第31回無機材料に関する最近の研究成果発表会
東海大学校友会館
January 27, 2014

表面ナノ構造を制御した半導体光触媒による水の可視光完全分解

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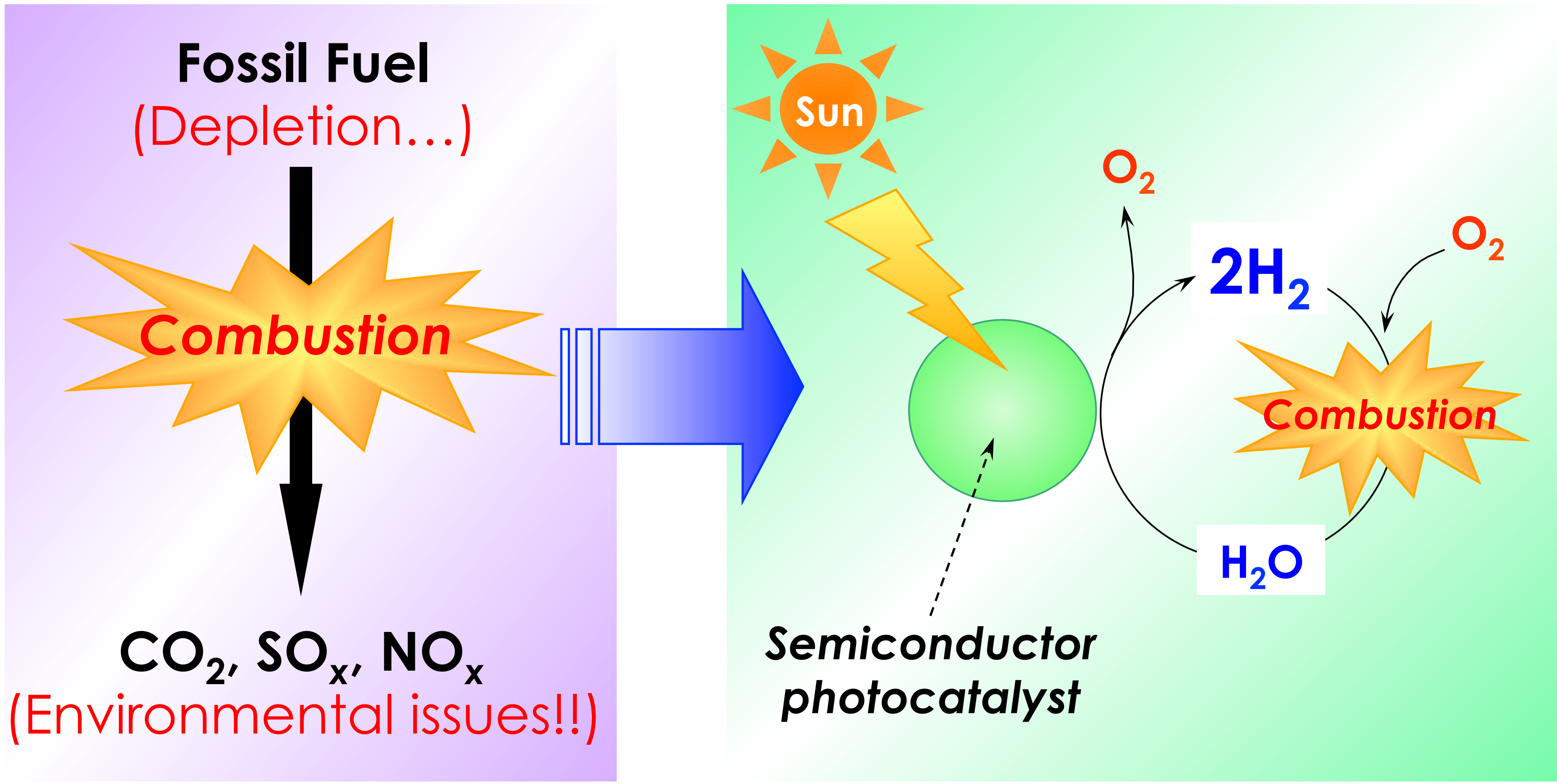
Research background

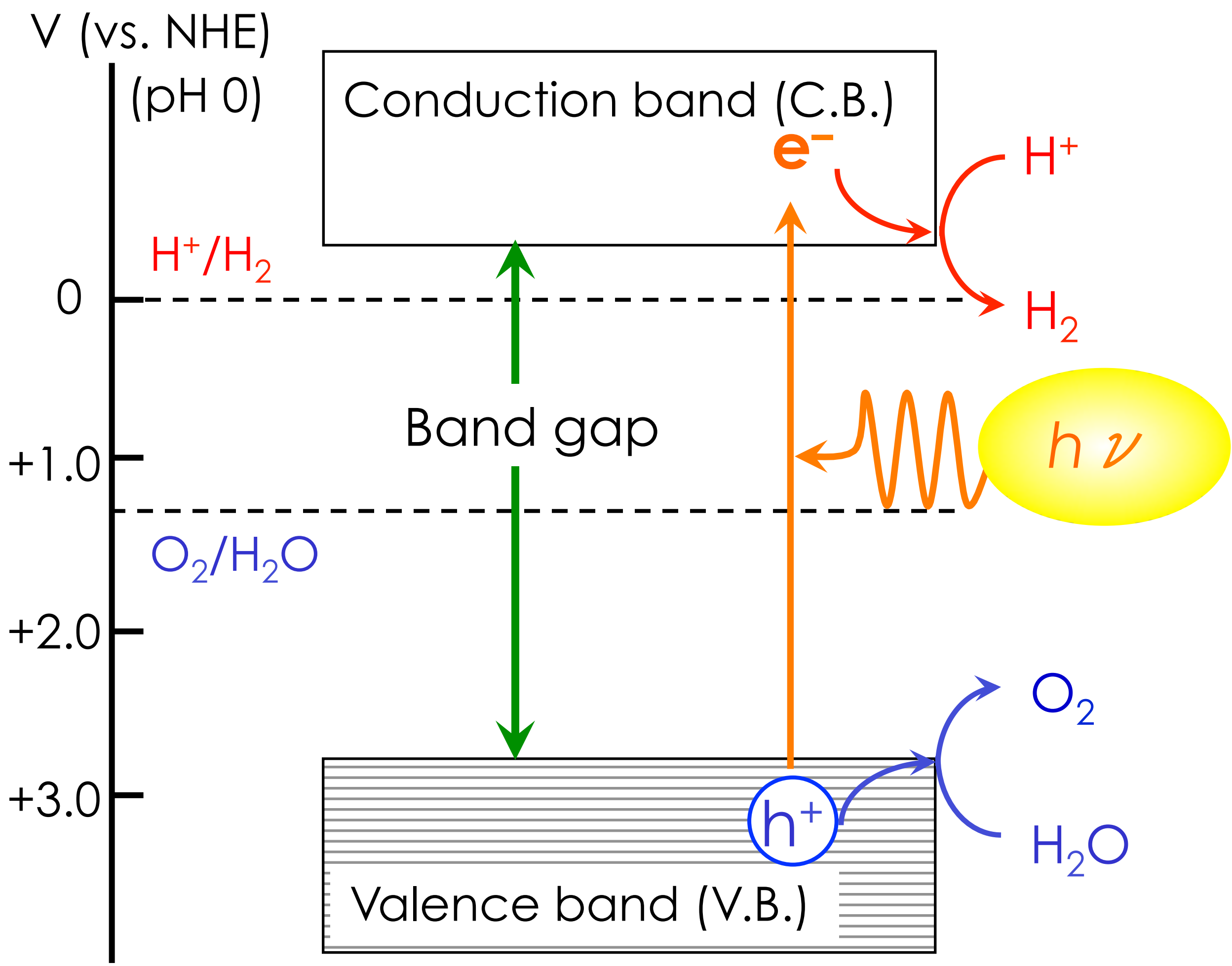
Conventional energy-production system

Photocatalytic H_2 production from water and solar energy



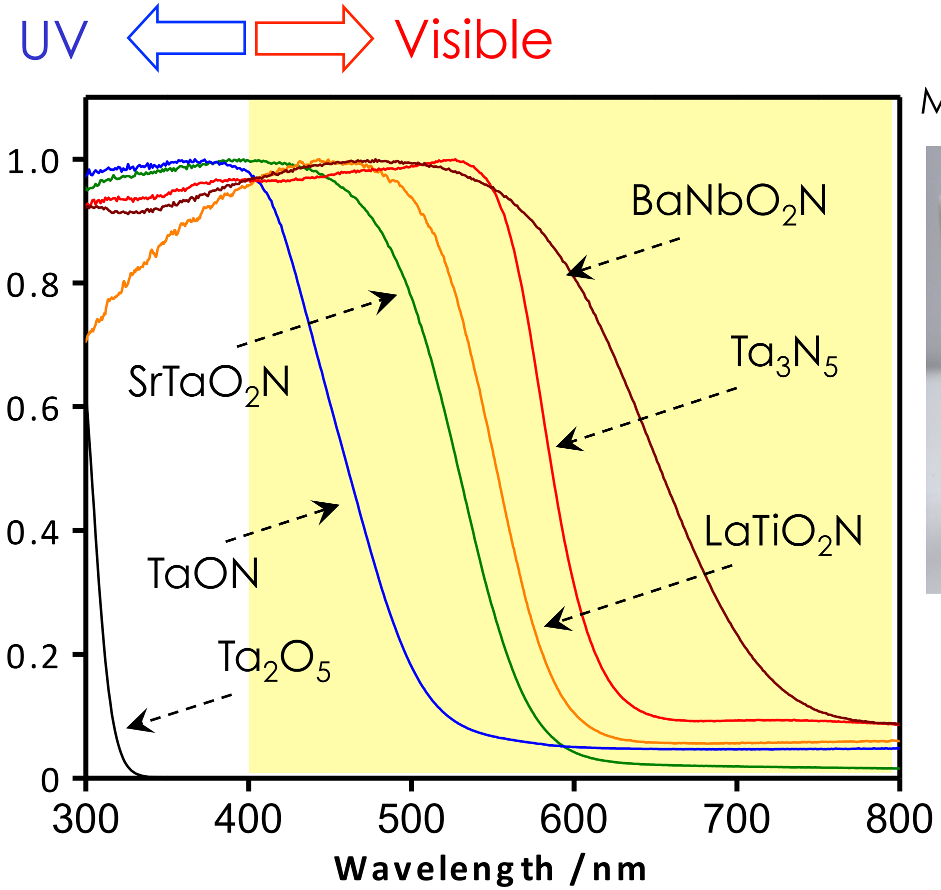
Basic principle of water splitting on a heterogeneous photocatalyst

$$H_2O \xrightarrow[\text{Photocatalyst}]{h\nu} H_2 + \frac{1}{2}O_2 \quad \Delta G^0 = 238\ \text{kJ/mol}$$



(Oxy)nitrides as water-splitting photocatalysts
…Production of H_2 as a renewable energy carrier

$$H_2O \xrightarrow[\text{Photocatalyst}]{\text{Sunlight}} H_2 + \frac{1}{2} O_2 \quad (\Delta G^0 = 238\ \text{kJ/mol})$$

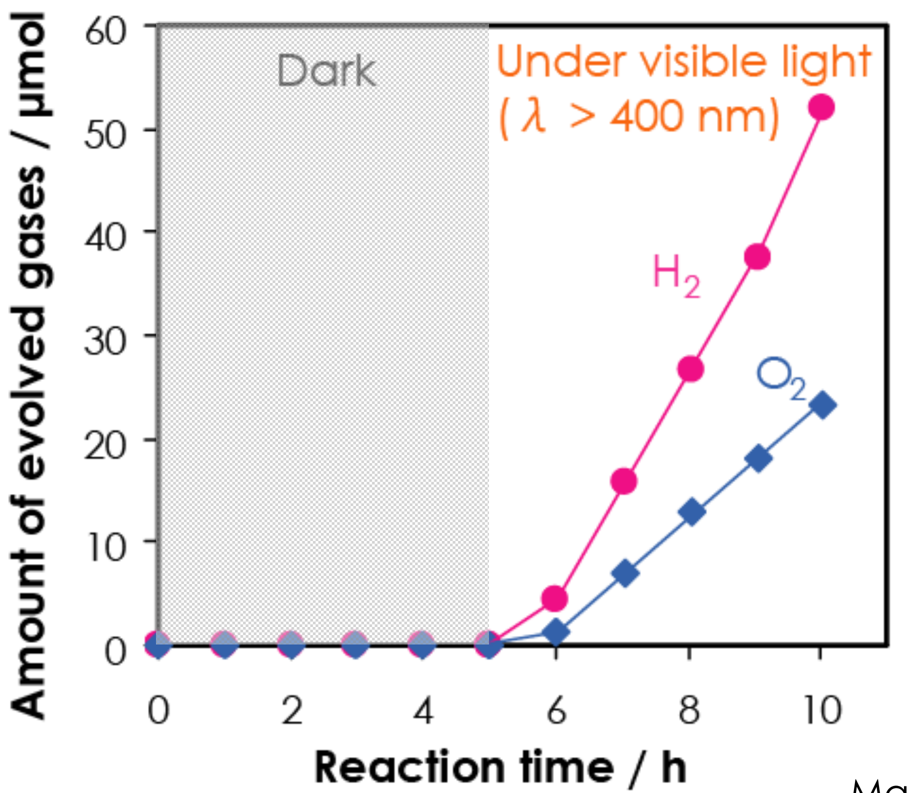


Maeda & Domen, *J. Phys. Chem. C* **2007**, *111*, 7851.

- Wide visible light absorption
- Suitable band structure
- Stable under irradiation

GaN–ZnO solid solution…the first “***reproducible***” example of achieving the visible-light-driven overall water splitting

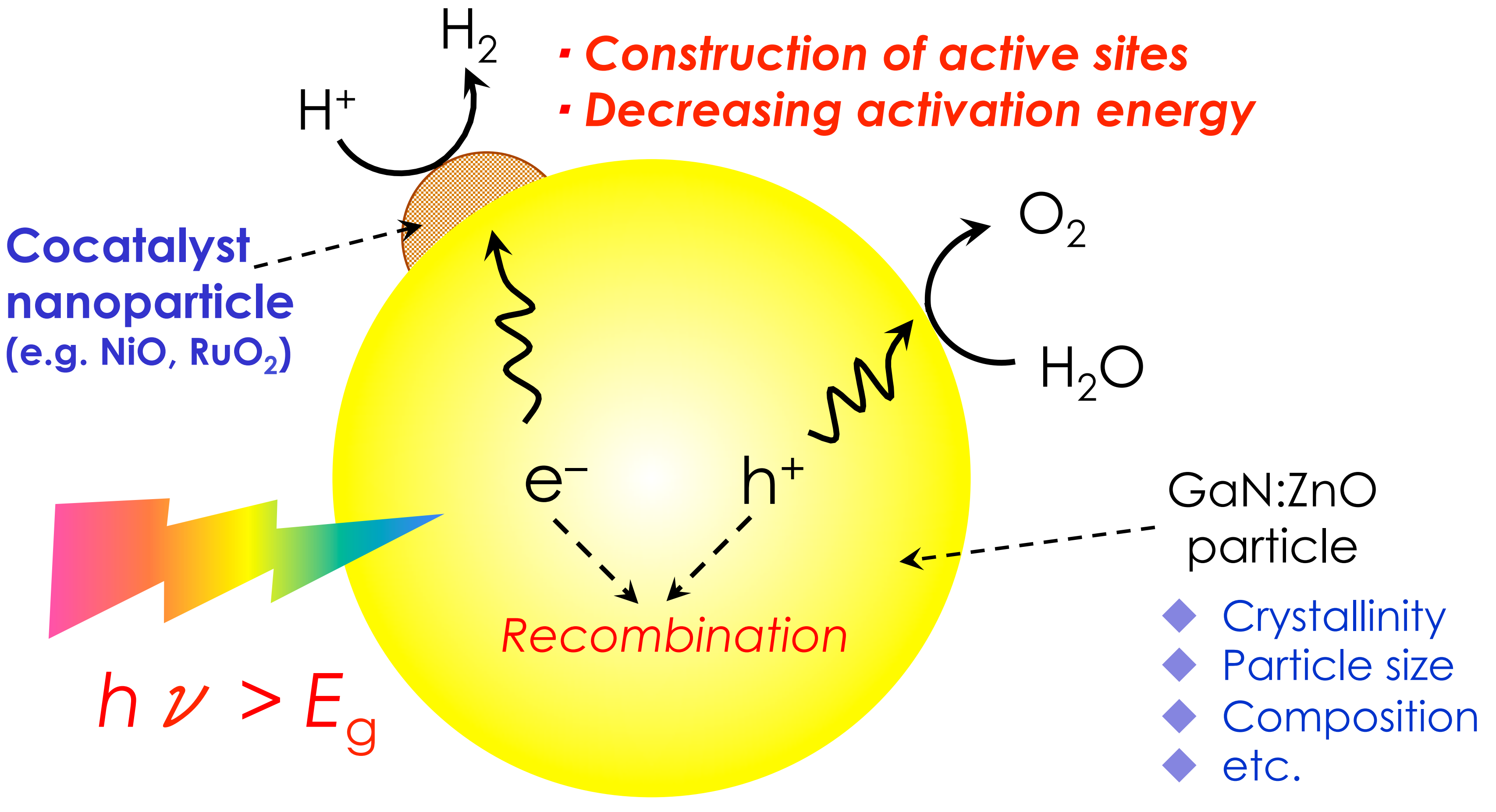
$$H_2O \xrightarrow{h\nu\ (< 3\ \text{eV})} H_2 + \frac{1}{2}O_2 \quad \Delta G^0 = 238\ \text{kJ/mol}$$



GaN $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ **(x = 0.42)** ZnO

Maeda et al., *J. Am. Chem. Soc.* **2005**, *127*, 8286.
Maeda et al., *Nature* **2006**, *440*, 295.
Maeda & Domen, *Chem. Mater. (Review)* **2010**, *22*, 612.

Strategy to develop an efficient photocatalyst

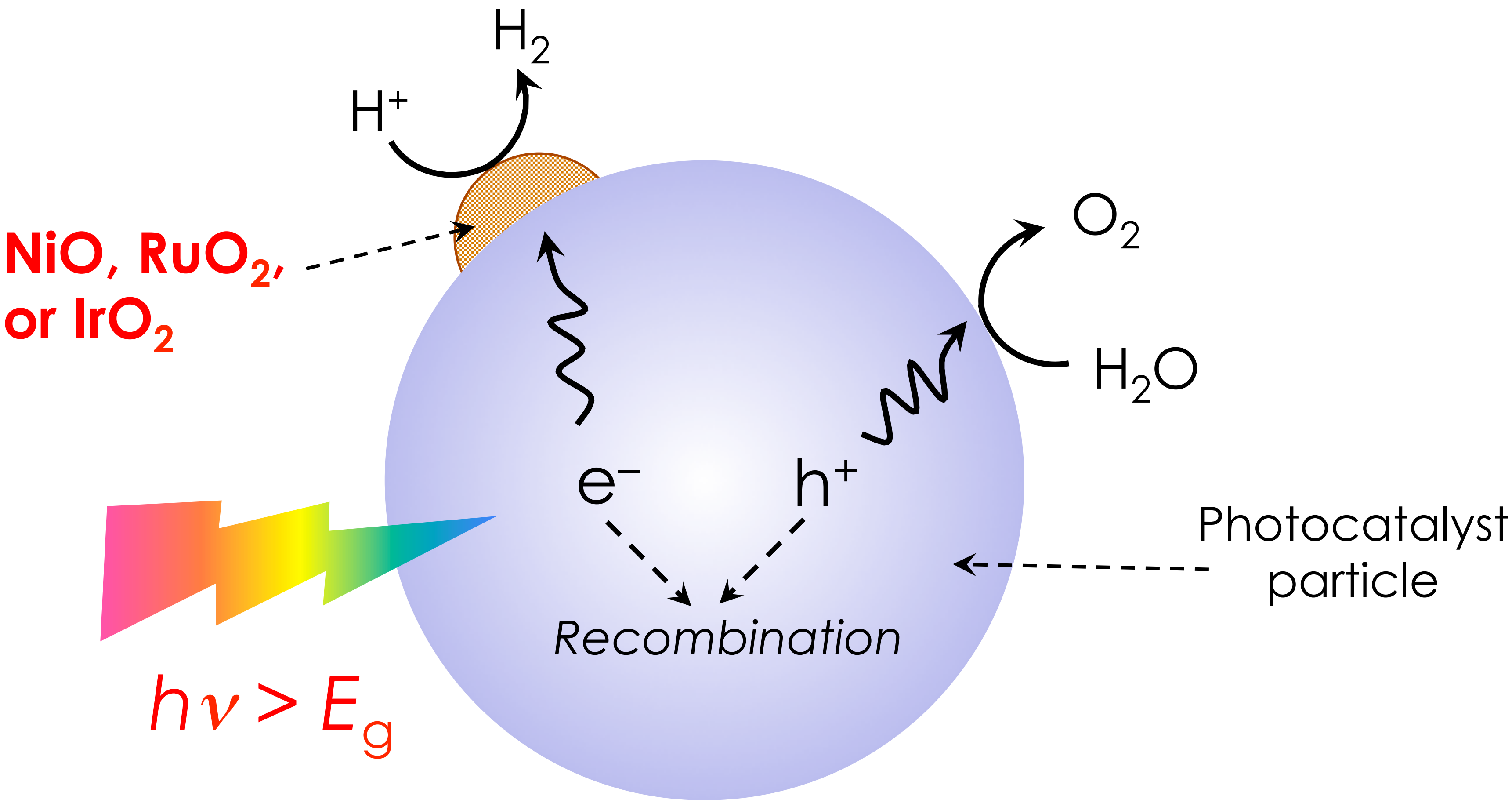


Development of a new cocatalyst that efficiently promotes the overall water splitting on GaN:ZnO

Development of a new cocatalyst for water splitting

Conventional cocatalysts

NiO, RuO_2, IrO_2..."***single***" component metal-oxides



Effect of Cr co-loading on water splitting activity

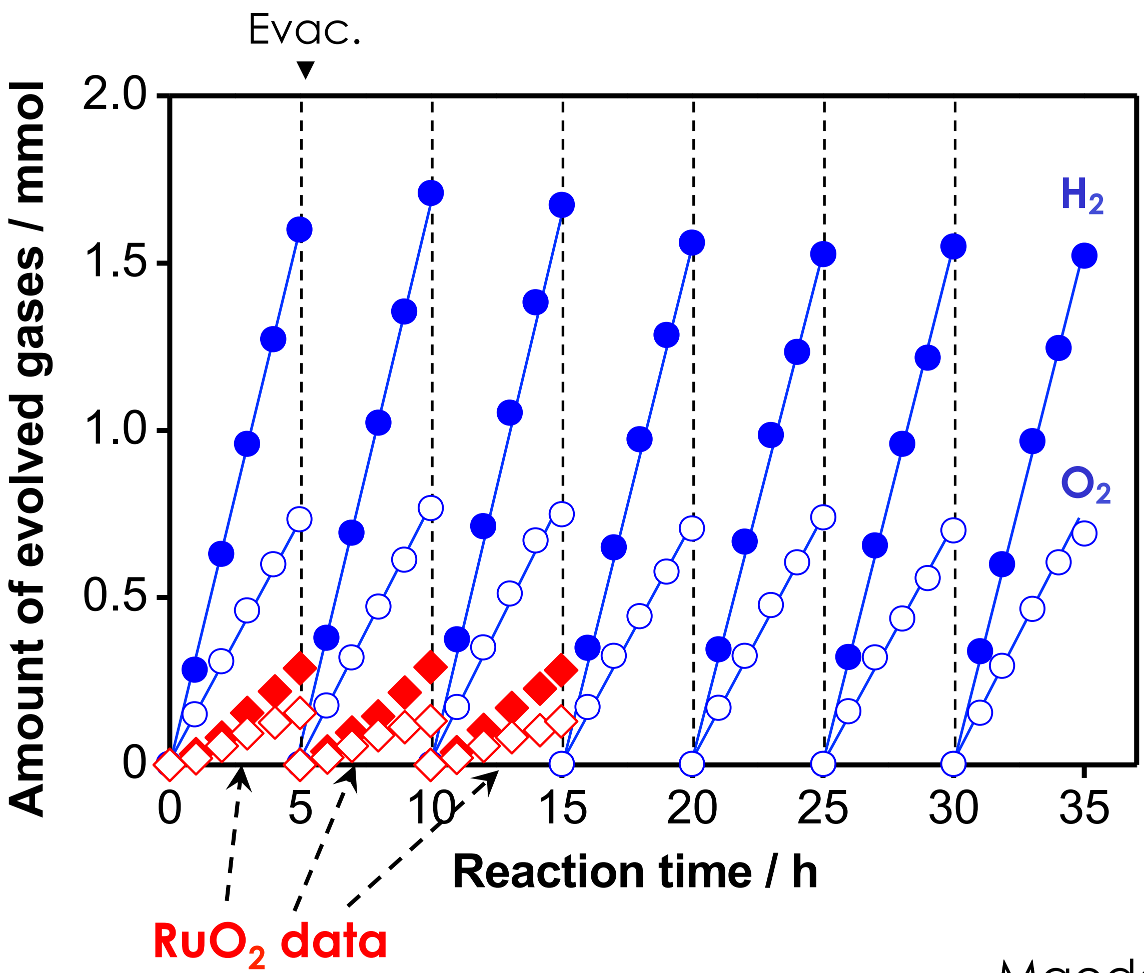
Maeda et al., *J. Catal.* **2006**, *243*, 303.

λ > 300 nm

Cocatalyst		Activity / μmol h^{-1}		Cr coloading amount / wt%	Activity / μmol h^{-1}	
Element (oxide)	Loading amount / wt%	H_2	O_2		H_2	O_2
None	-	0	0			
Cr	1	0	0			
Fe	1	0	0	1	73	36
Co	1	2.0	0	1	48	24
Ni	1.25	126	57	0.125	685	336
Cu	1	2.0	0	1	585	292
Ru	1	71	27	0.1	181	84
Rh	1	50	1.6	1.5	3835	1988
Pd	1	1.0	0	0.1	205	96
Ag	1	0	0	1	11	2.3
Ir	1.5	9.3	3.1	0.1	41	17
Pt	1	0.9	0.4	1	775	357

Catalyst: 0.3 g, Reactant soln.: distilled water 370~400 mL, Reaction vessel: Inner irradiation-type, Light source: 450 W high-pressure mercury lamp

Overall water splitting on $Rh_{2-y}Cr_yO_3$-loaded GaN:ZnO under visible light irradiation



λ > 400 nm

Used catalyst: 3.7 mmol
Evolved gases: 16.2 mmol

Catalytic cycle!!

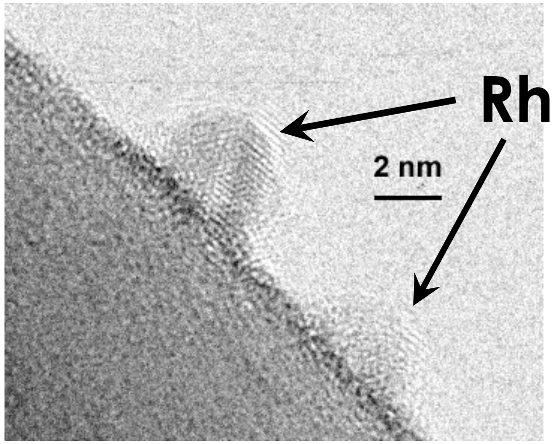
Maeda et al., *Nature*, **2006**, *440*, 295.

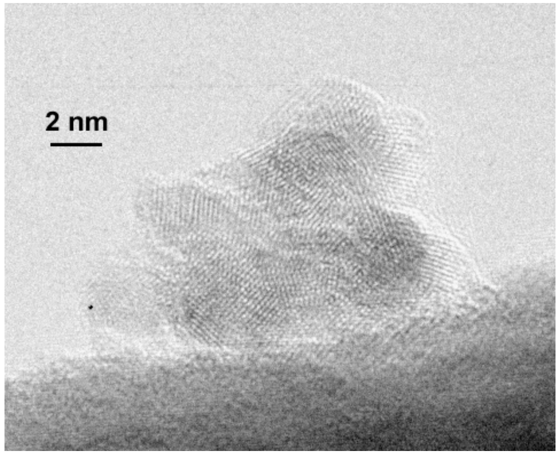
Catalyst: 0.3 g, Reactant soln.: H_2SO_4 aq. 370 mL (pH 4.5), Reaction vessel: Inner irradiation-type, Light source: 450 W high-pressure mercury lamp with a $NaNO_2$ aq. filter

TEM images of Rh-loaded GaN:ZnO before and after photodeposition of Cr_2O_3

Maeda et al., *Angew. Chem., Int. Ed.* **2006**, *45*, 7806.
Maeda et al., *J. Phys. Chem. C* **2007**, *111*, 7554.
Maeda et al., *Chem. Eur. J.* **2010**, *16*, 7750.

Revealed by XAFS and XPS

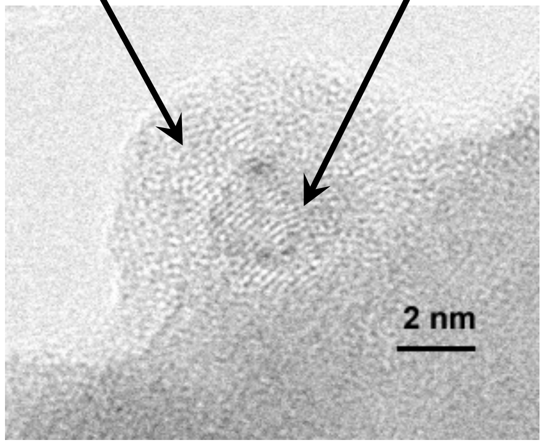


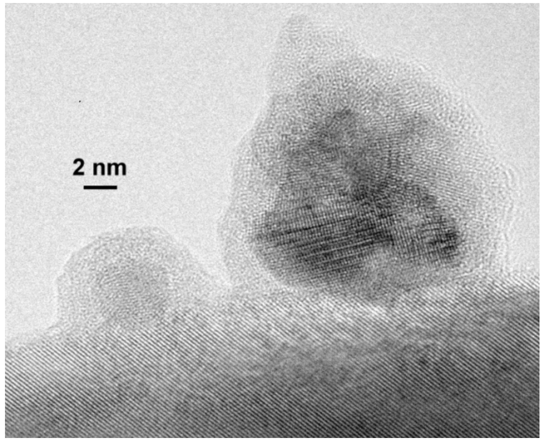


Rh/GaN:ZnO
(before Cr_2O_3 deposition)

Photoreduction of Cr^{6+}

Cr_2O_3 (shell) **Rh (core)**

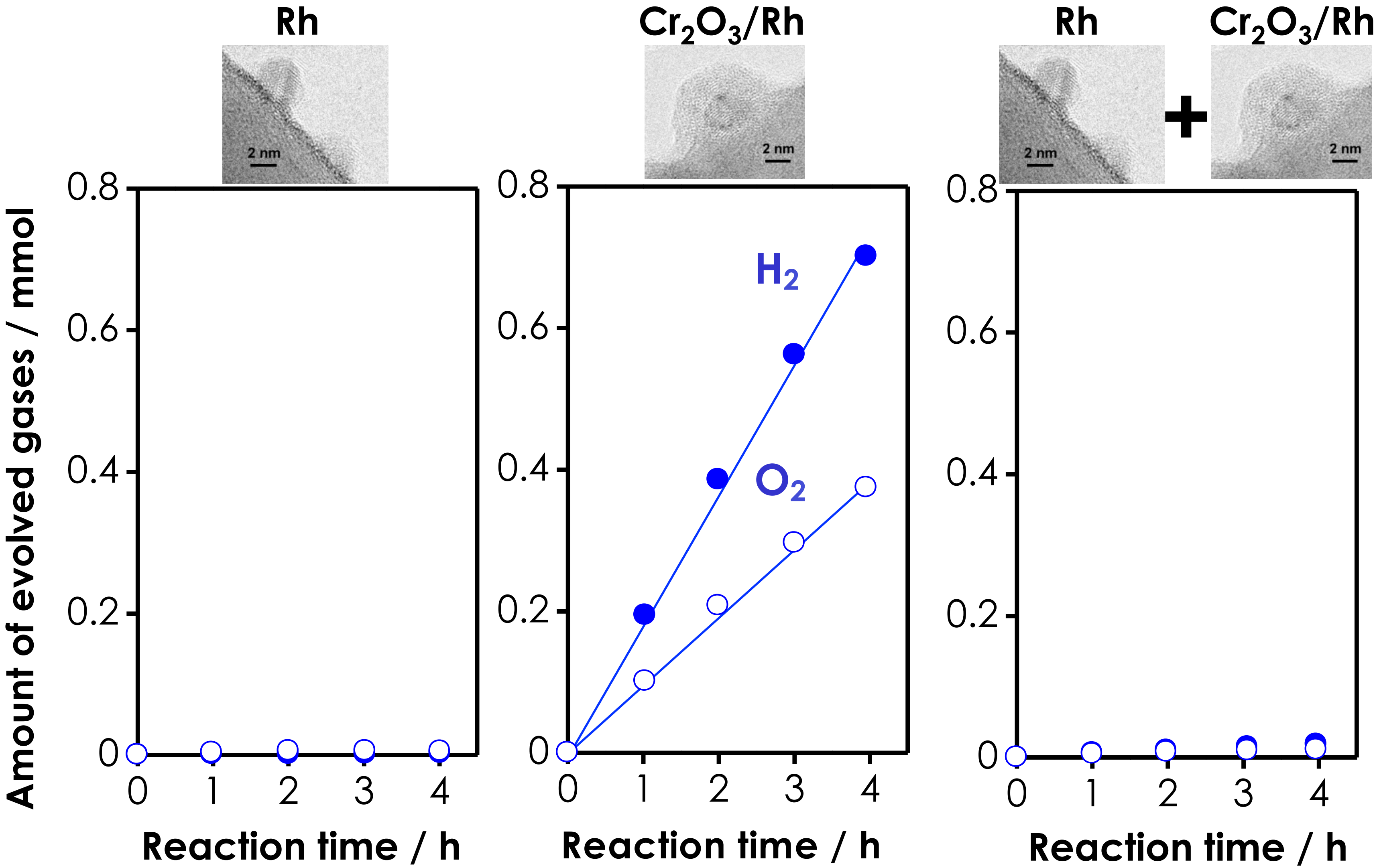




Cr_2O_3/Rh/GaN:ZnO

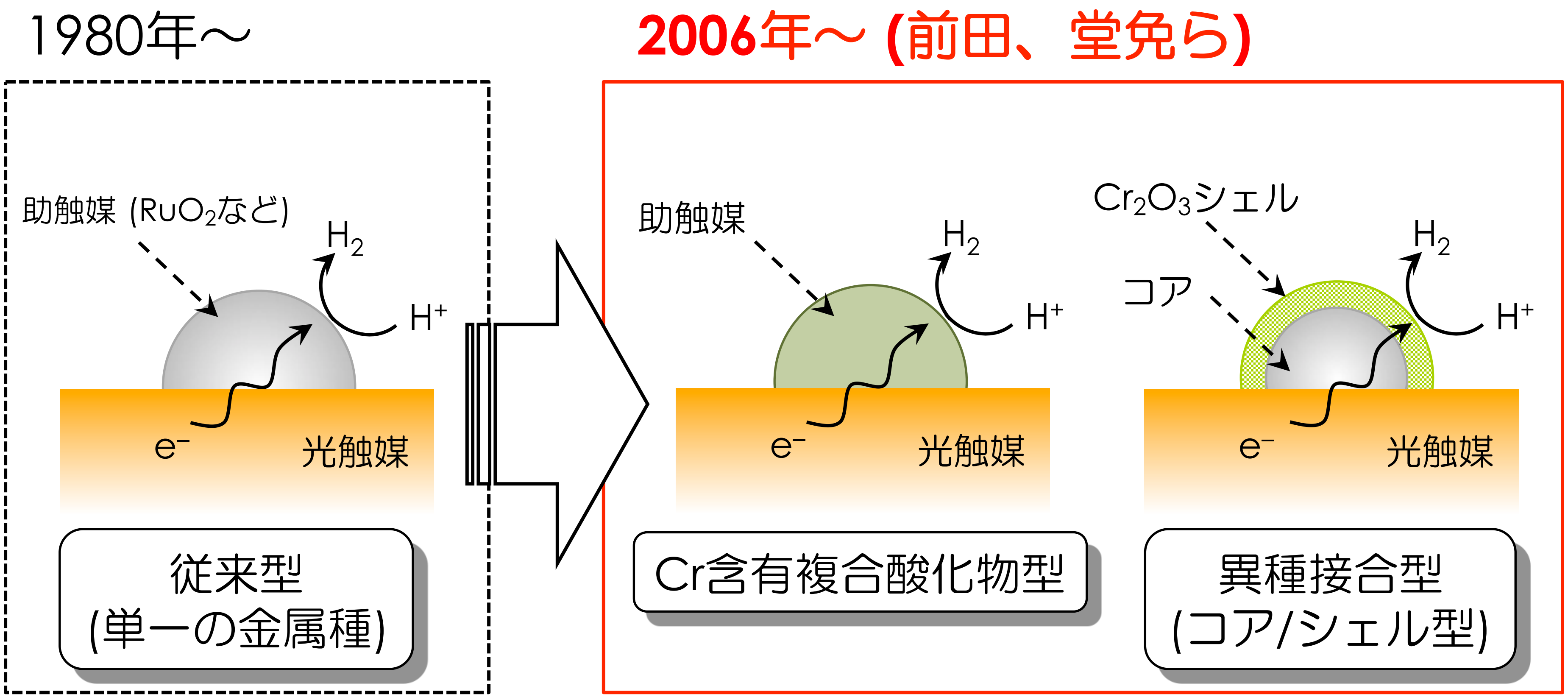
Time course of overall water splitting on core/shell-structured Cr_2O_3/Rh/GaN:ZnO

λ > 400 nm



Catalyst: 0.15 g, Reactant soln.: pure H_2O 370 mL, Reaction vessel: Pyrex inner irradiation-type, Light source: 450 W high-pressure Hg lamp with a $NaNO_2$ aq. (2 M) filter

水分解光触媒における助触媒研究

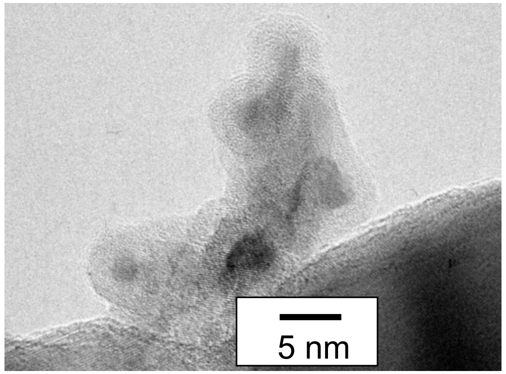


水分解光触媒研究の分野に助触媒開発という一大研究領域を確立

Major problem in the nanoparticulate core/shell system

Photodeposition

Aggregated Rh



Attempts to have Rh well-dispersed

- Impregnation method

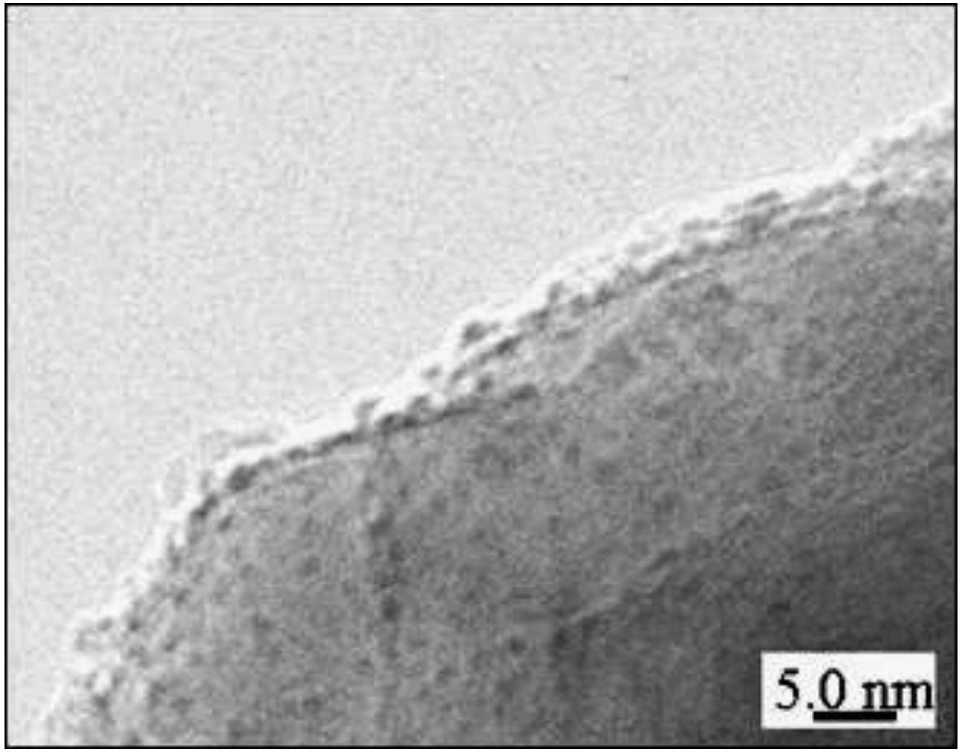
→ No positive effect!!

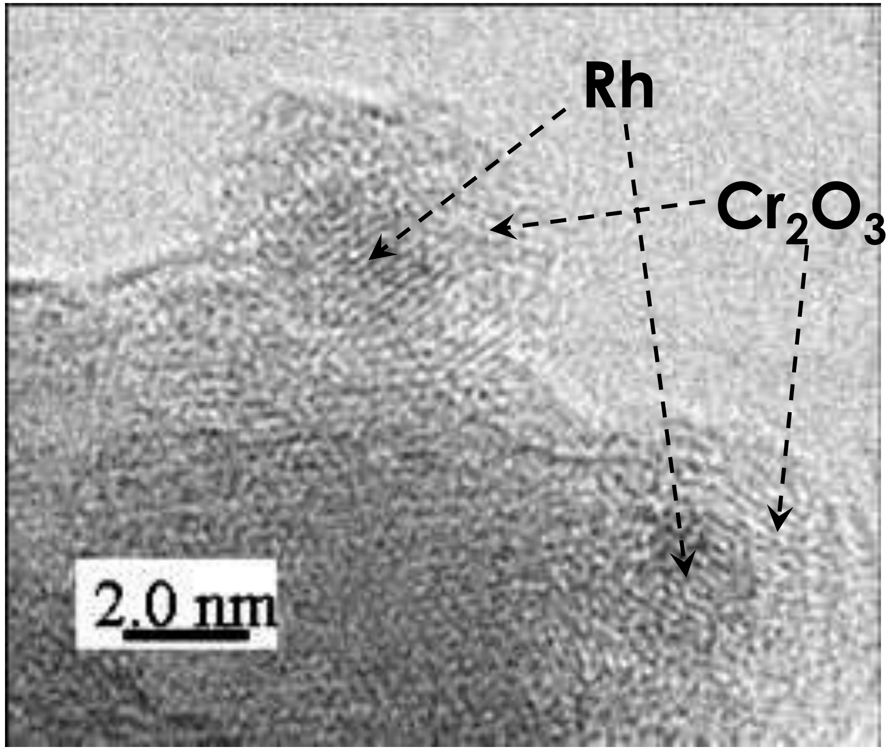
- New method

→ **Adsorption**

To increase the activity of Cr_2O_3/Rh/GaN:ZnO by introduction of ***Rh nanoparticle core with higher dispersion***

TEM images of GaN:ZnO modified with Rh/Cr_2O_3 (core/shell) nanoparticles by an adsorption method



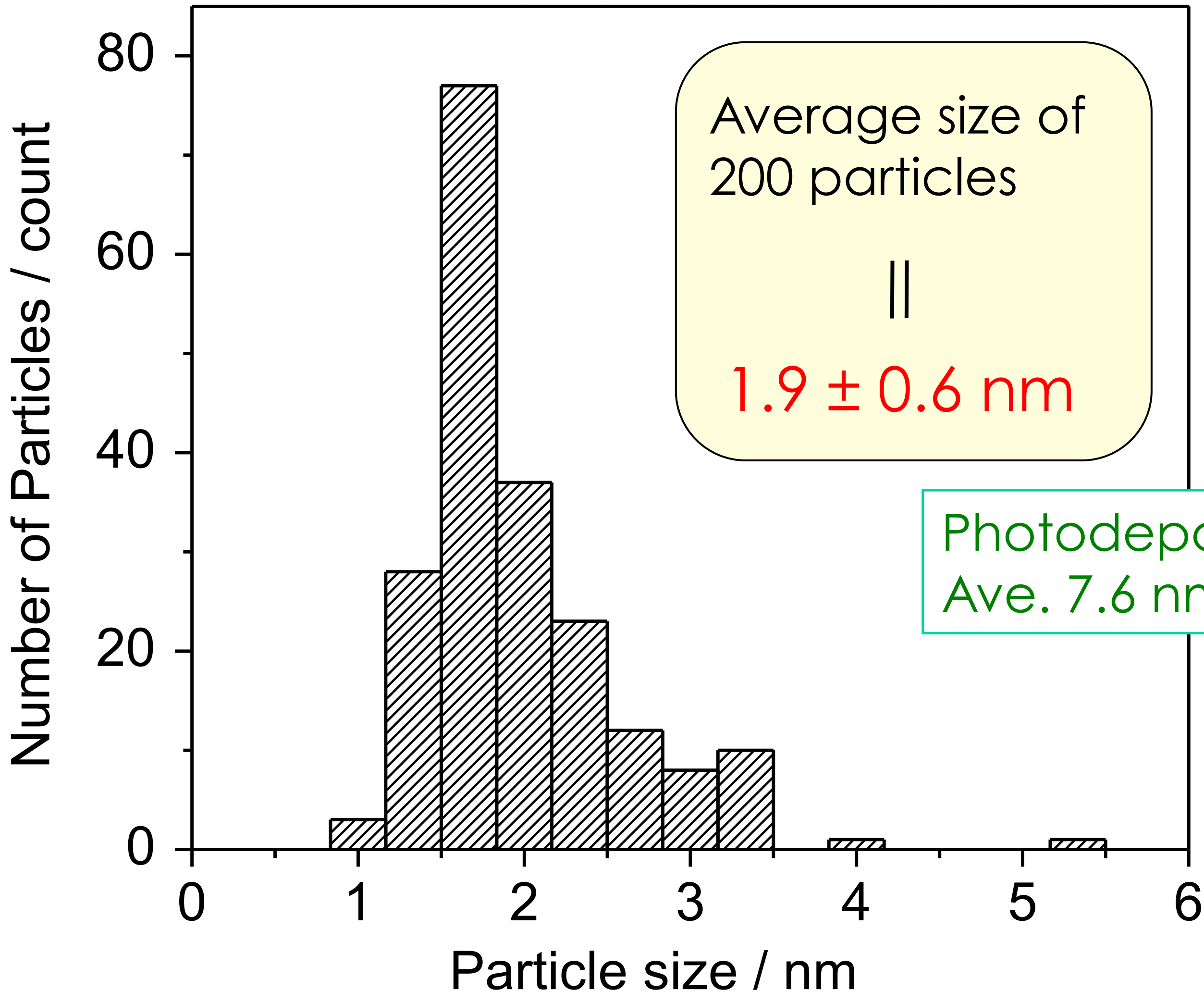


High-dispersion!!

Size: 1~3 nm

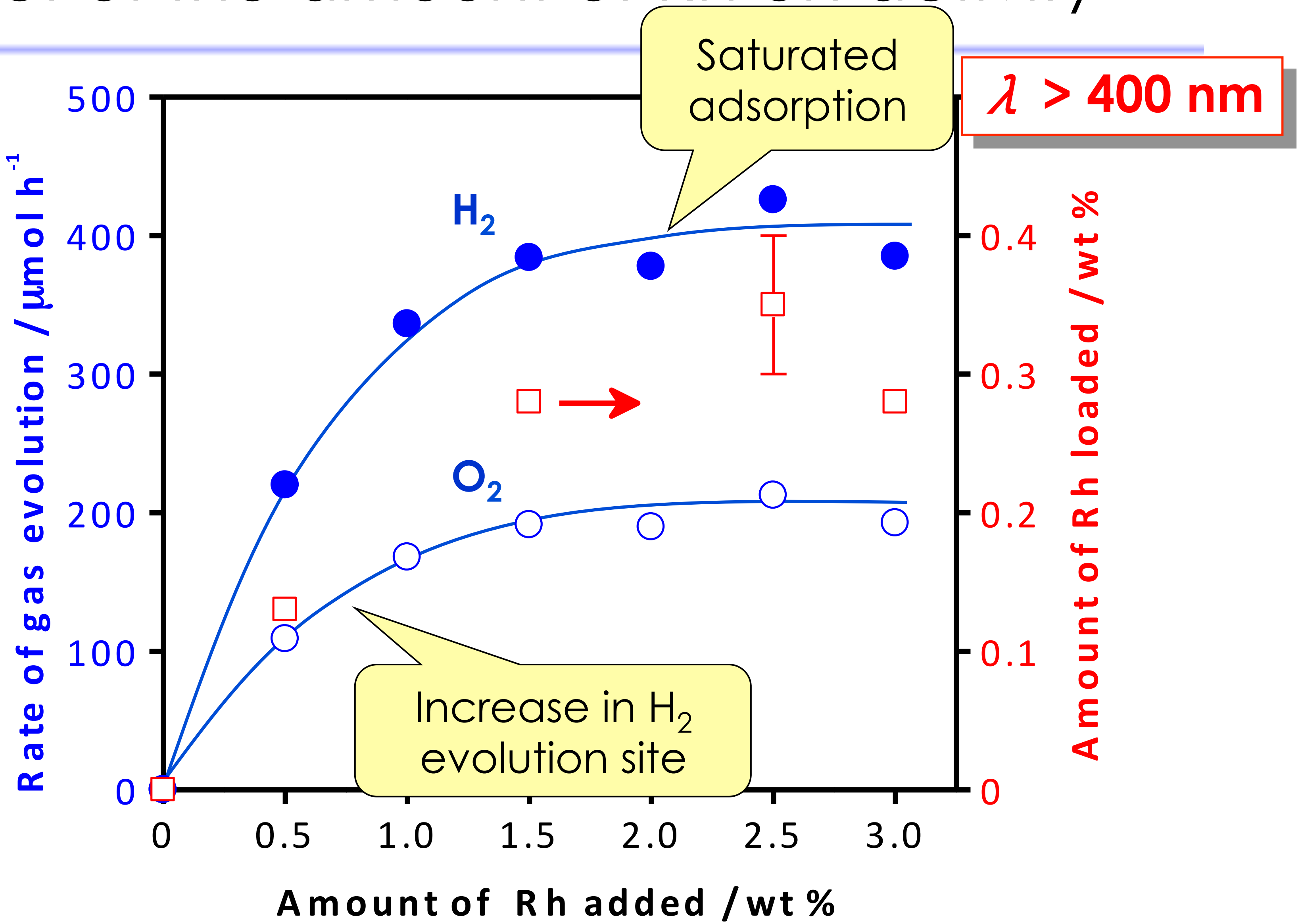
Sakamoto et al., *Nanoscale,* **2009**, *1*, 106.
Maeda et al., *Chem. Eur. J.,* **2010**, *16*, 7750.

Size distribution of Rh nanoparticles adsorbed on the surface of GaN:ZnO



Photodeposition method
Ave. 7.6 nm (50 particles)

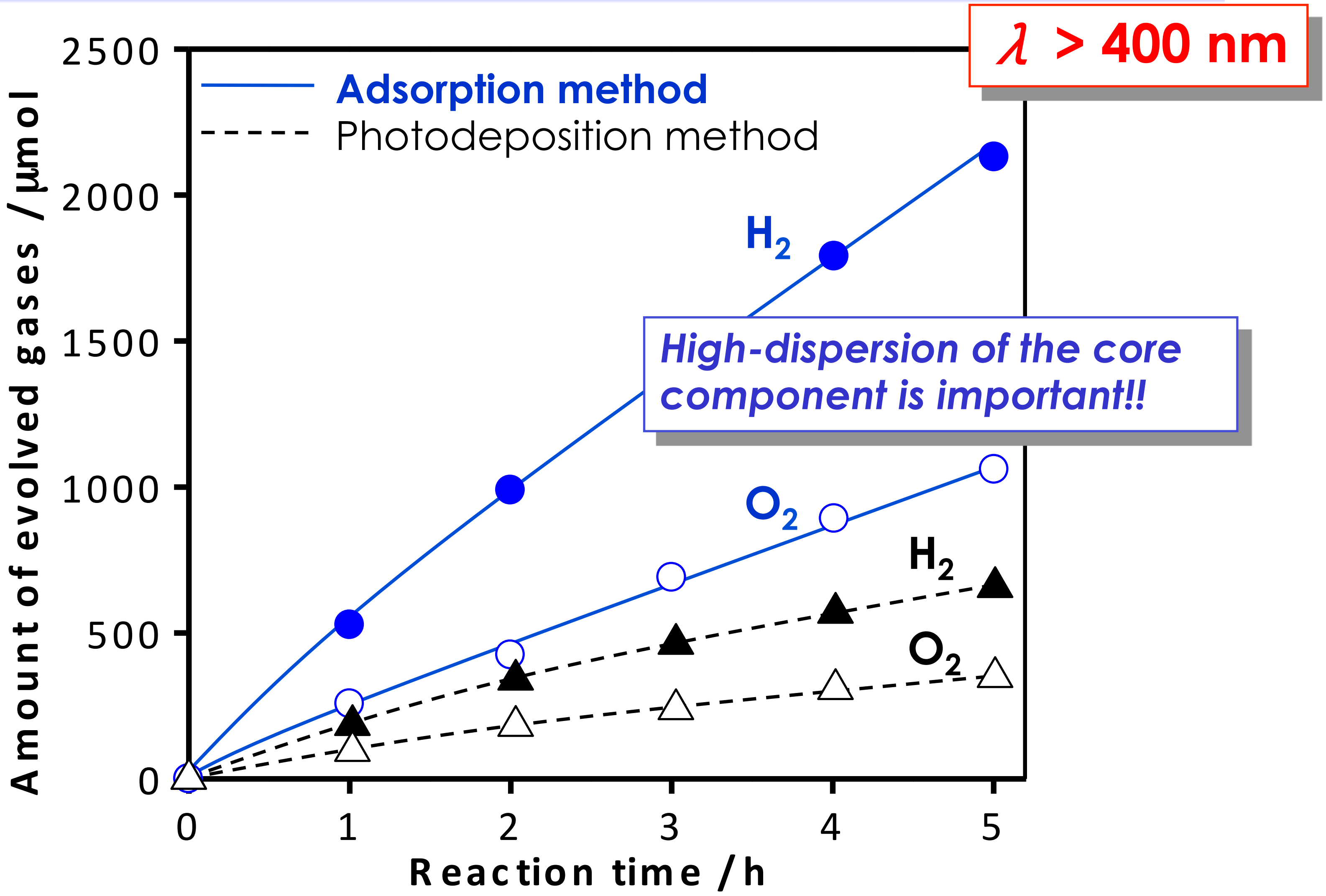
Effect of the amount of Rh on activity



Catalyst: 0.15 g, Reactant soln.: pure H_2O 400 mL, Reaction vessel: Pyrex inner irradiation-type, Light source: 450 W high-pressure Hg lamp with a $NaNO_2$ aq. (2 M) filter

Comparison of activity

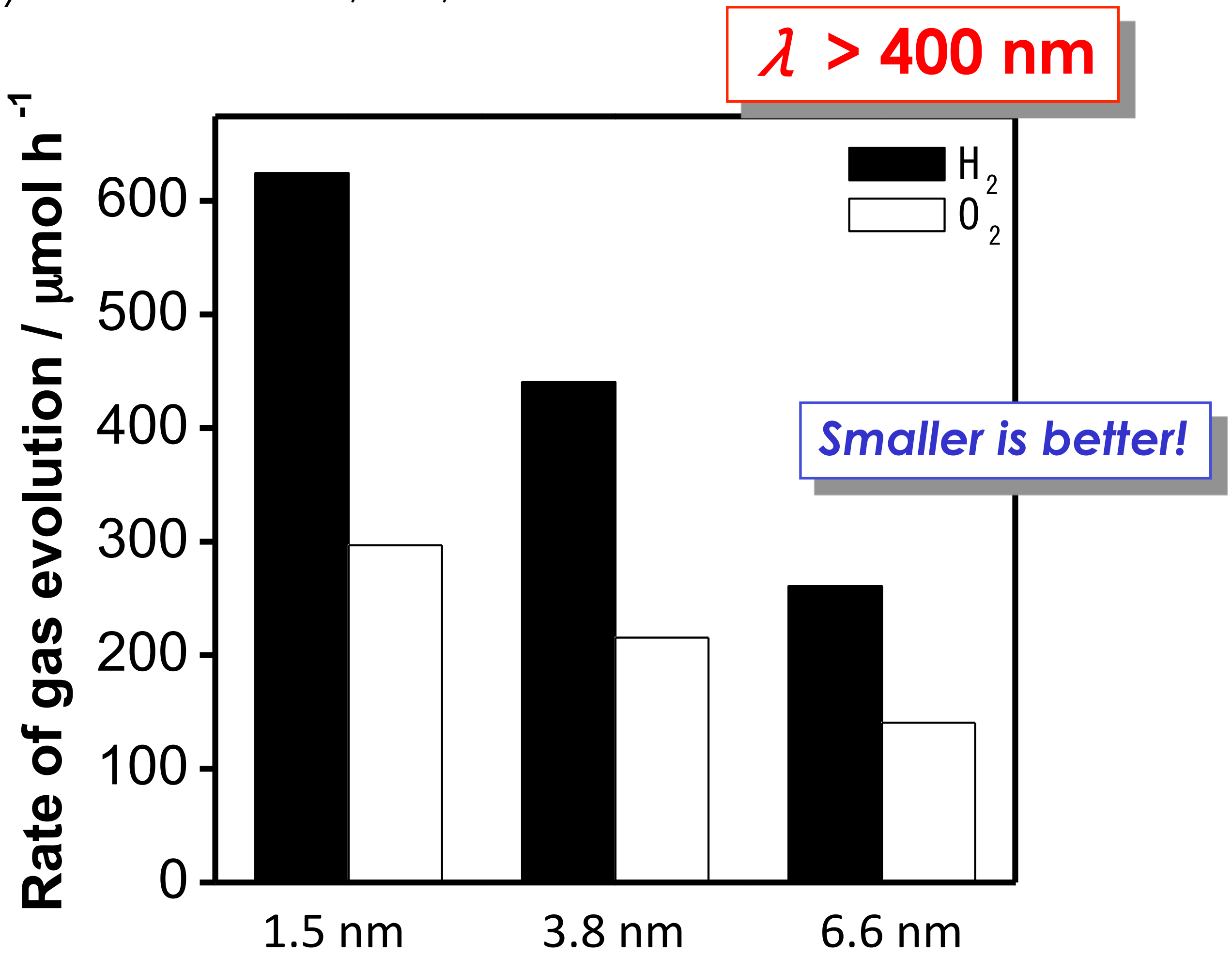
…Rh loading amount: 0.3~0.4 wt%



Catalyst: 0.15 g, Reactant soln.: pure H_2O 400 mL, Reaction vessel: Pyrex inner irradiation-type, Light source: 450 W high-pressure Hg lamp with a $NaNO_2$ aq. (2 M) filter

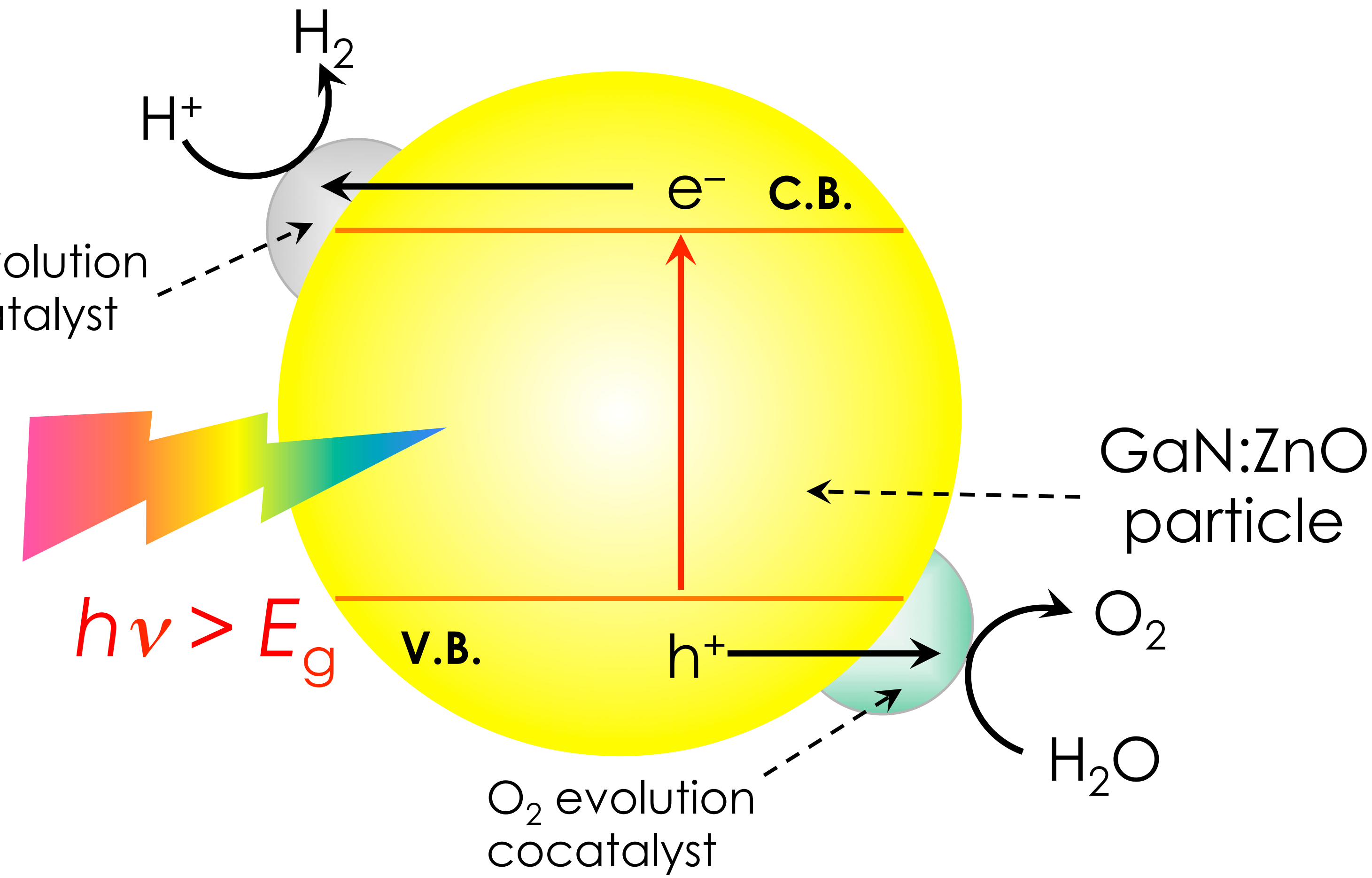
Effect of the size of Rh nanoparticles on activity

Ikeda et al., *J. Phys. Chem. C* **2013**, *117*, 2467.



Catalyst: 0.15 g, Reactant soln.: H_2SO_4 aq. 400 mL (pH 4.5), Reaction vessel: Pyrex inner irradiation-type, Light source: 450 W high-pressure Hg lamp with a $NaNO_2$ aq. (2 M) filter

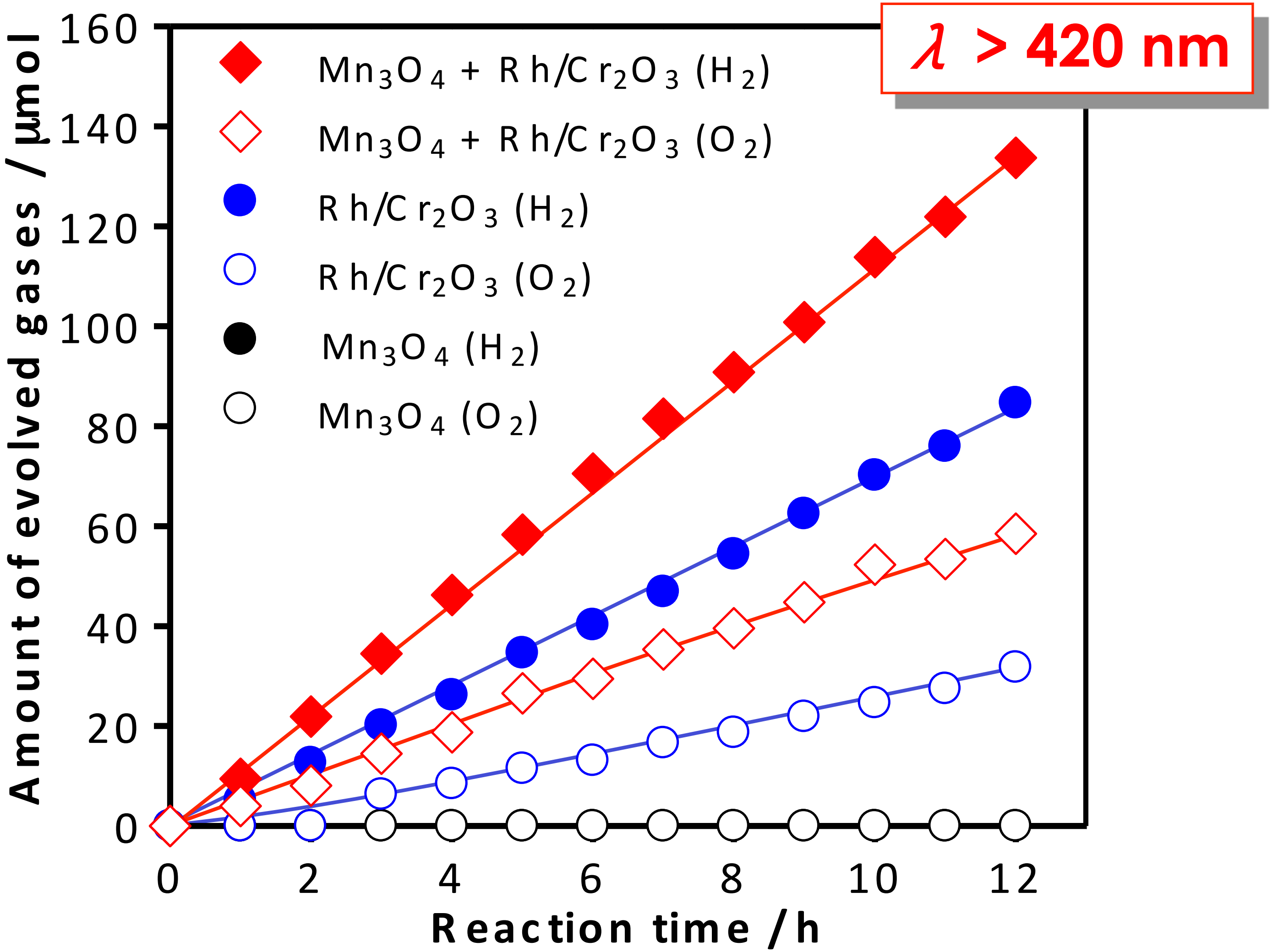
Overall water splitting on a particulate photocatalyst promoted by two different types of cocatalysts



Introduction of both H_2 and O_2 evolution cocatalysts to improve activity!
…But no successful example for constructing such a structure…

Visible light water splitting
…Effect of coloading Mn_3O_4

Mn_3O_4 0.05 wt %



Catalyst: 0.1 g of each, Reactant solution: distilled water 100 mL, Top-irradiation type with a 300 W Xe lamp and a cutoff filter

Summary

- Precise control of Rh core size in Rh/Cr_2O_3 nanoparticles
  - ✓ Successful introduction of size-controlled Rh nanoparticles onto the surface of GaN:ZnO photocatalyst
  - ✓ For application in the core component, smaller Rh works better.
  - ✓ Loading another oxygen evolution cocatalyst of Mn_3O_4 nanoparticles further enhances the water-splitting activity.

- Mechanism of H_2 evolution on Rh/Cr_2O_3 nanoparticles
  - ✓ The core hosts active sites for H_2 formation, while the Cr_2O_3 shell functions as a selective permeable membrane.

Modification of surface structure in nano-scale is highly important for enhancing water-splitting activity with visible light!

Acknowledgement

- Prof. K. Domen…The Univ. of Tokyo

  The boss

- Prof. T. Teranishi, T. Ikeda, T. Yoshinaga…Kyoto Univ. & Tsukuba Univ.
- Dr. M. Yoshida, N. Sakamoto, A. Xiong…(former) students of our group

  Collaboration on the core/shell cocatalyst project

- Dr. D. Lu…Tokyo Institute of Technology

  TEM observations

- 日本板硝子材料工学助成会, 日本学術振興会, 科学技術振興機構さきがけ

  Funding support