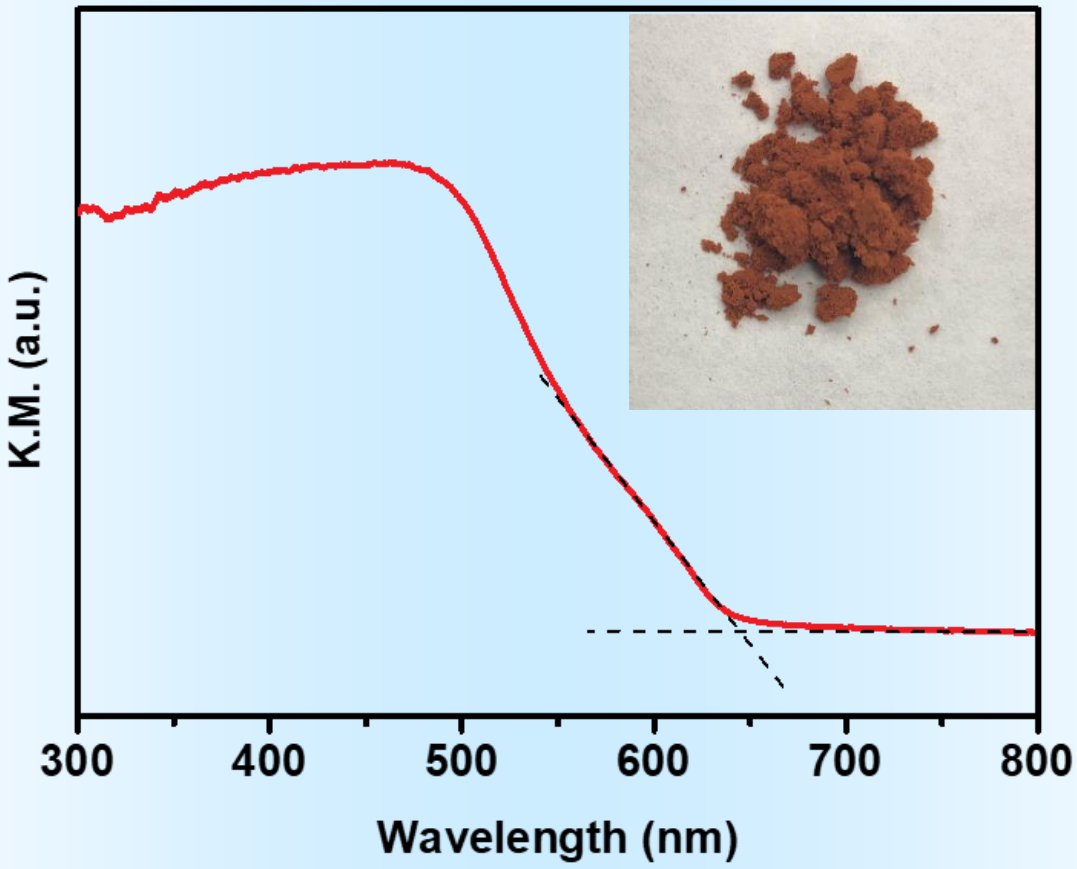
UV-vis DRS of $Y_2Ti_2O_5S_2$



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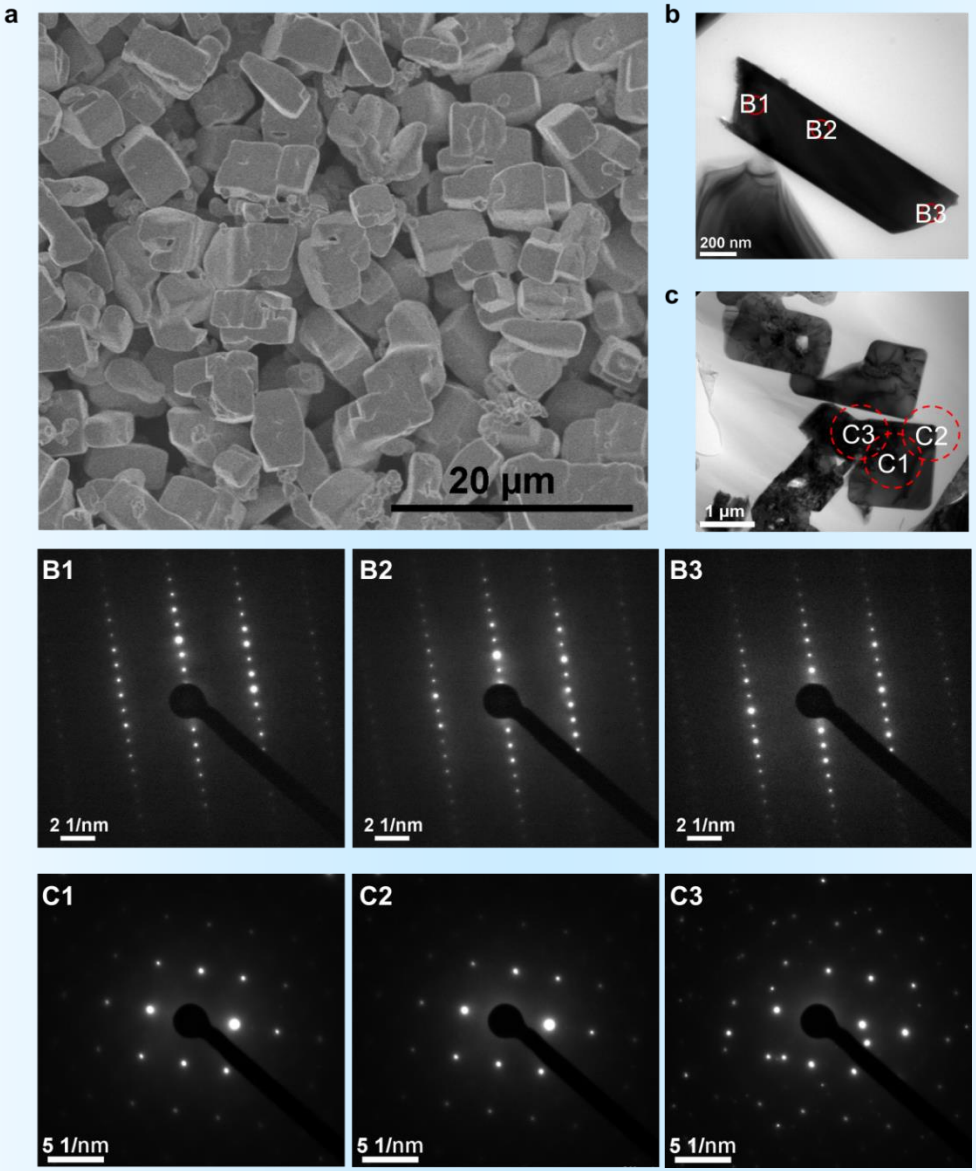
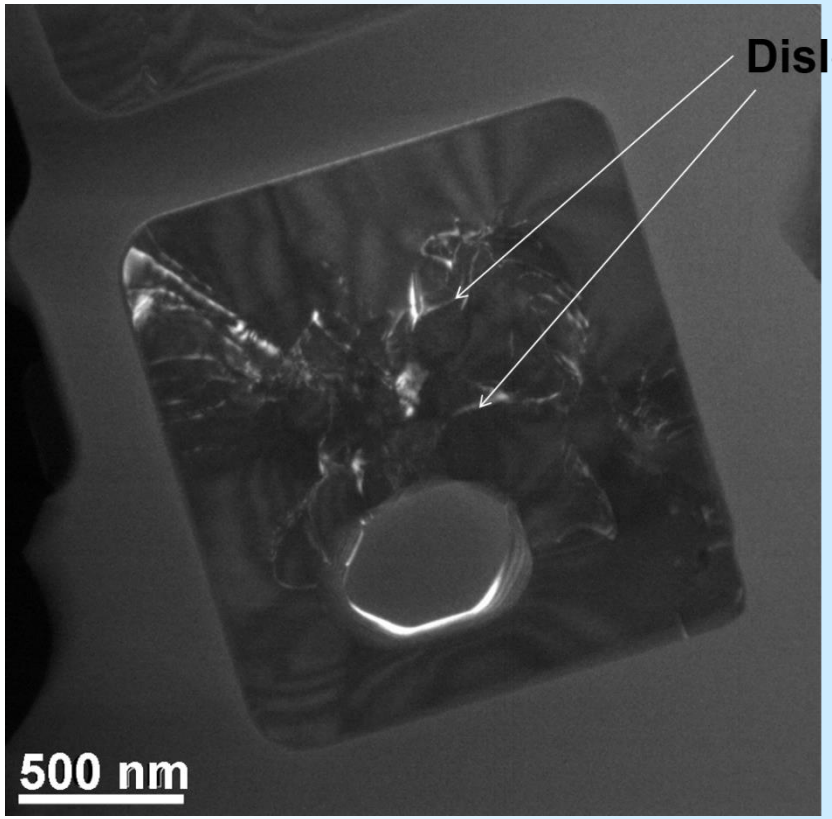
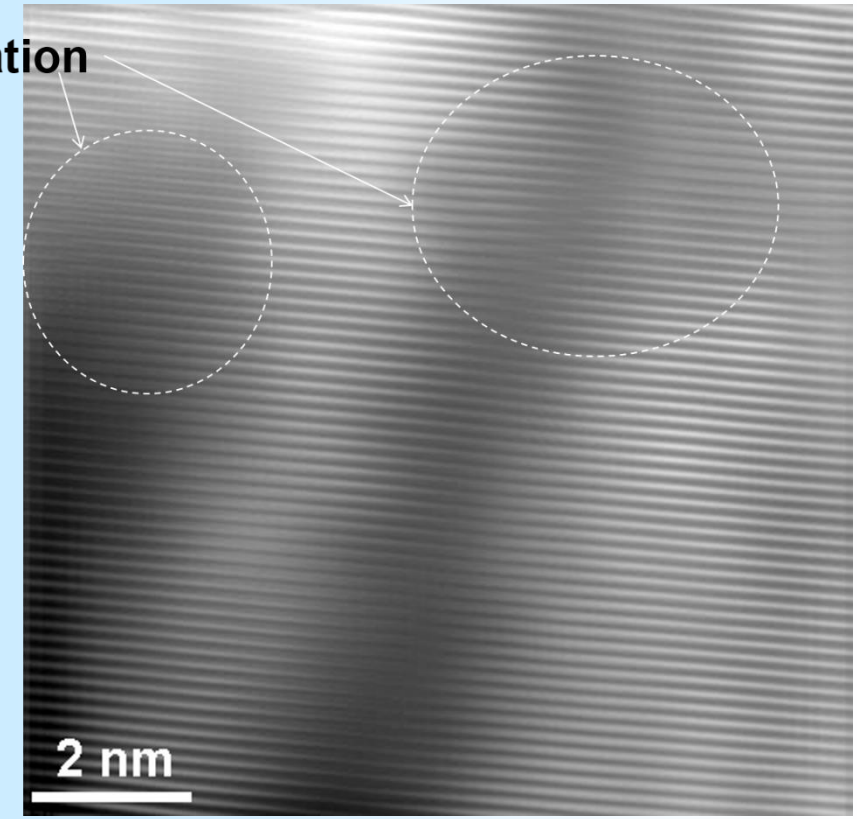
SEM image and ED patterns of $Y_2Ti_2O_5S_2$

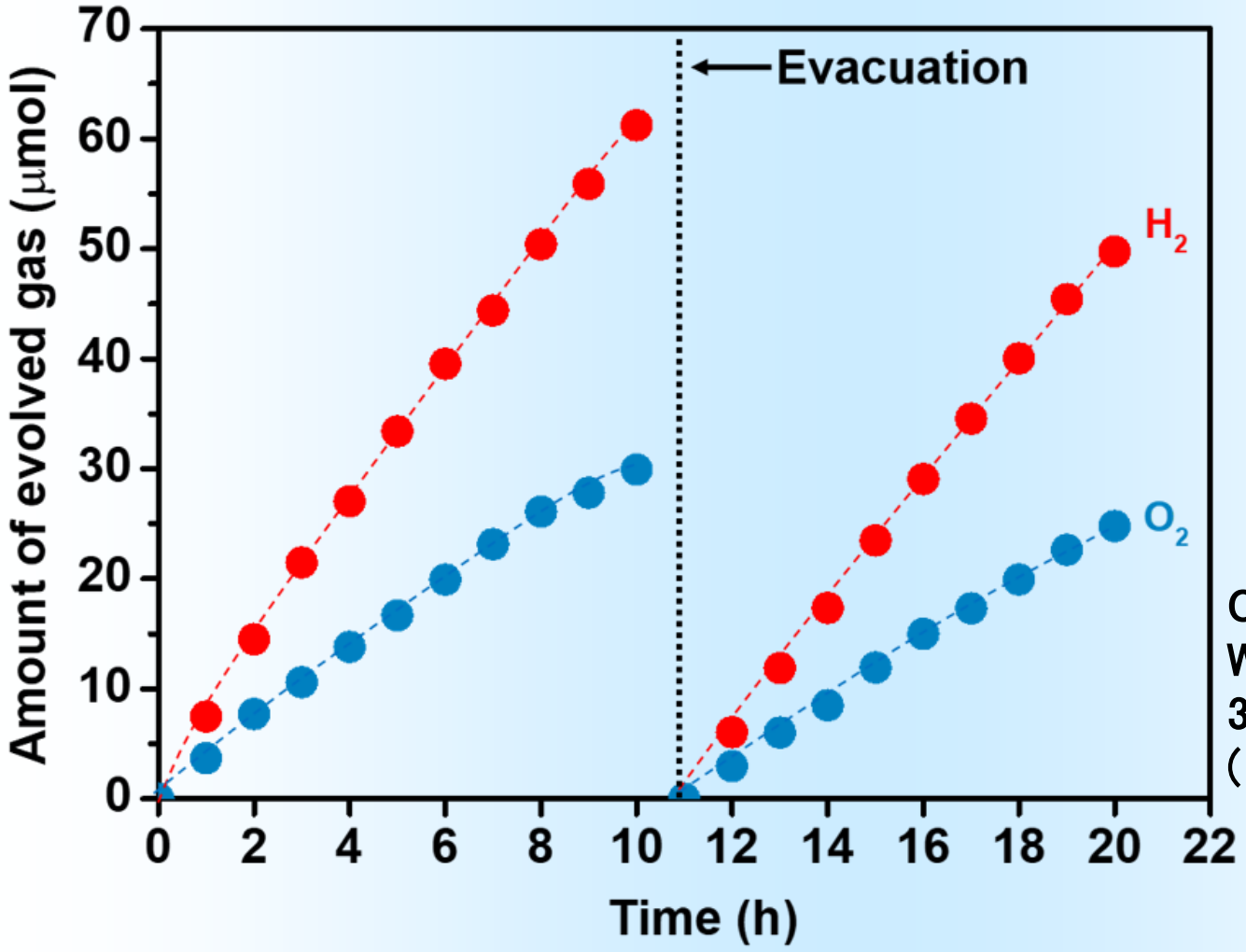


Confirmation of defect structure by STEM





Water splitting on $Cr_2O_3/Rh/Y_2Ti_2O_5S_2/IrO_2$



AQY = 0.2 %
at 500 nm

Cat: 0.2g
Water (150 mL, pH 8.5)
300 W Xenon lamp
(λ > 420 nm: visible light)

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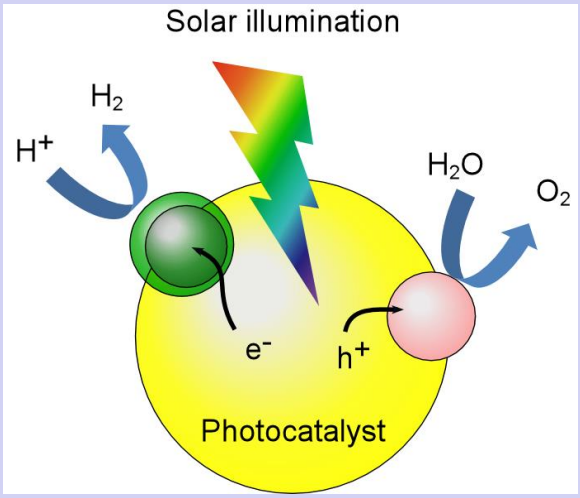
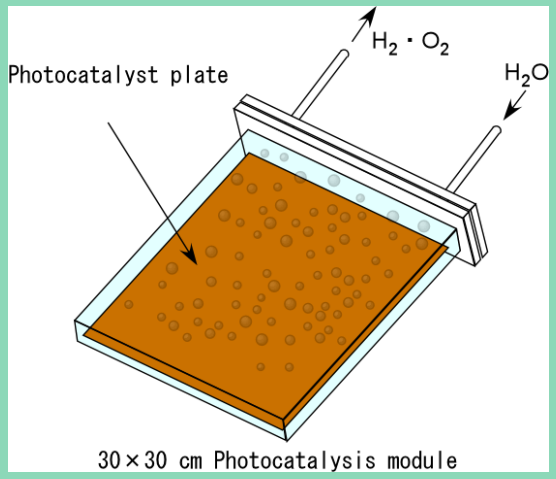
Image of large scale application



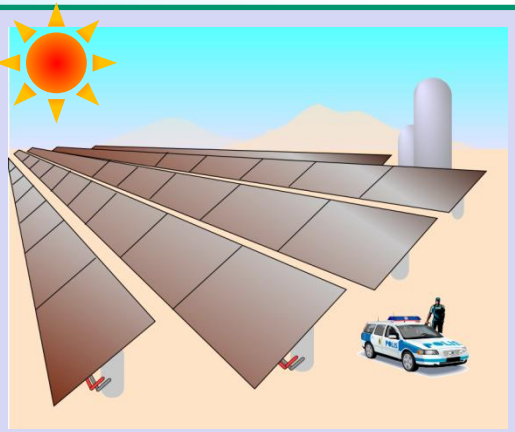
Microscopic Scale

Development of materials
Development of cocatalysts
Mechanism analysis



Medium Scale

Immobilization of photocatalysis
Reactor design
H_2/O_2 gas separation



Large Scale

Feasibility study
Chemical plant design

"Water splitting panel"

⇒ Photocatalyst sheet

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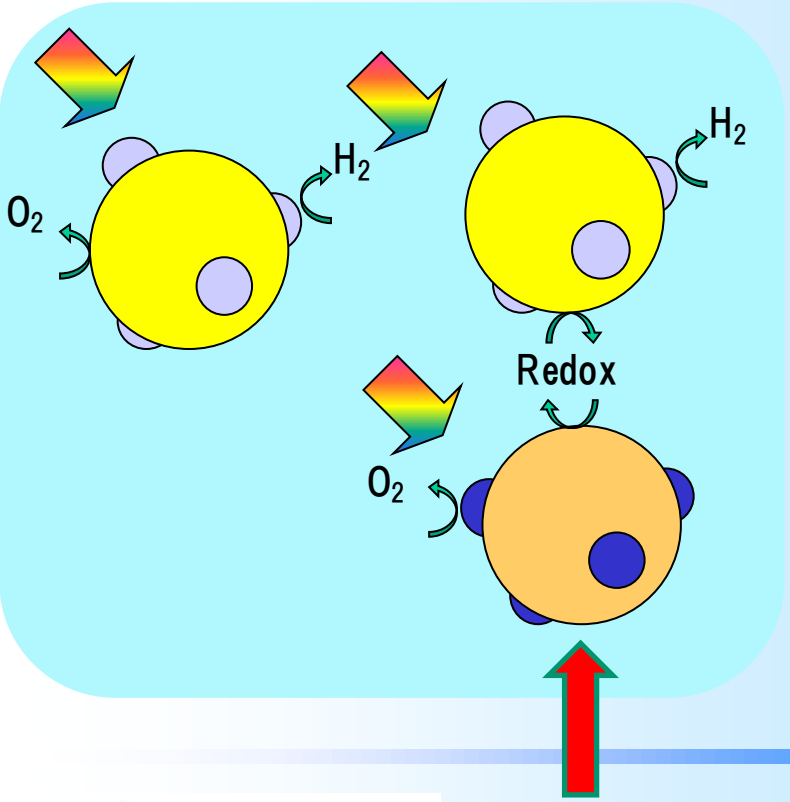
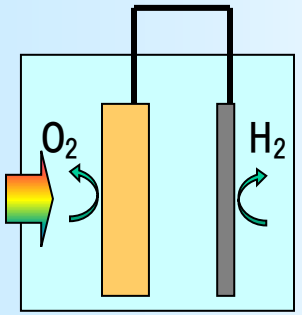
Photocatalytic & Photoelectrochemical water splitting

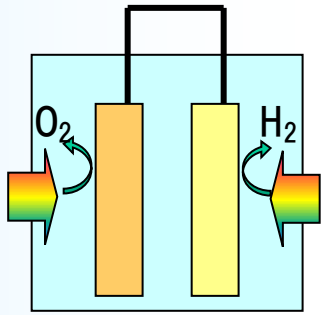
Photocatalysts | **Photocatalyst sheet** | **Photoelectrodes**

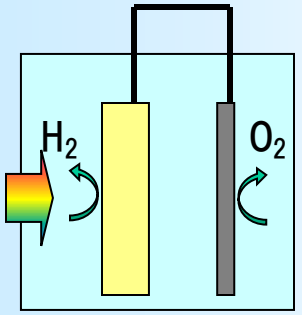
1-step 2-step



1-step 2-step







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Photocatalysts for H_2 and O_2 evolution

$SrTiO_3$:La,Rh
(H_2)

$BiVO_4$:Mo
(O_2)

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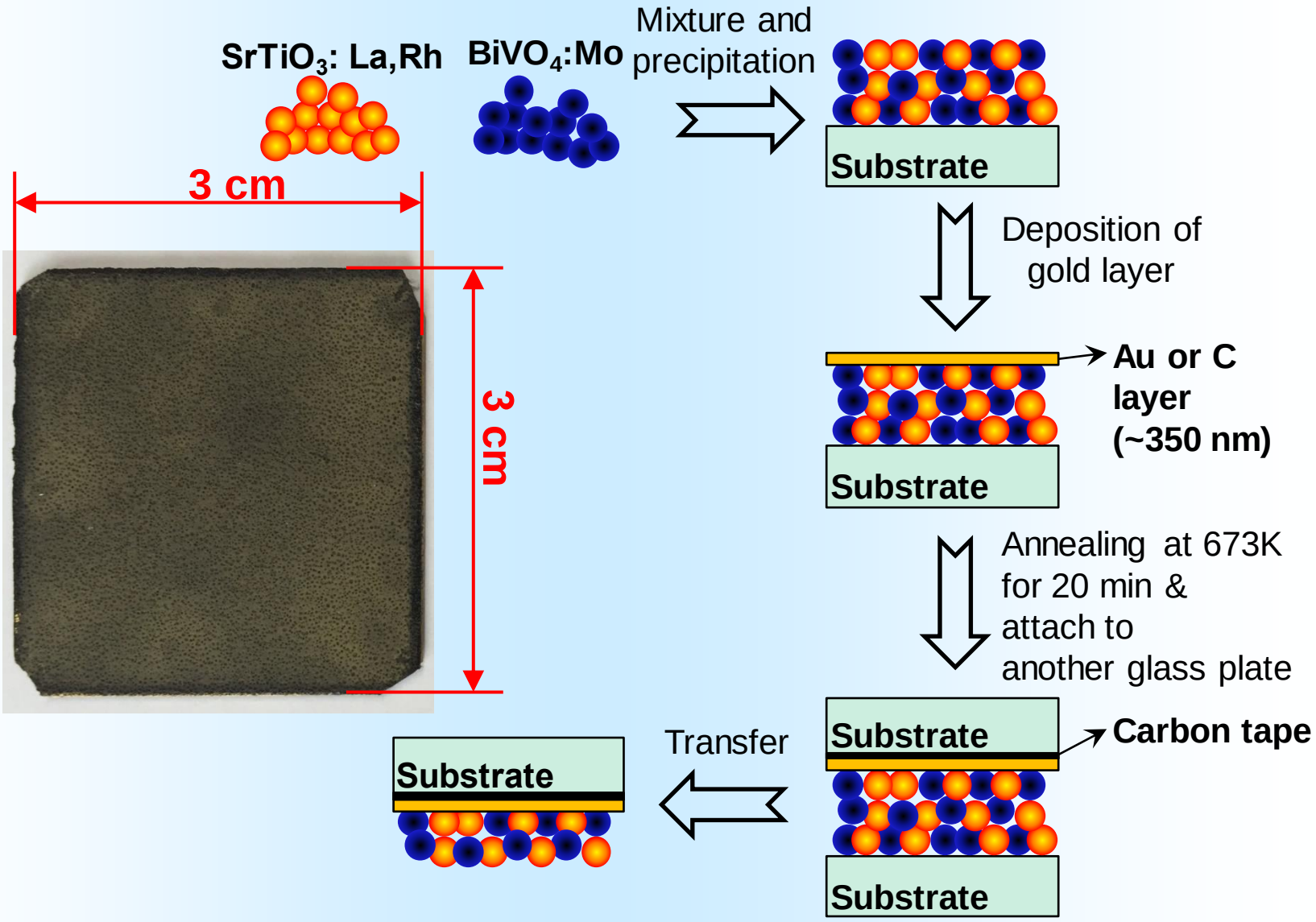
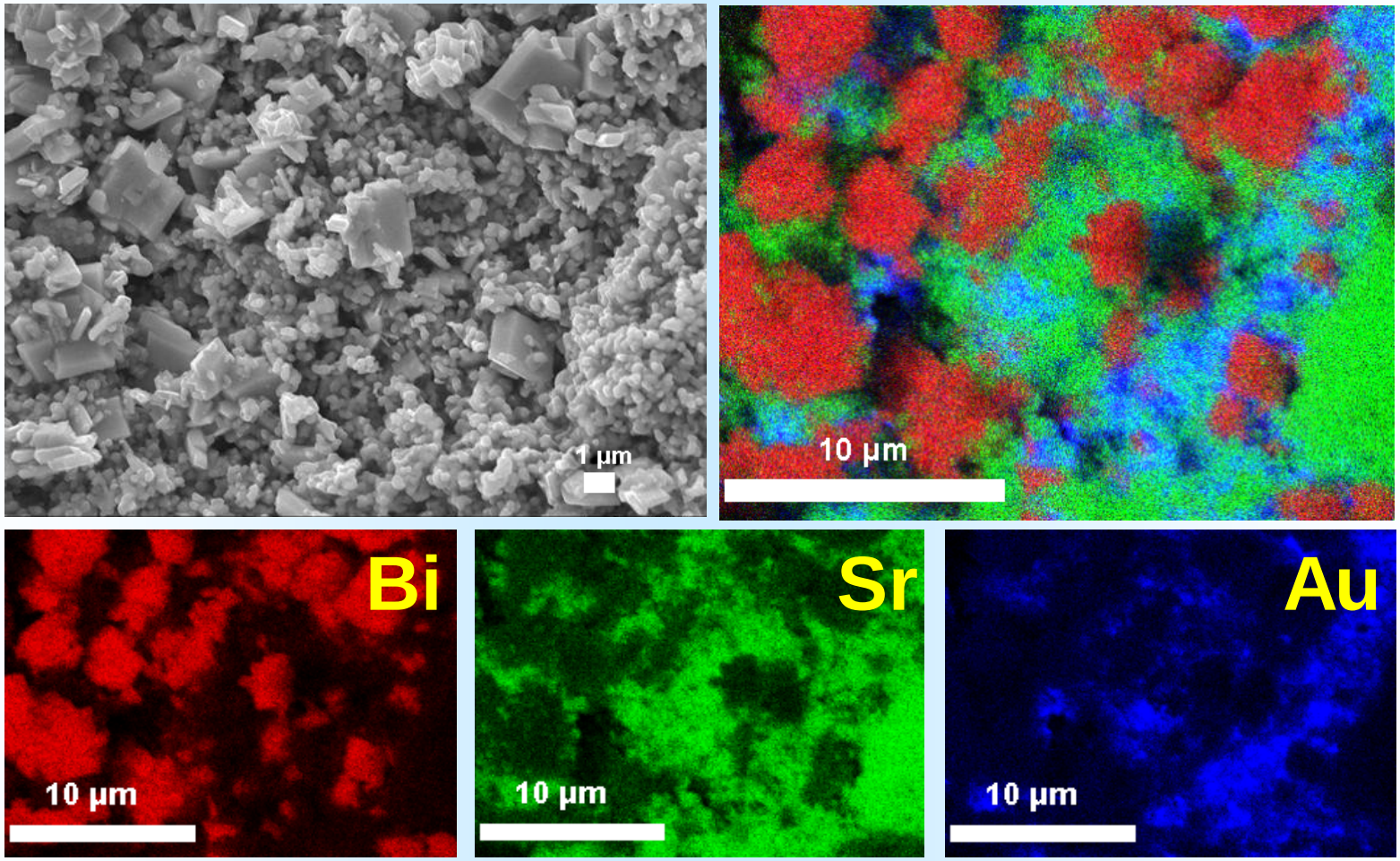
Preparation procedure of photocatalyst sheet



SEM-EDX Elemental Mapping of ($Ru/SrTiO_3$:La,Rh/Au/$BiVO_4$:Mo) Photocatalyst Sheet



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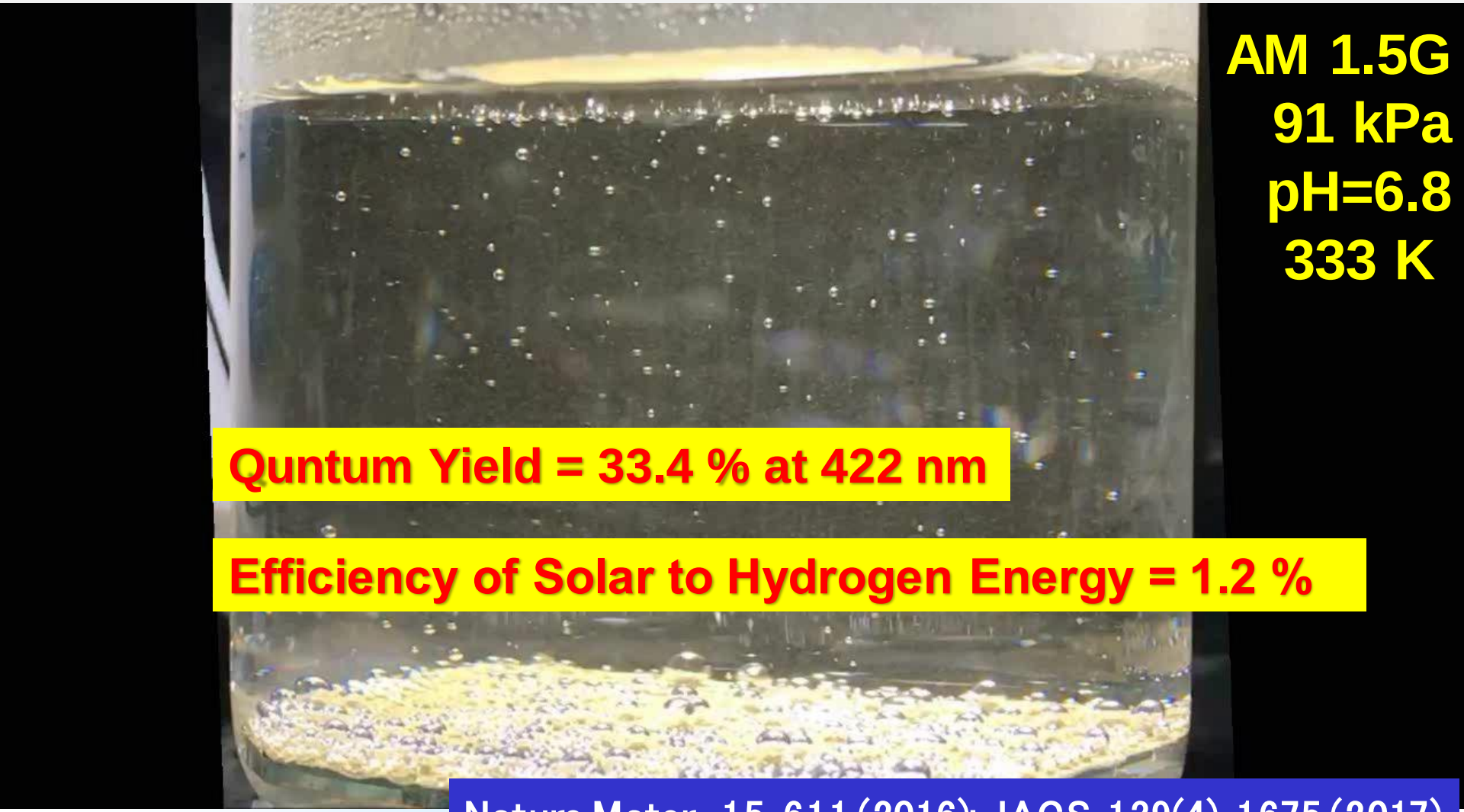
Water splitting on photocatalyst sheet ($SrTiO_3$:Rh,La / C / $BiVO_4$:Mo)



Nature Mater., 15, 611 (2016); JACS, 139(4), 1675 (2017)

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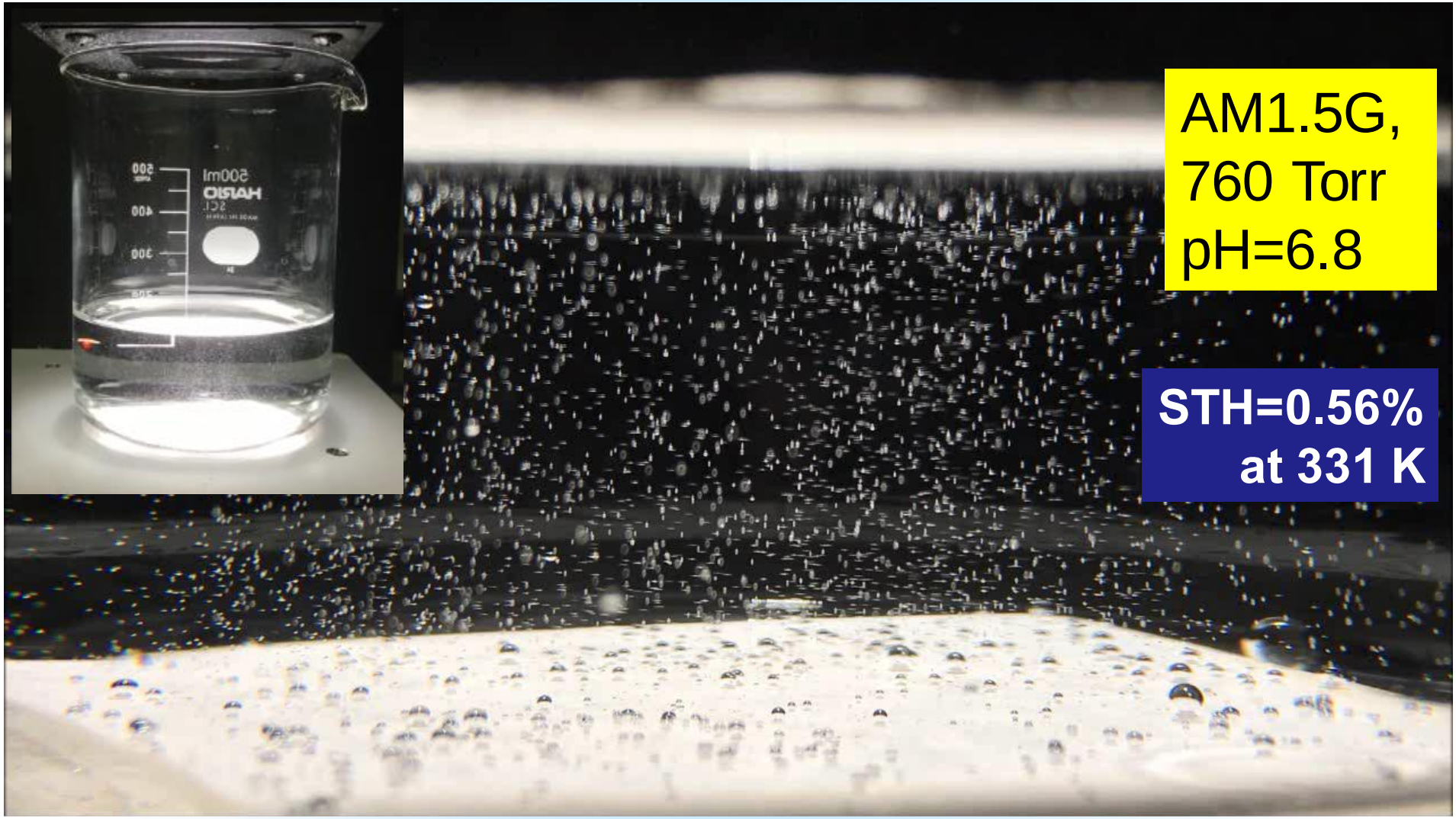
Water splitting on $RhCrO_x/SrTiO_3$:Al + SiO_2 photocatalyst sheet



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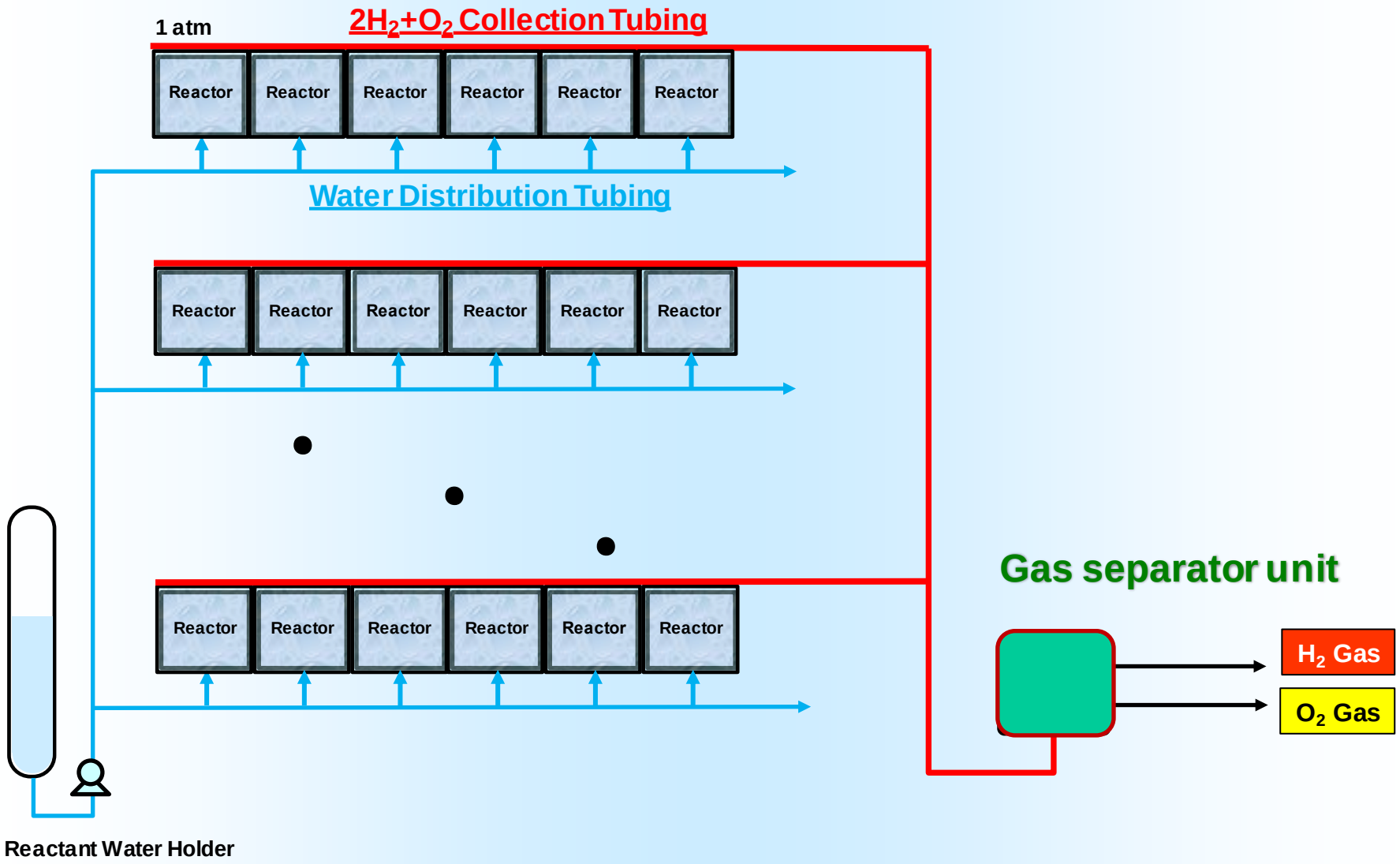
Schematic Diagram of Solar H_2 Plant
(1 atm Thin-layer reactor, Low-pressure-gradient tubing, and H_2/O_2 Gas separation device)



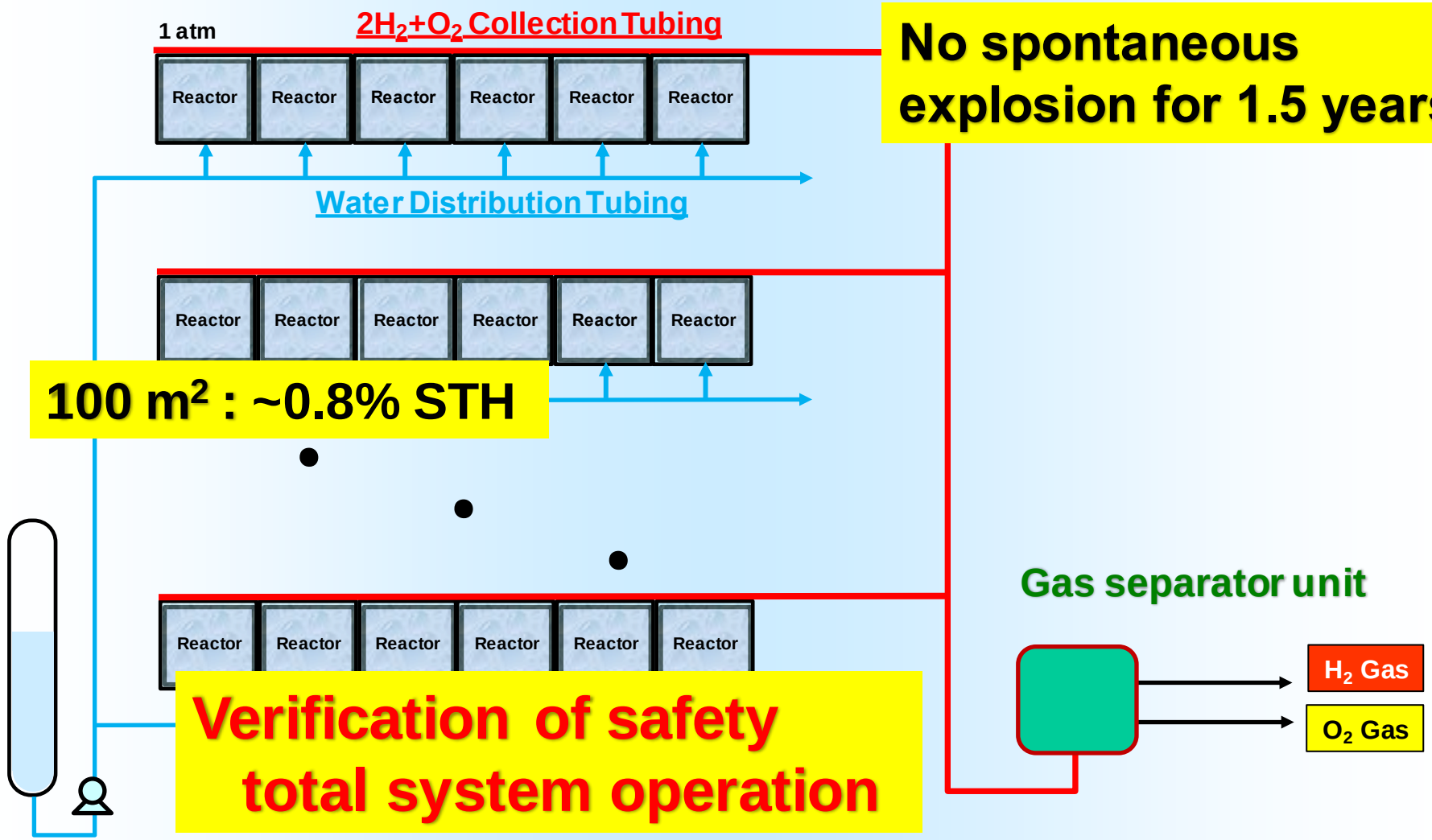
3 m^2 prototype water splitting panel

September 7, 2019, 9:45 am, 304 K at Kakioka Research Facility

STH:0.78%

214 mL(H_2+1/2O_2)/min

Design of prototype solar H_2 production system



Outline

[1] Introduction

[2] Particulate photocatalysts for water splitting

- *Al-doped $SrTiO_3$*
- *$Y_2Ti_2O_5S_2$*

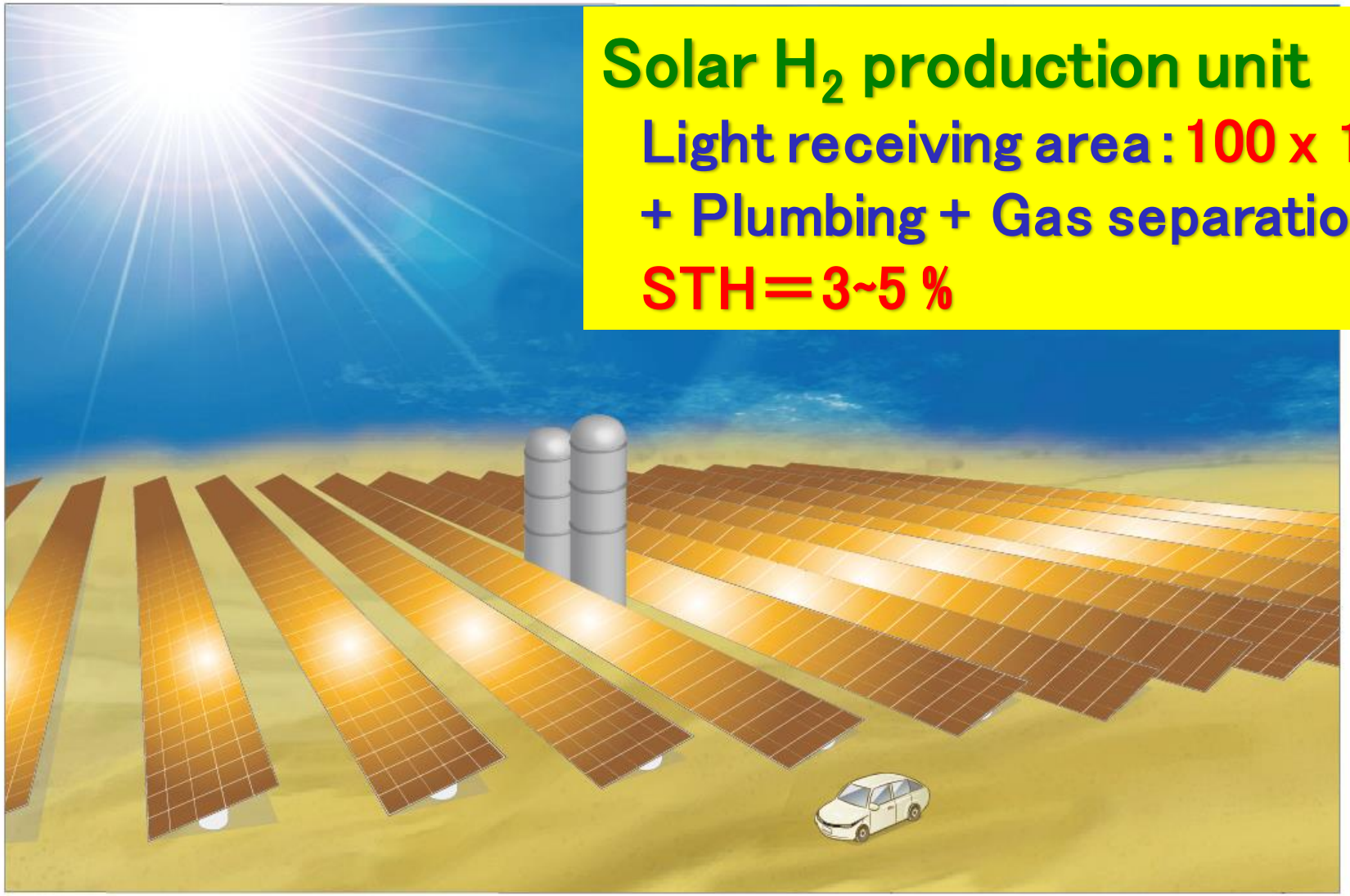
[3] Photocatalyst sheets & water splitting panel

- *La, Rh-doped $SrTiO_3$ & Mo-doped $BiVO_4$*
- *Al-doped $SrTiO_3$*

[4] Construction of a prototype solar hydrogen production system

[5] Summary

Image of future implementation into the real world



Solar H_2 production unit

Light receiving area : 100 x 100 m^2

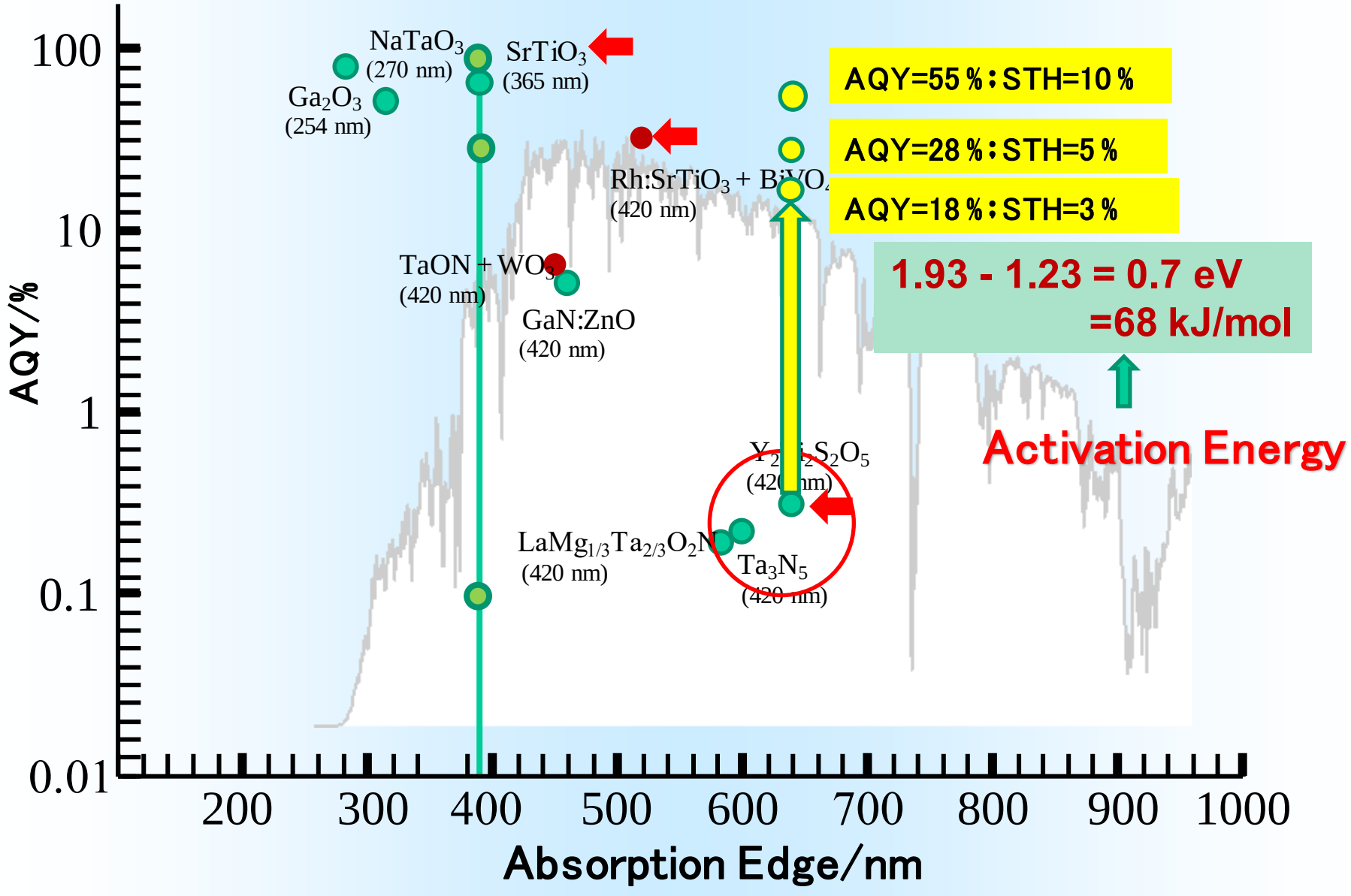
+ Plumbing + Gas separation unit

STH＝3~5 %

SHINSHU UNIVERSITY

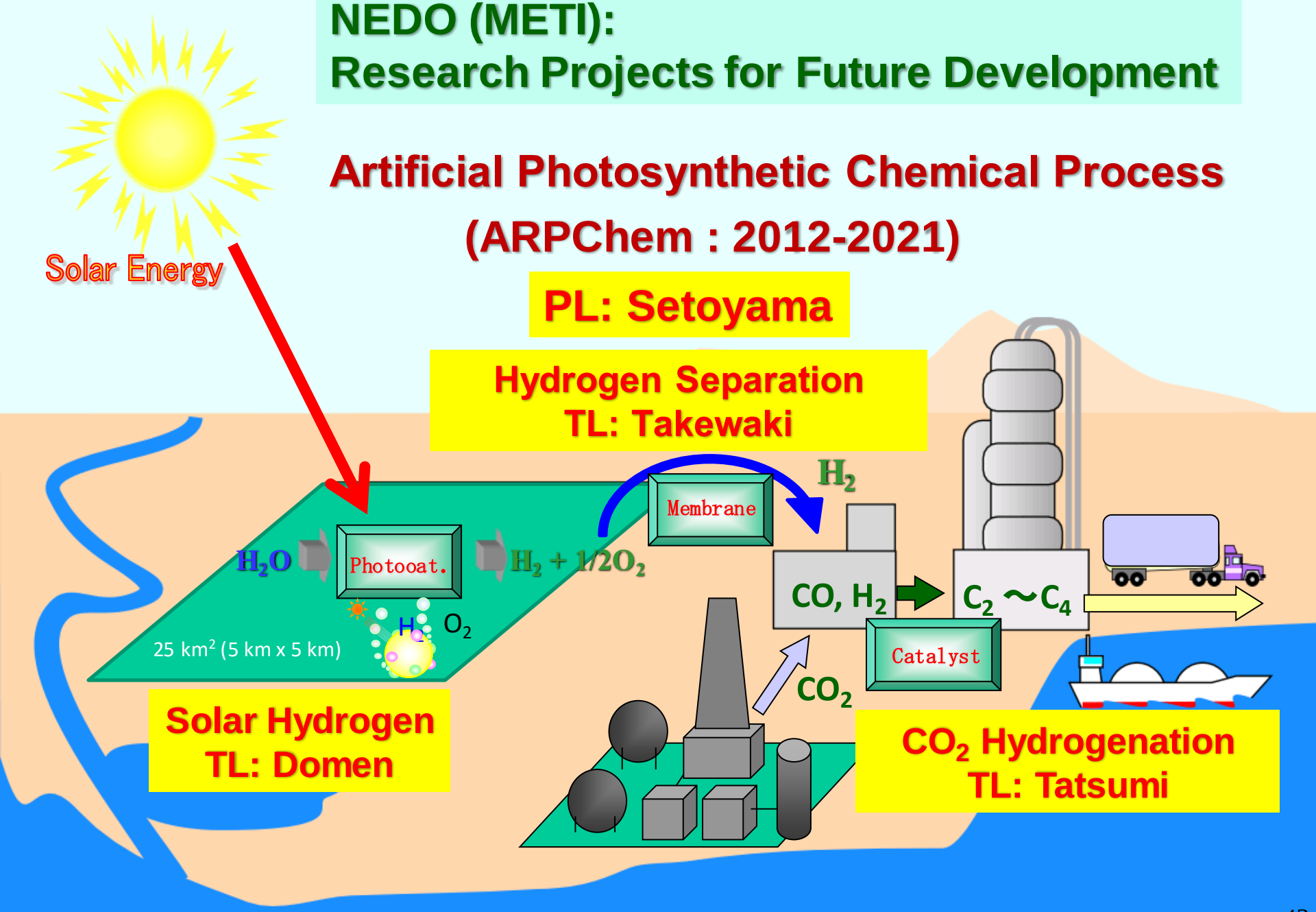
THE UNIVERSITY OF TOKYO

Absorption edge vs AQY for overall water splitting reaction



NEDO (METI):
Research Projects for Future Development

Artificial Photosynthetic Chemical Process
(ARPChem : 2012-2021)



Research Projects for Future Development:

"Artificial Photosynthetic Chemical Process" (ARPChem)"

(NEDO, METI: 2012-2021)

ARPChem Association

- Mitsubishi Chemicals
- Mitsui Chemicals
- Fuji Films
- TOTO
- INPEX

- AIST
- Fine Ceramic Center

- Univ. Tokyo
- Tokyo Univ. Science
- Kyoto Univ.
- Shinshu Univ.
- Meiji Univ.
- Nagoya Inst. Tech.
- Yamaguchi Univ.