November 9, 2021: CBMM (Webinar)

Niobium Technology for Clean Energy

Niobium-based Photocatalysts for Water Splitting Reaction

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Shinshu University & The University of Tokyo

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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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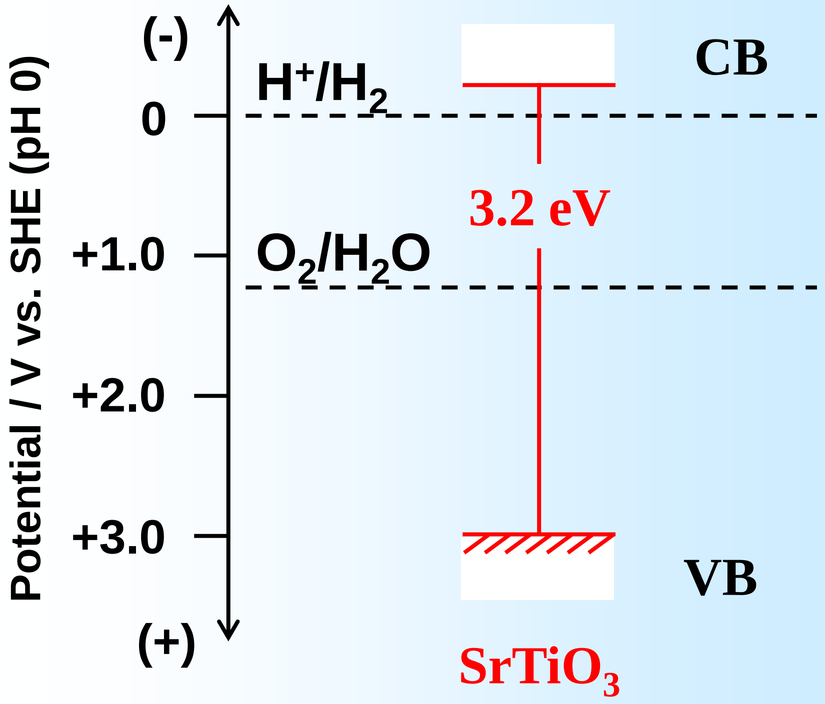
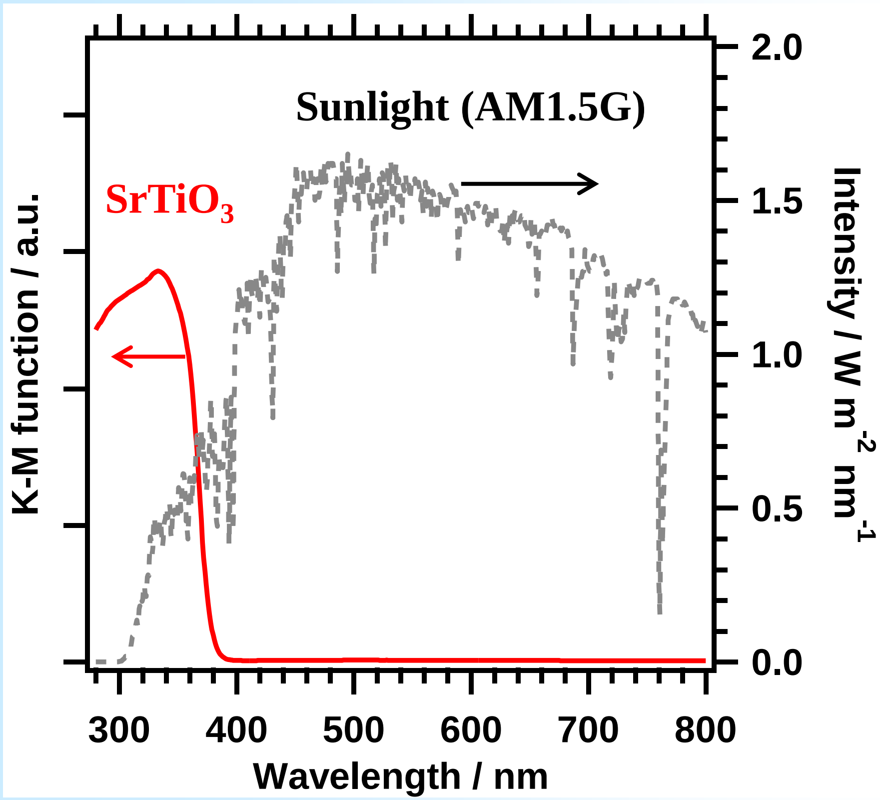
Potential of $SrTiO_3$ as photocatalyst





UV light responsive photocatalyst

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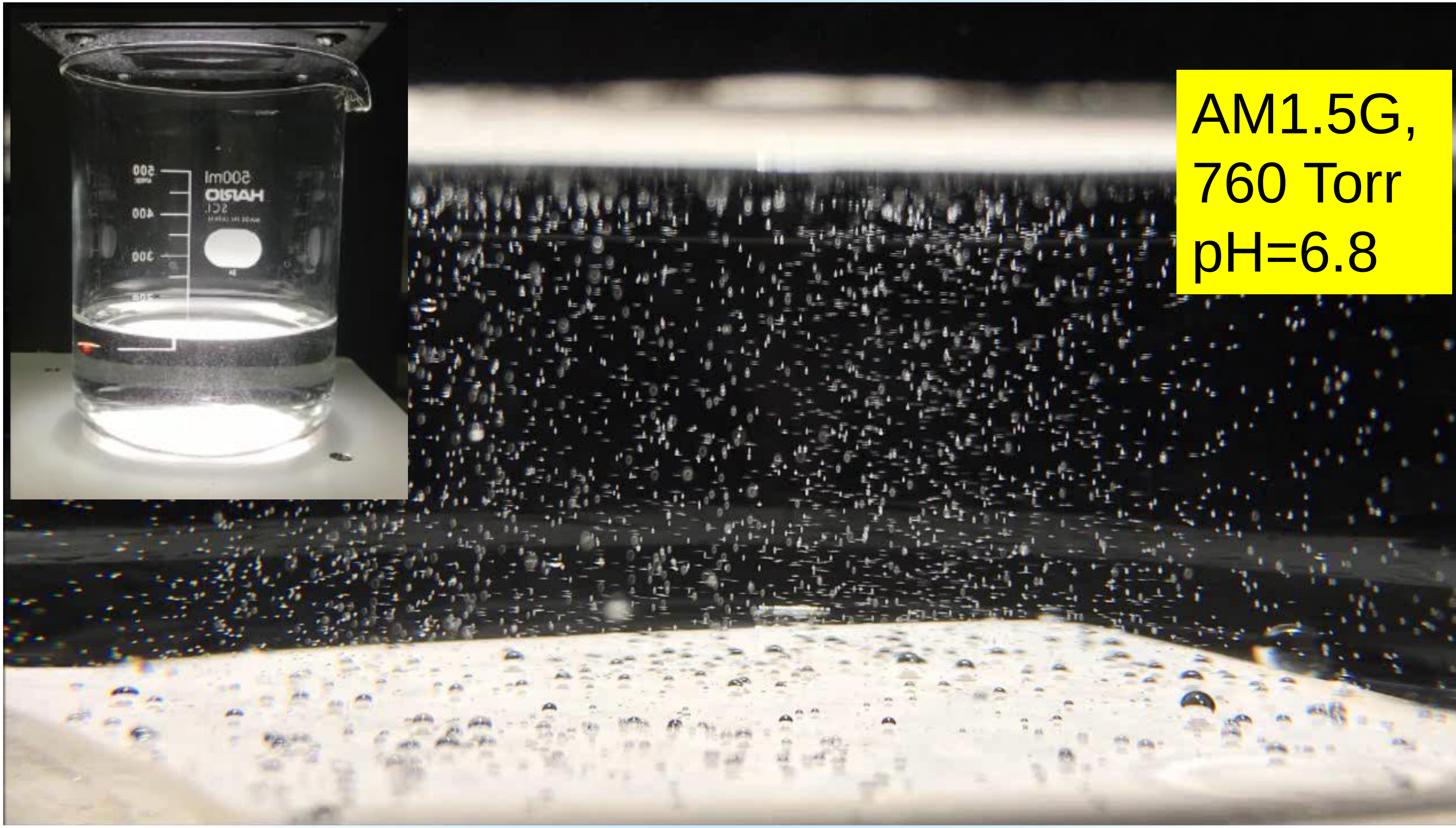
Water splitting on $RhCrCoO_x/SrTiO_3:Al + SiO_2$ photocatalyst sheet



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100 m^2 prototype water splitting panel

November 6, 2019, 15:20 am at Kakioka Research Facility

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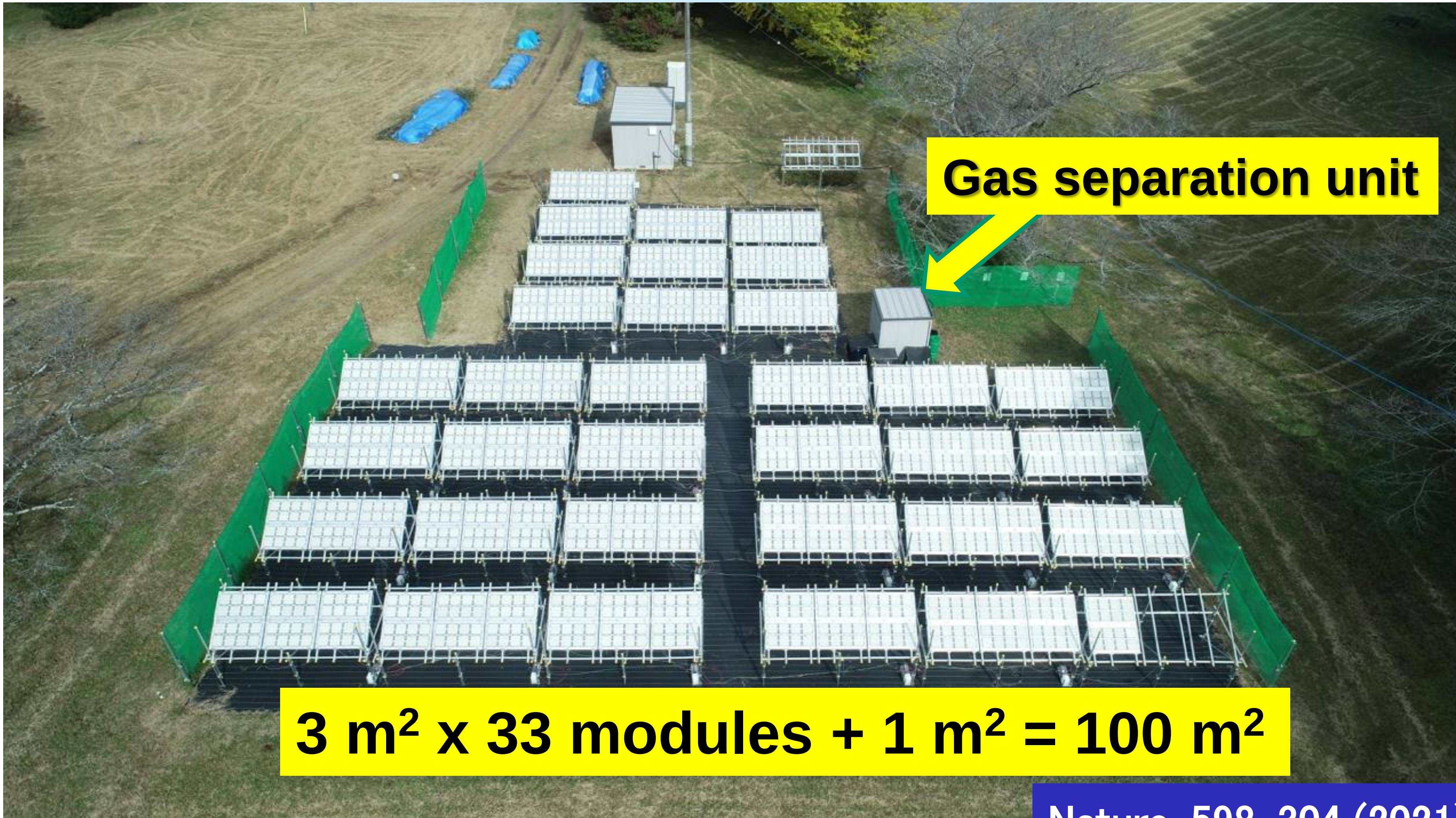
$100\ m^2$ prototype water splitting panel

November 6, 2019, 15:20 am at Kakioka Research Facility



Nature, 598, 304 (2021)

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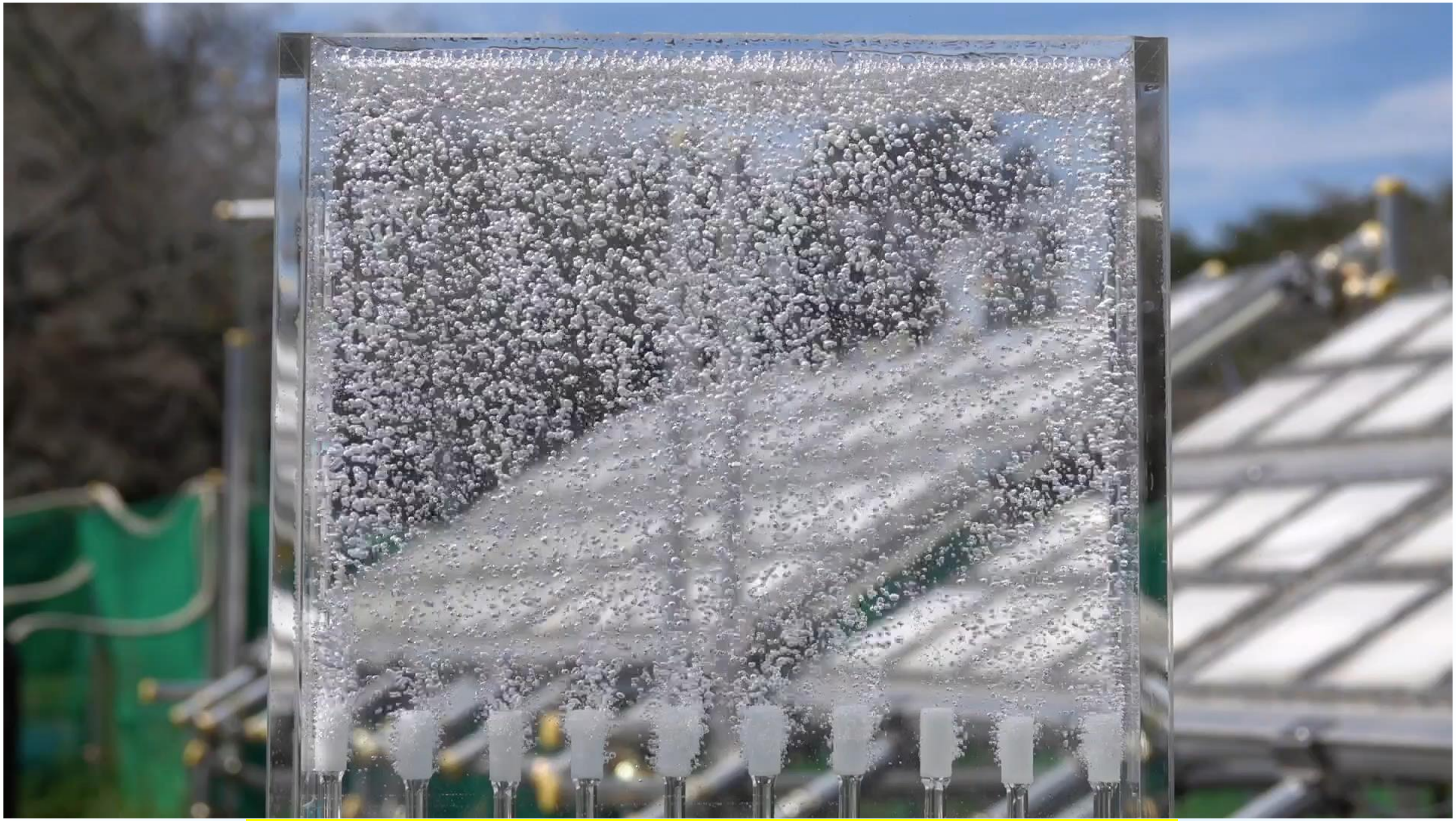
100 m^2 prototype water splitting panel

September 30, 2020, 11:30 am at Kakioka Research Facility



3.6～3.7 L/min (H_2+1/2O_2)

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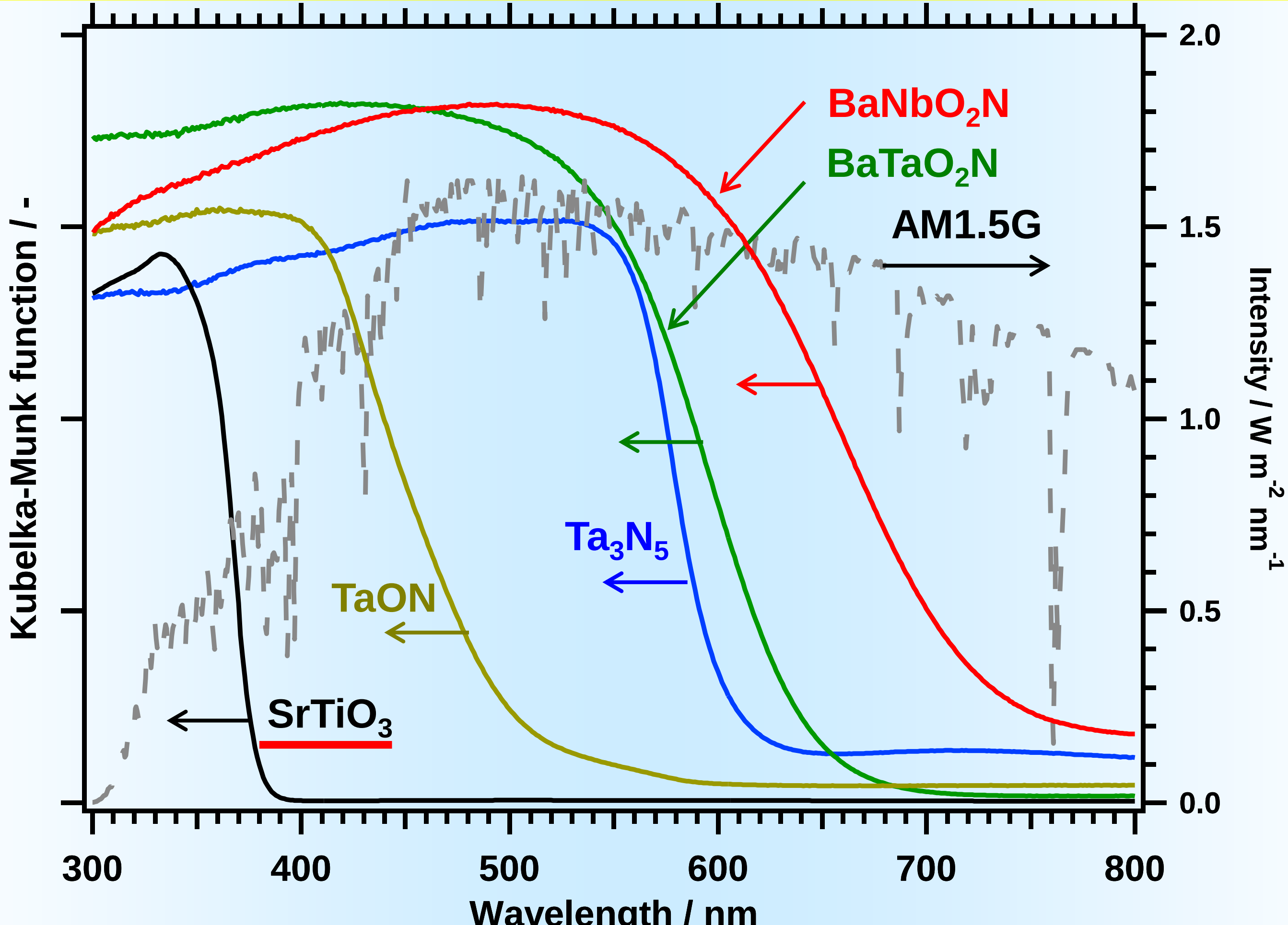
Comparison of solar light absorption among various materils

Nb-based materials are one of the ultimate targets as photocatalysts.



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Conventional preparation of $BaNbO_2N$

$BaCO_3$ + Nb_2O_5 (Ba/Nb=5/4)

↓ + NaCl flux
Calcination (1173 K, 5 h)
Washing

$Ba_5Nb_4O_{15}$

↓ + $BaCO_3$ (Ba/Nb=1.25–2.00)
Nitridation (1202 K, 15 h)

$BaNbO_2N$ + impurity

↓ Aqua regia treatment
Washing

$BaNbO_2N$

$BaNbO_2N$

↓ Impregnation
$Co(NO_3)_2$ aq (Co 2 wt%)
Nitridation
(773 K, 1 h)

$CoO_x/BaNbO_2N$ **O_2 evolution**

$BaNbO_2N$

↓ Impregnation
H_2PtCl_6 aq (Pt 1 wt%)
Hydrogen reduction
(573 K, 1 h)

$Pt/BaNbO_2N$ **H_2 evolution**

Energy Environ. Sci. 2013, 6, 3595.

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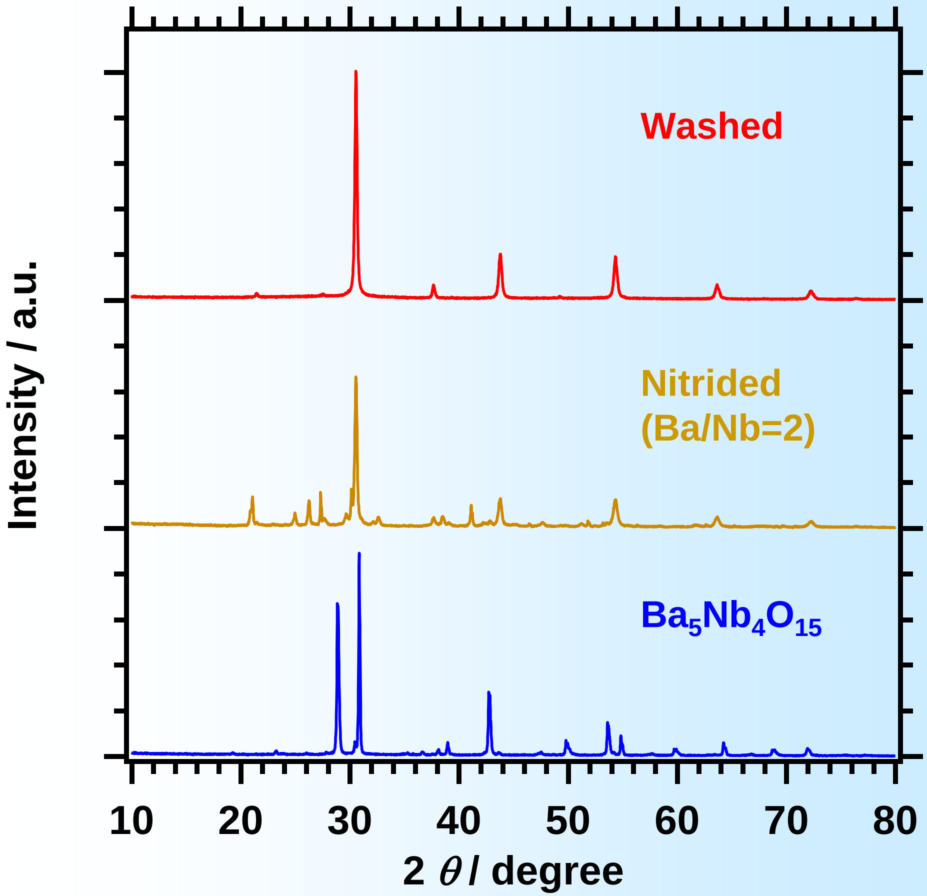
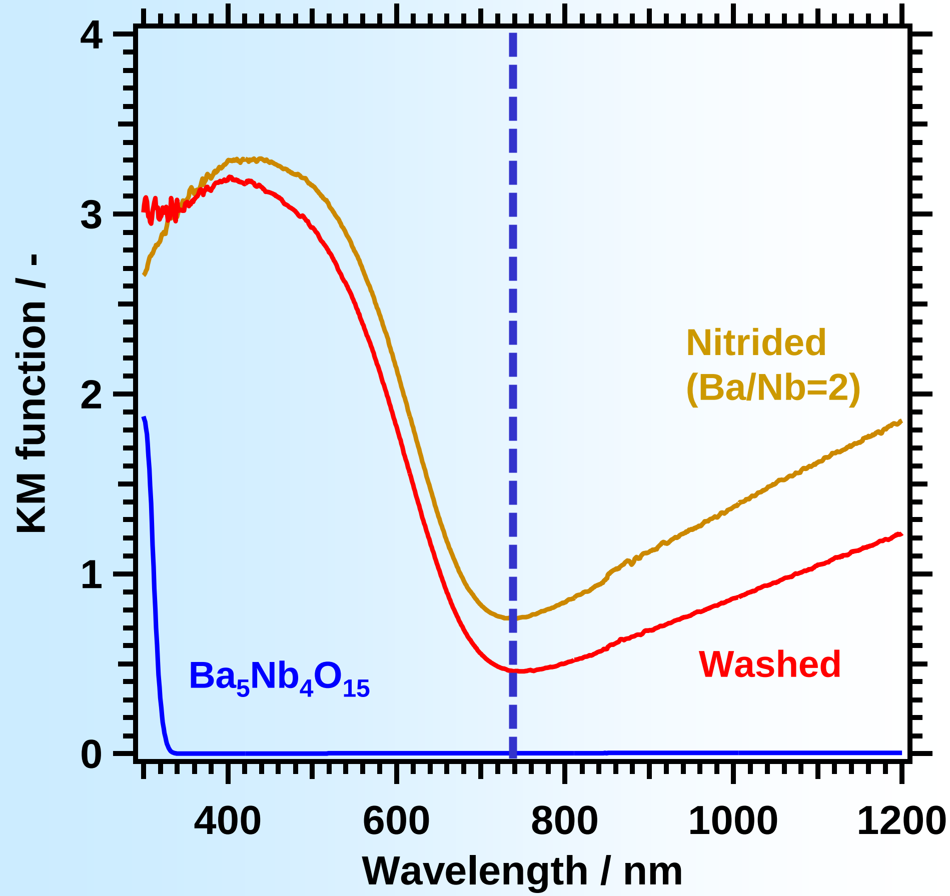
XRD patterns and DR spectra of $BaNbO_2N$





Removal of excessive Ba-containing impurities

Absorption edge at 740 nm

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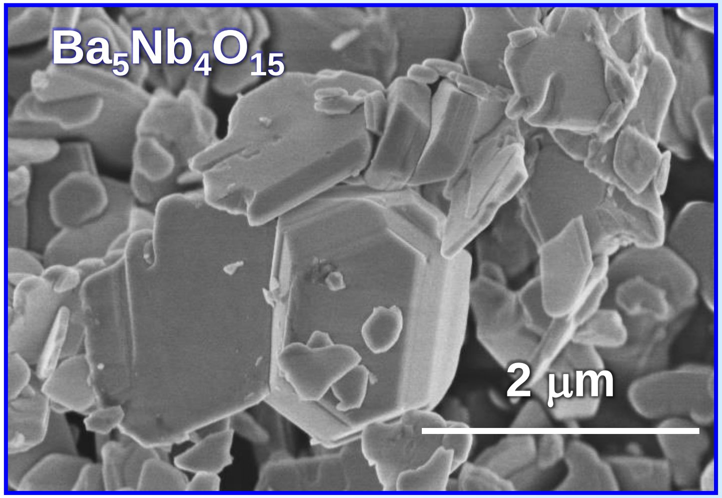
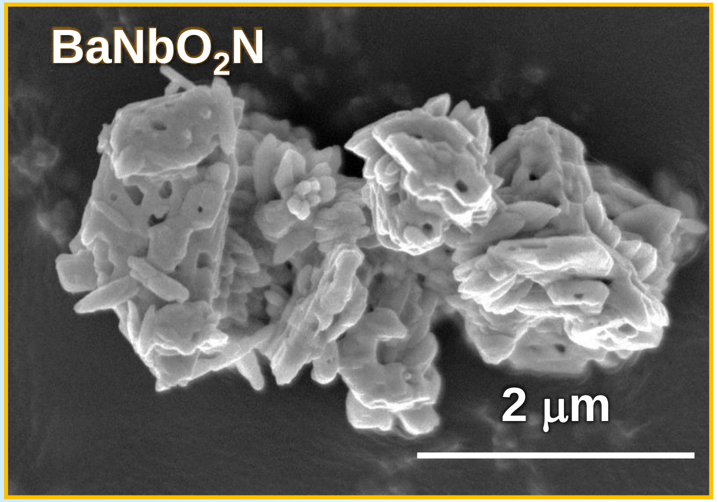
SEM images of $BaNbO_2N$

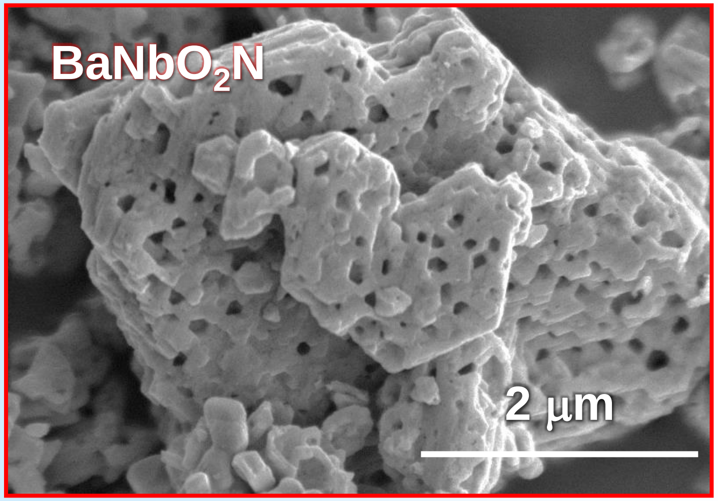


Nitridation ⇨



Fragmentation of particles
(due to excessive Ba species)

Washed ⇨



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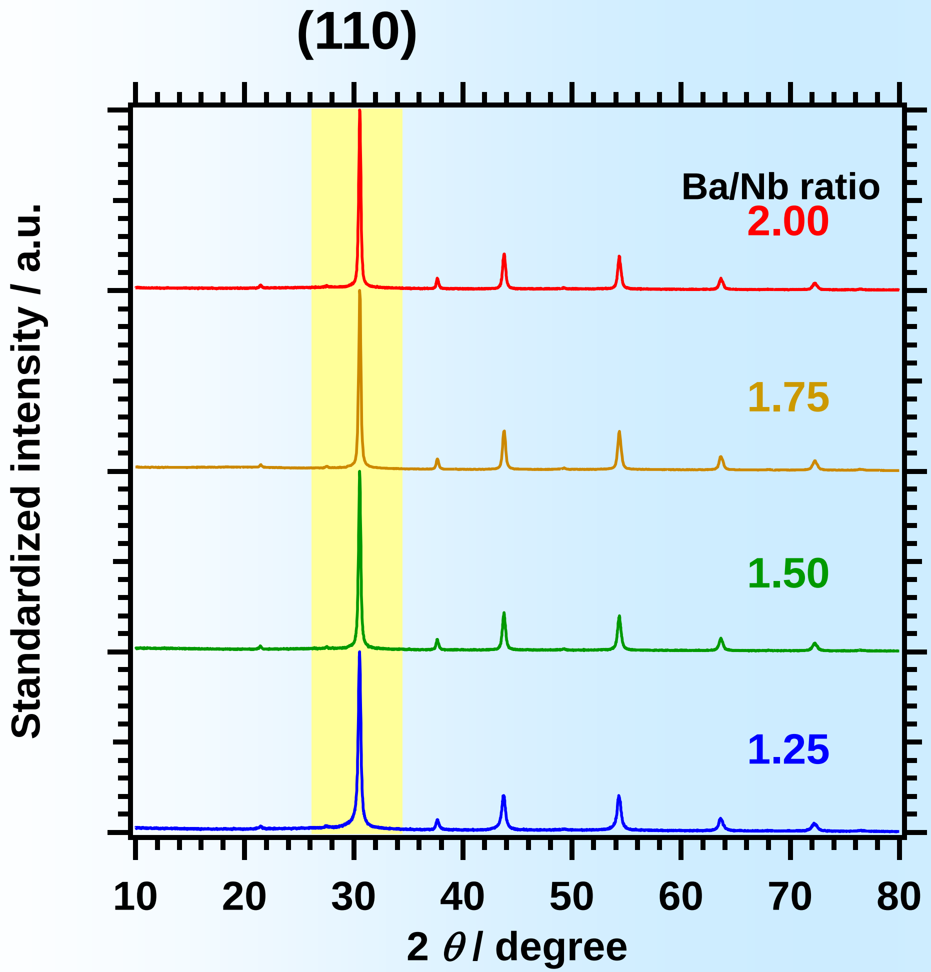
Effect of excess $BaCO_3$-addition during the nitridation of $Ba_5Nb_4O_{15}$



Single phase of $BaTaO_2N$

FWHM of (110)

0.207°

0.210°

0.213°

0.246°

Improvement of crystallinity/ homogeneity

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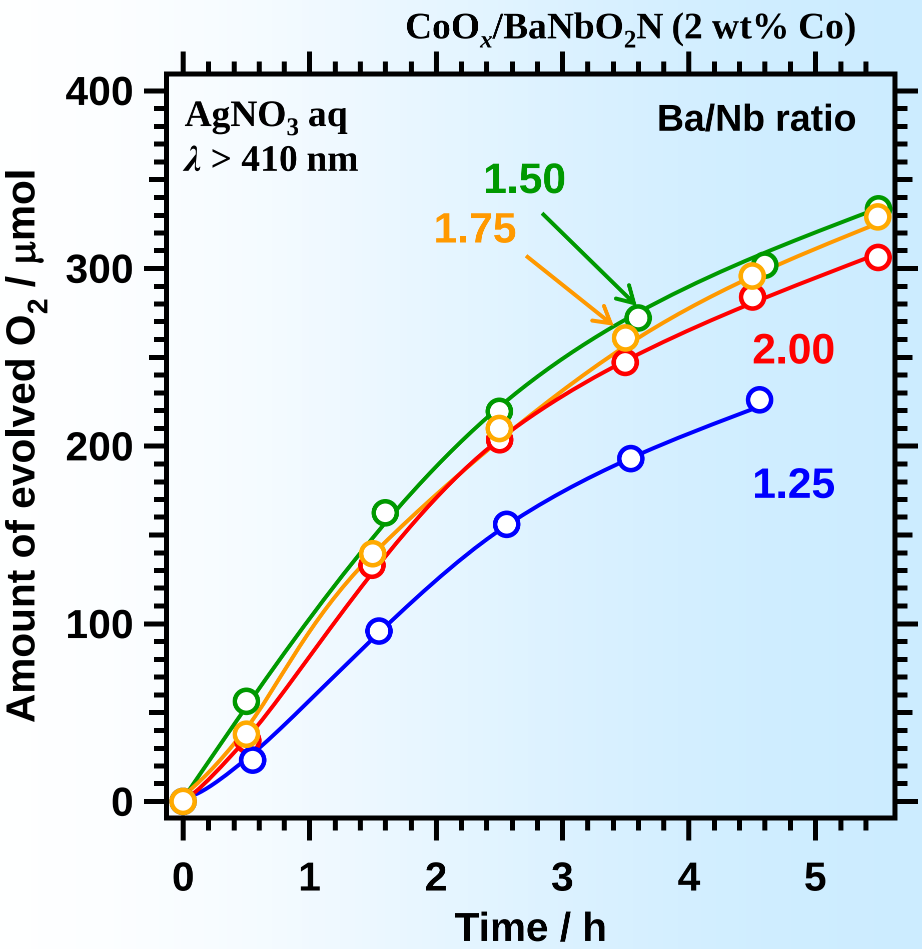
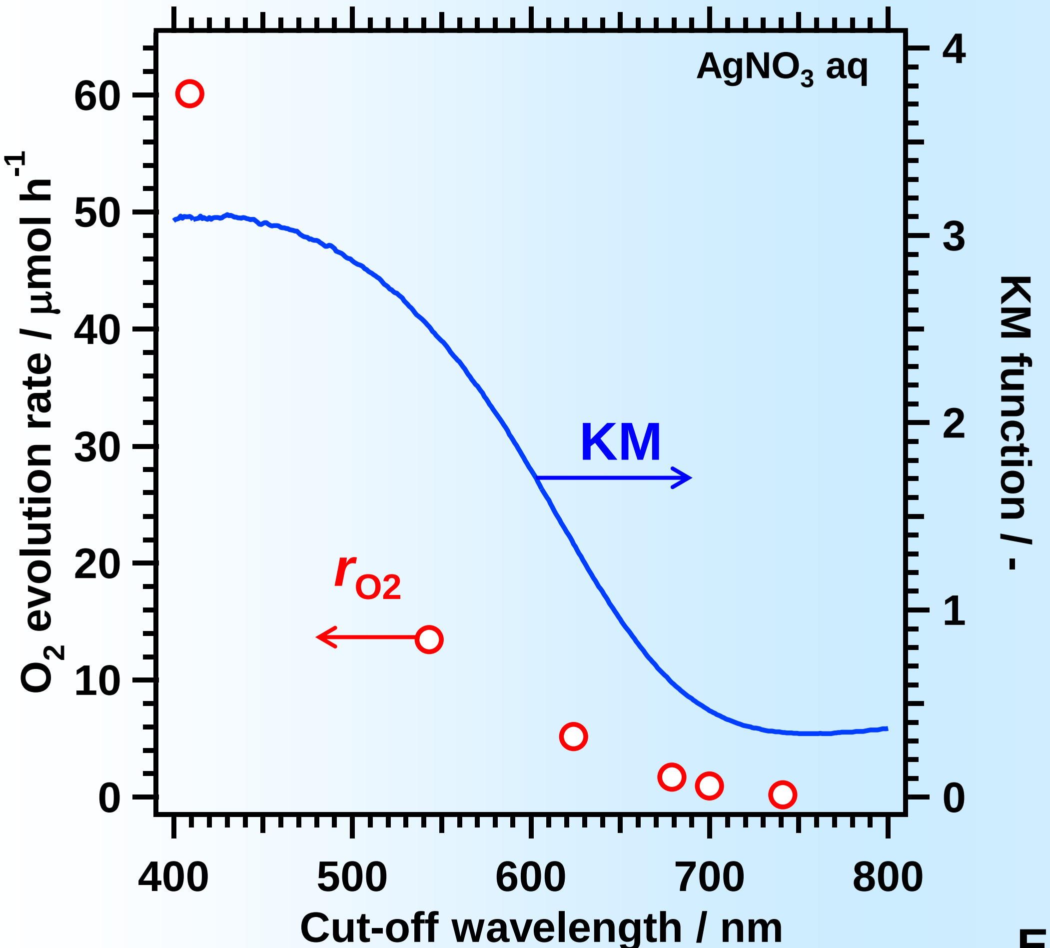
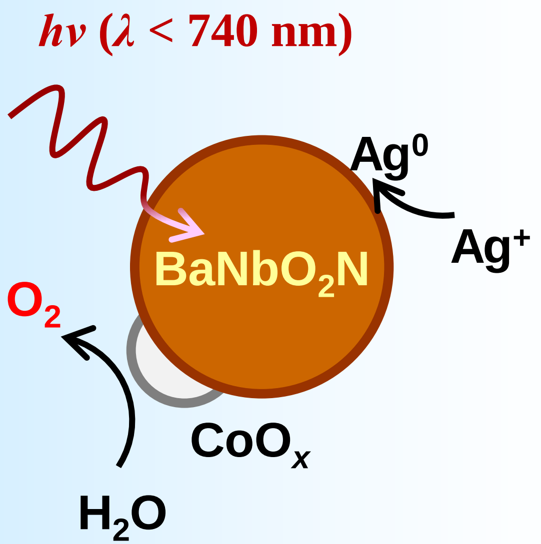
Effect of $BaCO_3$-addition on the O_2 evolution activity of $CoO_x/BaNbO_2N$



Improvement of the activity by $BaCO_3$-addition:
Ba/Nb=1.5

Wavelength-dependence of O_2 evolurion activity on $CoO_x/BaNbO_2N$





Active under red light
(AQY: 0.4%, 420 nm)

Energy Environ. Sci.; 2013, 6, 3595.

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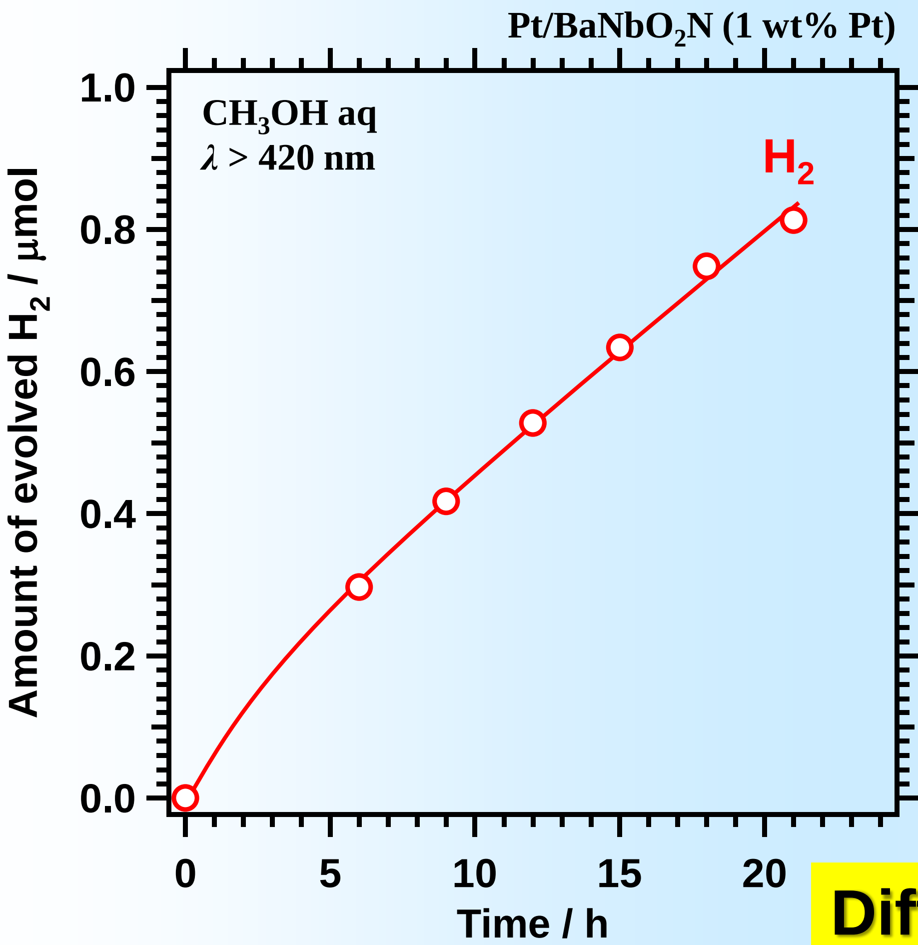
H_2 evolution activity of Pt/$BaNbO_2N$



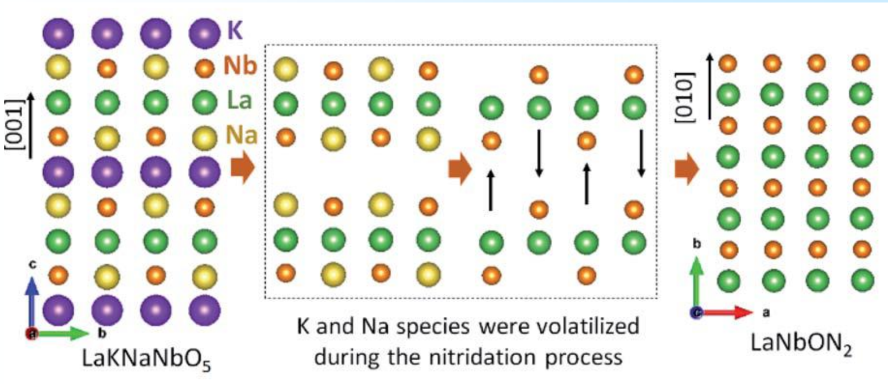
Very low activity of H_2 evolution

But band gap is suitable for overall water splitting under visible light

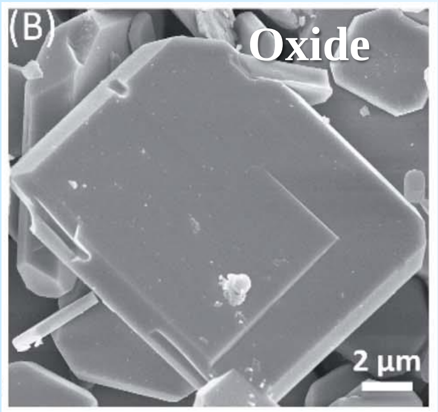
Different Nb-based materials ?

$LaNbON_2$ prepared fromlayered $LaKNaNbO_5$

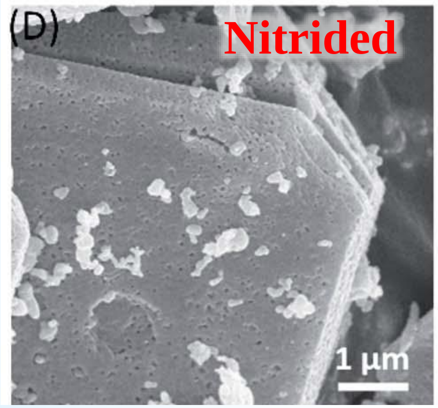
Side view



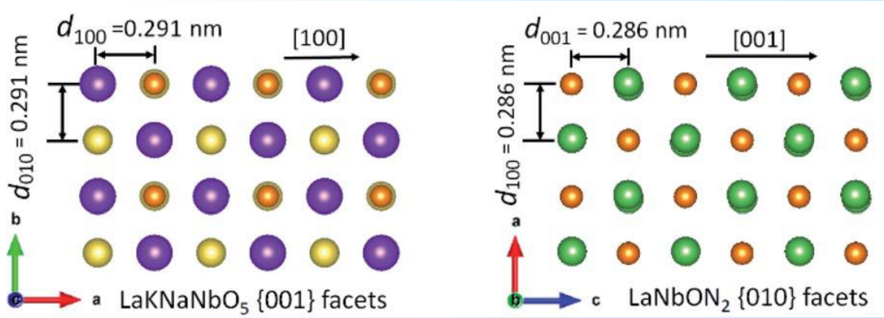
Oxide



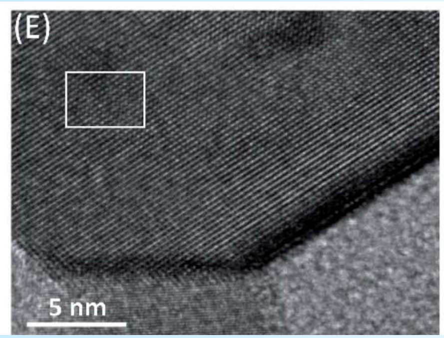
Nitrided



Top view



Nitrided



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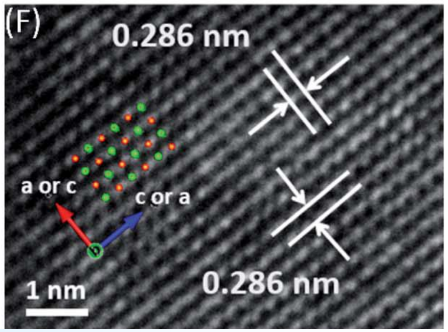

Matching of the cation arrangements

Oriented $LaNbON_2$ crystallites formed

J. Mater. Chem. A; 2020, 8, 11743.

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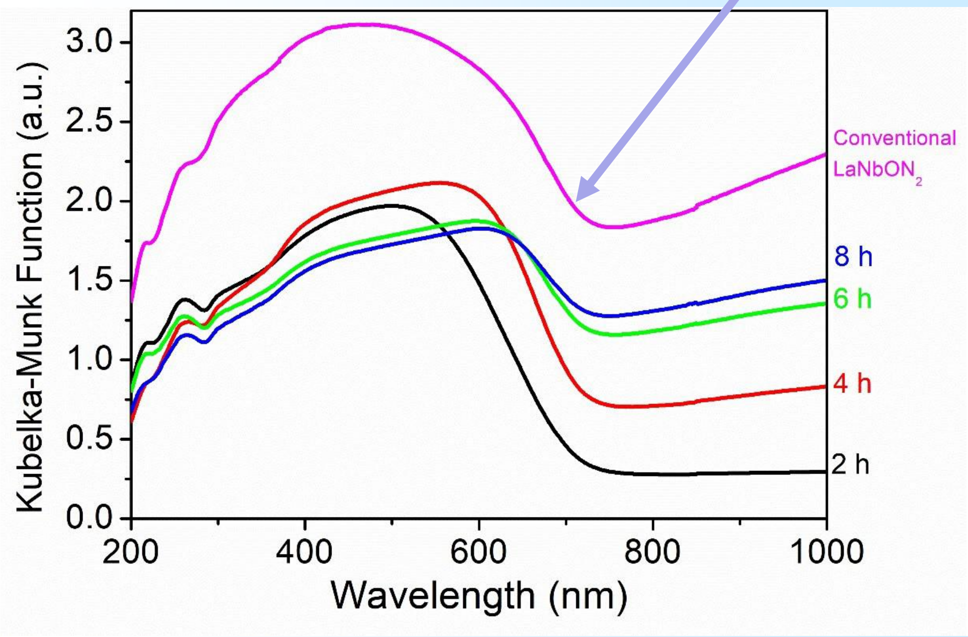
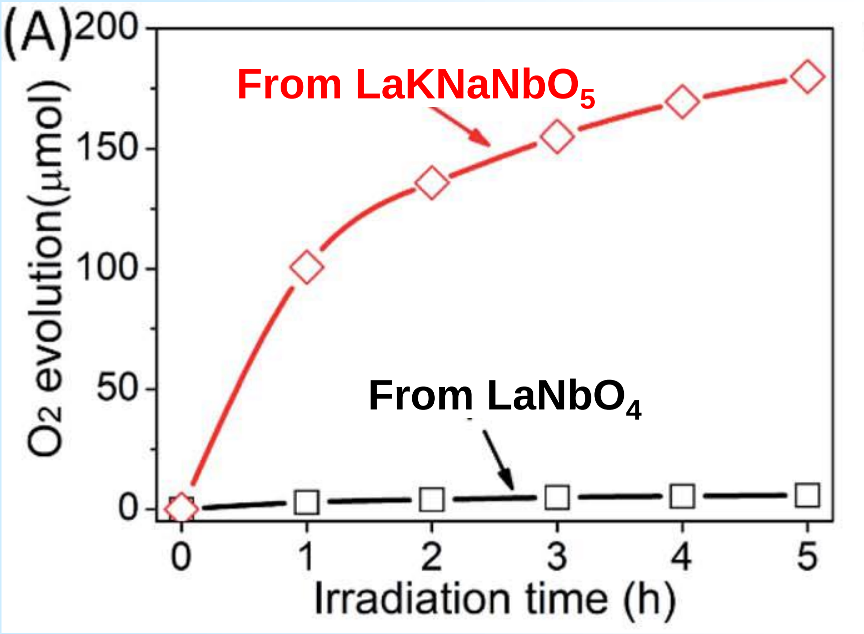
$LaNbON_2$ prepared from layered $LaKNaNbO_5$

$LaNbO_4$ is usual precursor.



AgNO$_3$ aq, λ > 420 nm



Weaker background absorption

Higher O_2 evolution activity (AQY = 0.85%, 420 nm)

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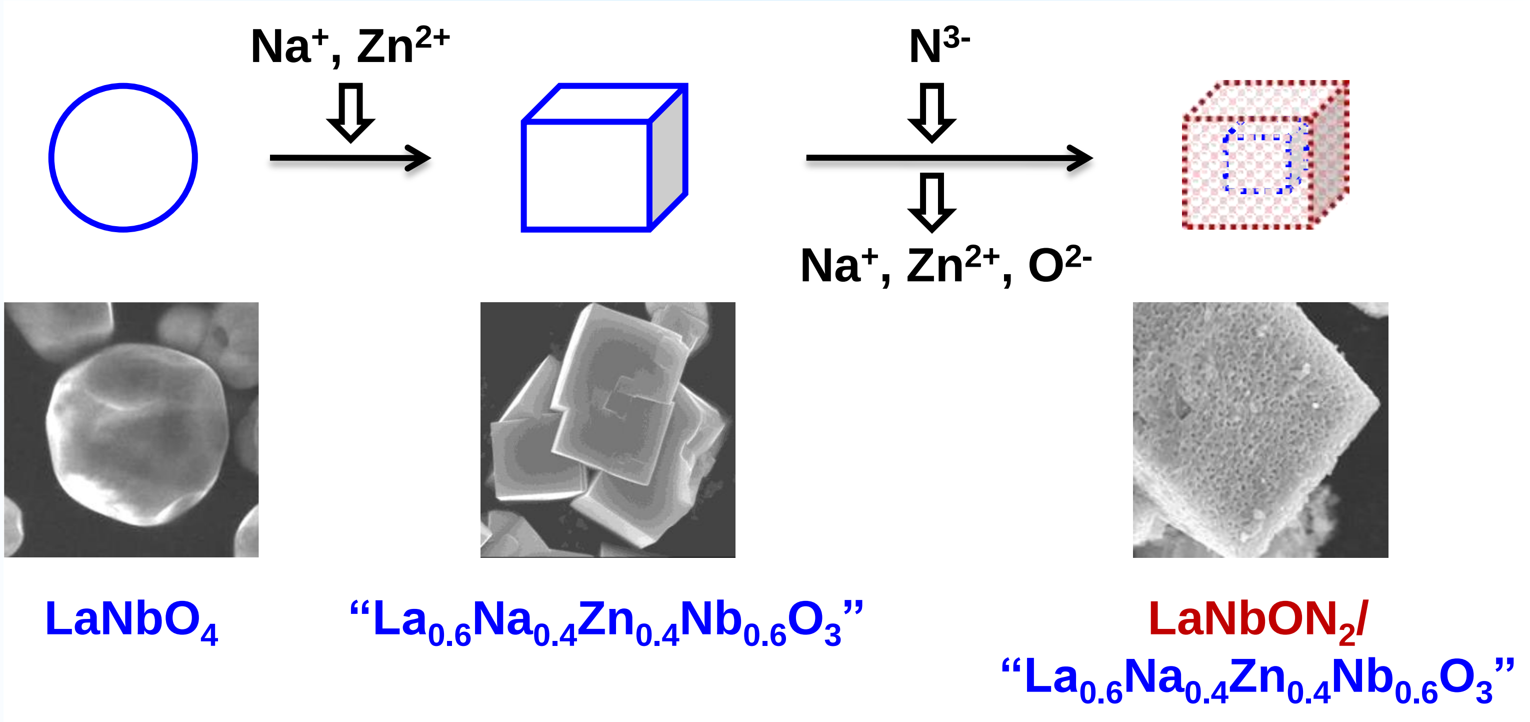
$LaNbON_2$ prepared from perovskite-type "$La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$"



Catalysis; 2021, *11*, 566.

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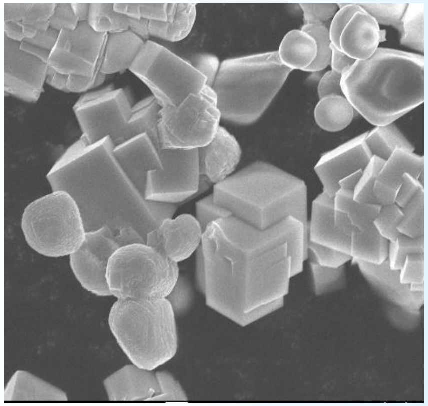
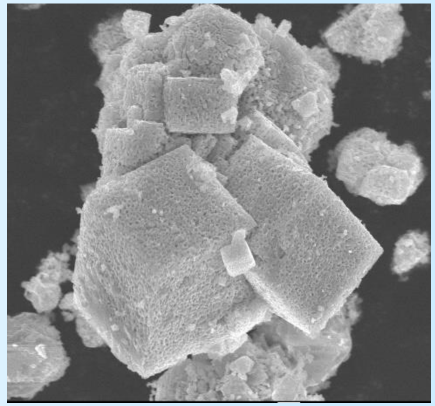
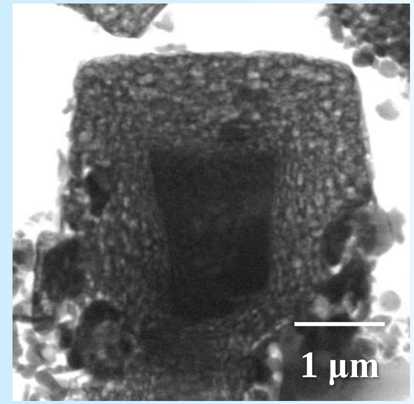
$LaNbON_2$ prepared from "$La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$" & $LaNbO_4$

"$La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$"

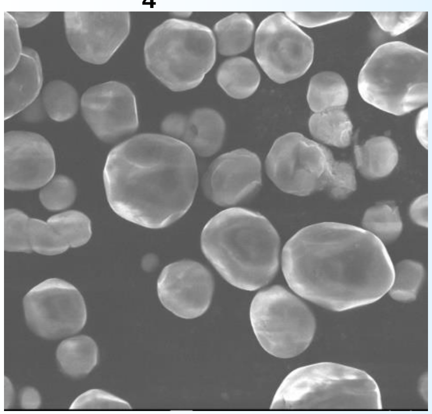


Nitridation product

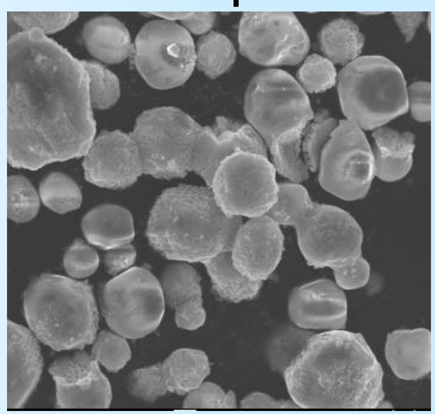




$LaNbO_4$

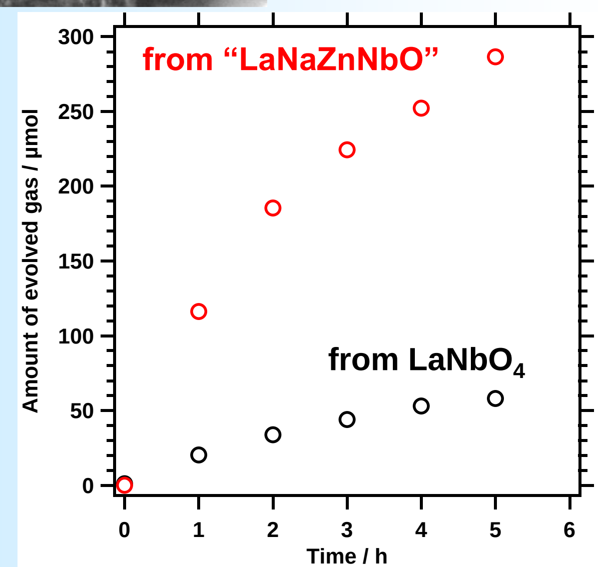


Nitridation product



2 µm

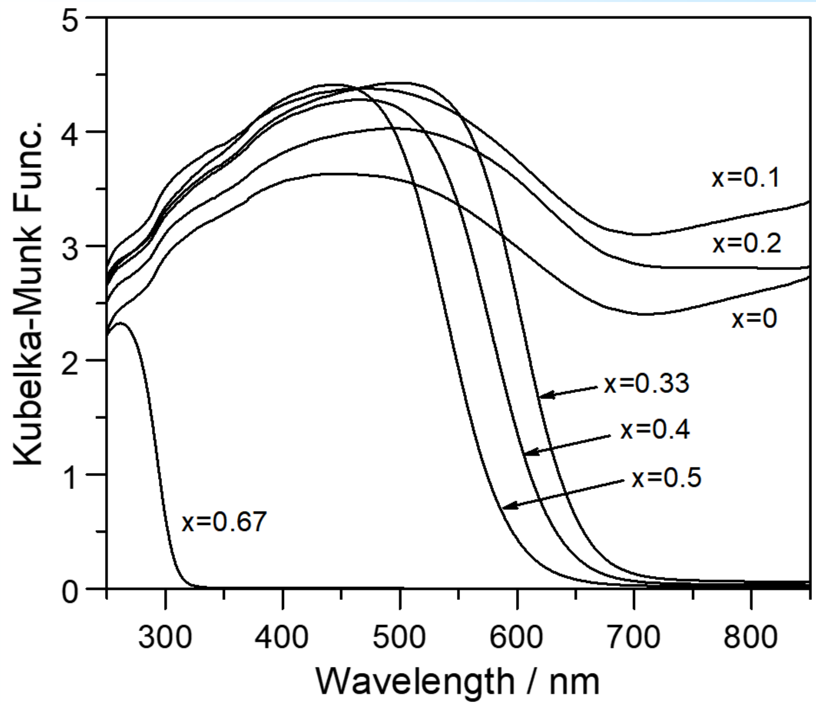
$AgNO_3$ aq
λ > 420 nm

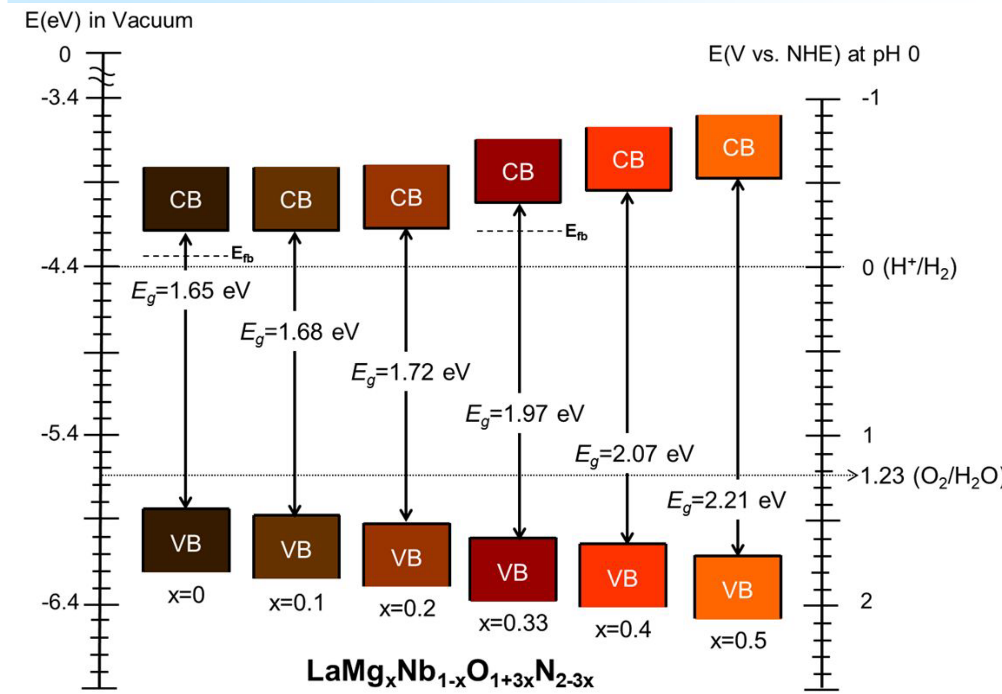


O_2 evolution activity for $LaNbON_2$
AQY: 1.7% (420 nm)

Effect of Mg-doping on $LaMg_xNb_{1-x}O_{1+3x}N_{2-3x}$

Challenge for overall water splitting”





Increase of Mg-doping causes increase of bandgap energy.

J. Mater. Chem. A. 2021, *9*, 8655.

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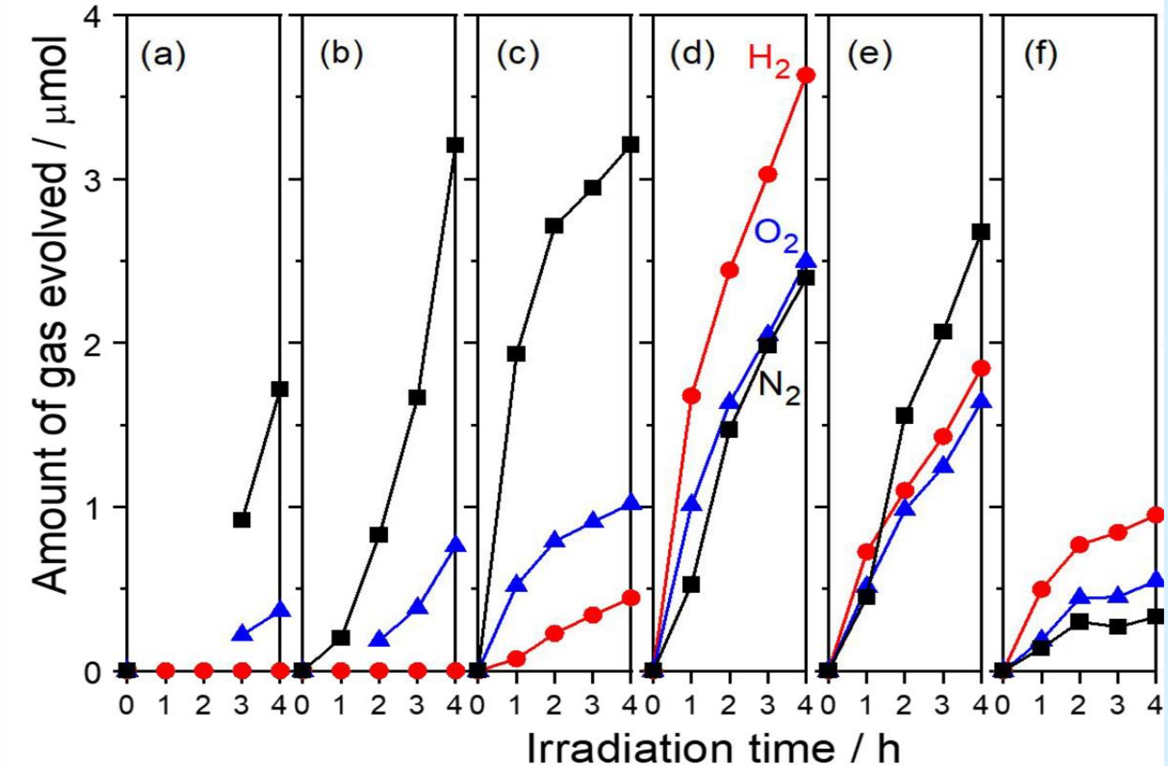
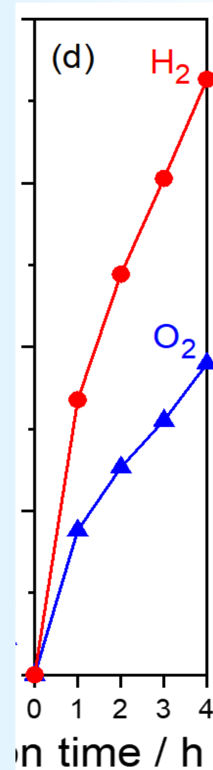
Water splitting on $LaMg_xNb_{1-x}O_{1+3x}N_{2-3x}$ *(x=0-0.5)*

→ Mg-rich

x = 0 *x* = 0.1 *x* = 0,2 *x* = 0.33 *x* = 0.4 *x* = 0.5



x = 0.33



Air subtracted

λ≤680 nm

$RhCrO_y$-CoO_z/$LaMg_xNb_{1-x}O_{1+3x}N_{2-3x}$,
pure water, Xe lamp (*λ* > 380 nm)

The first example of overall water splitting on Nb-based photocatalyst.

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Summary

- Niobium-based photocatalysts are attractive candidates for solar hydrogen production from water.
- Absorption edge of $BaNbO_2N$ extended up to 760 nm (1.6 eV), which is almost theoretical limit of overall water splitting.
- Preparation procedure of $LaNbON_2$ significantly affects O_2 and H_2 evolution activity.
- Mg-doping to $LaNbON_2$ ($LaMg_{1/3}Nb_{2/3}O_2N$) has achieved overall water splitting, which is the first example using Nb-based photocatalysts of ～700 nm absorption edge.

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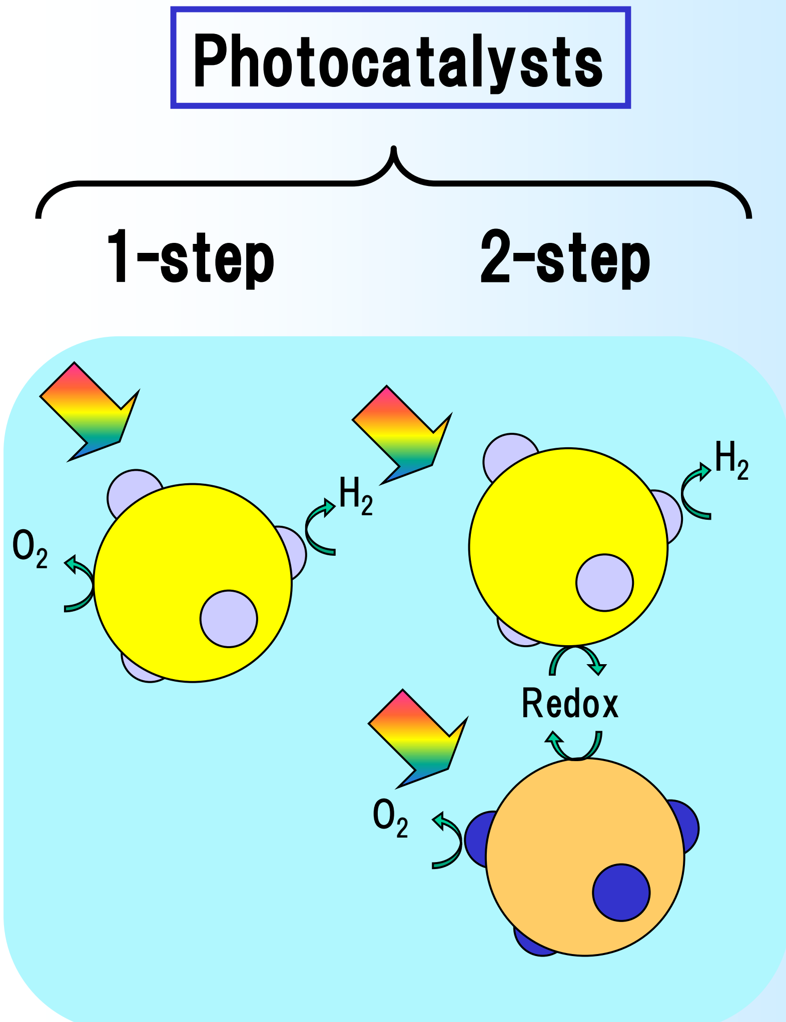
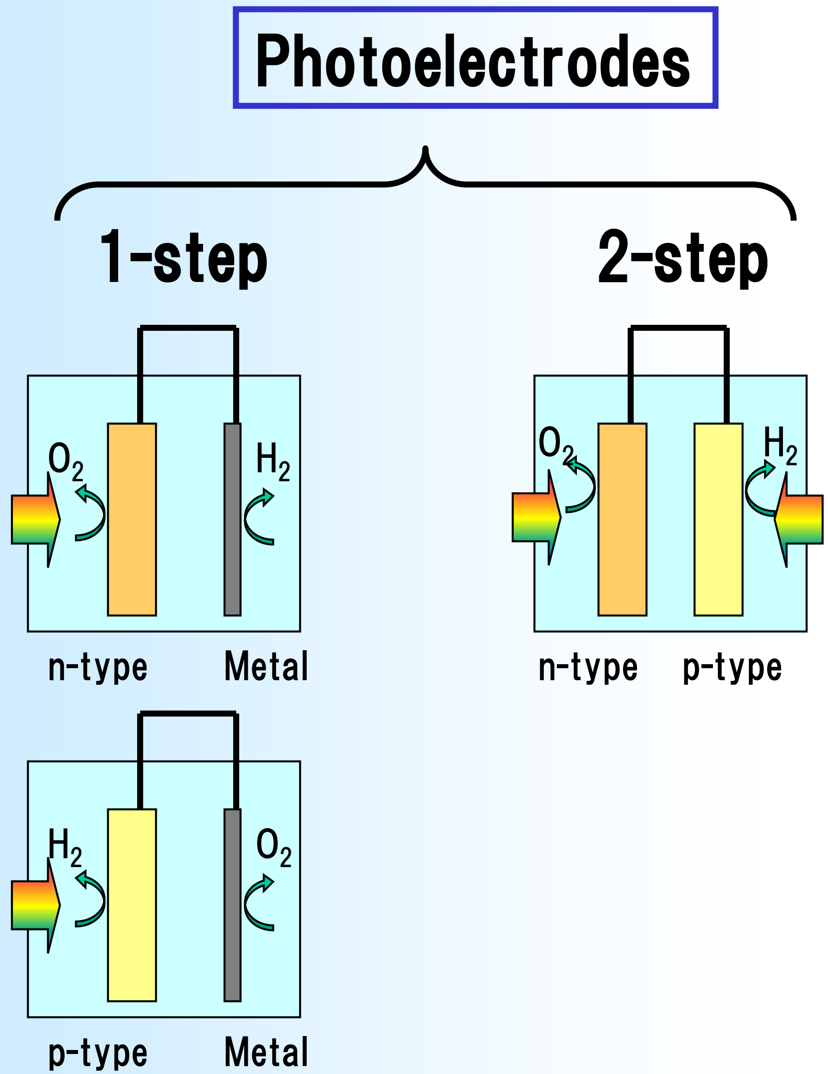
Photocatalytic & Photoelectrochemical water splitting





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