

# 可視光応答性光触媒RhドーパドSrTiO<sub>3</sub>の電子状態: 軟X線吸収・発光分光による研究

東大物性研  
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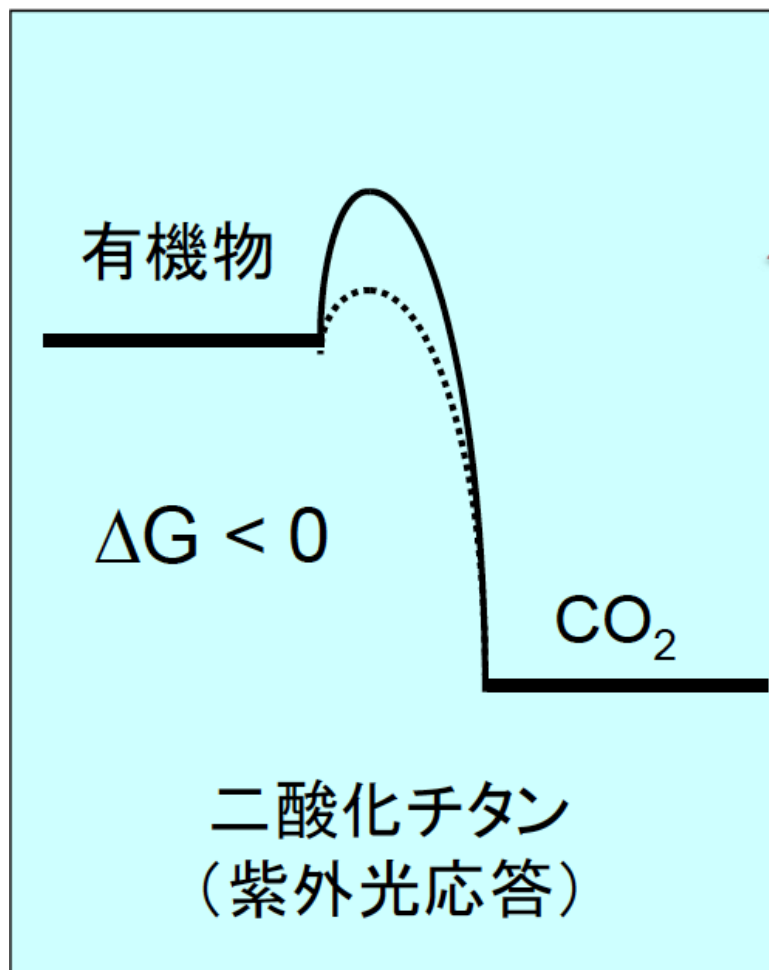
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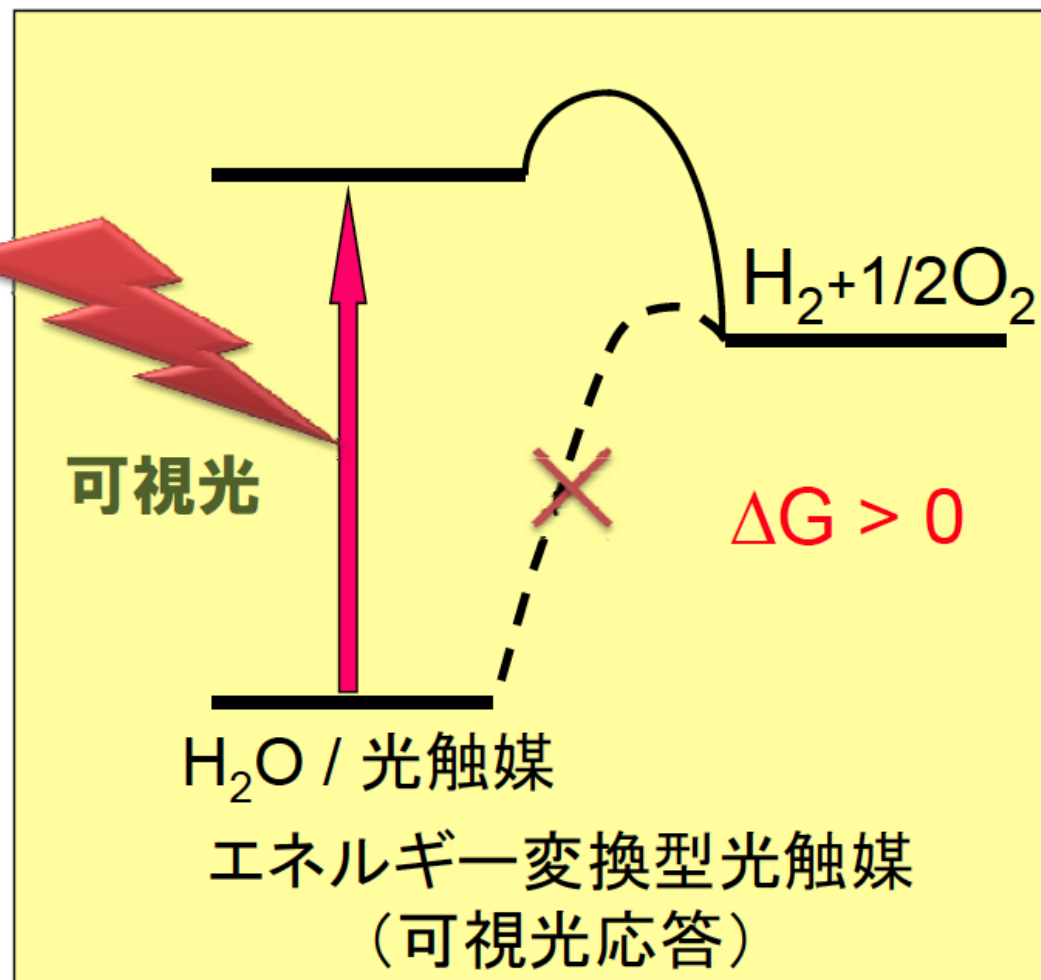
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東北大WPI  
赤木和人

# 環境浄化型光触媒とエネルギー変換型光触媒



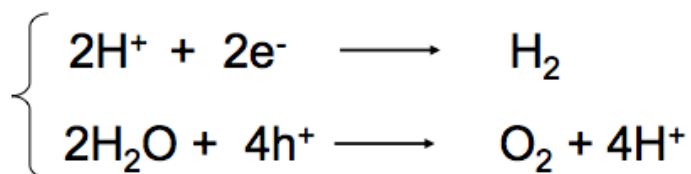
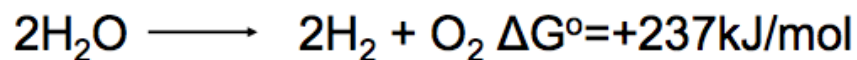
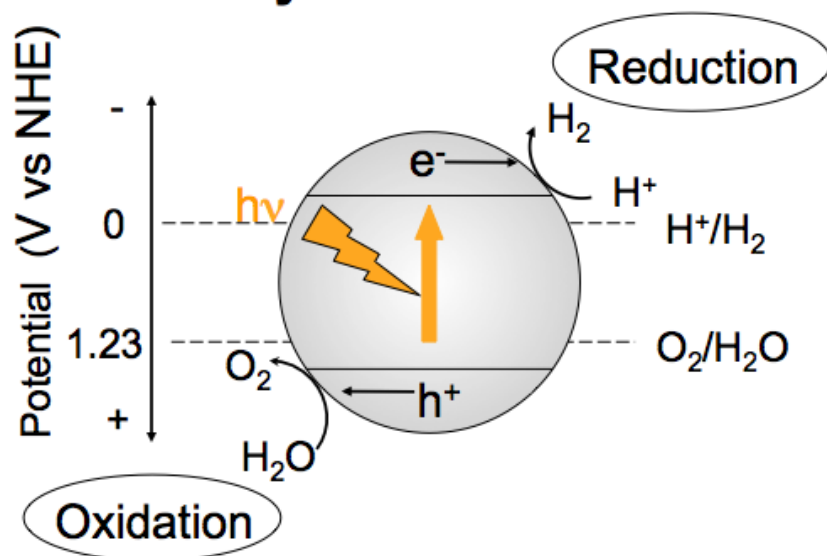
有機物の光分解



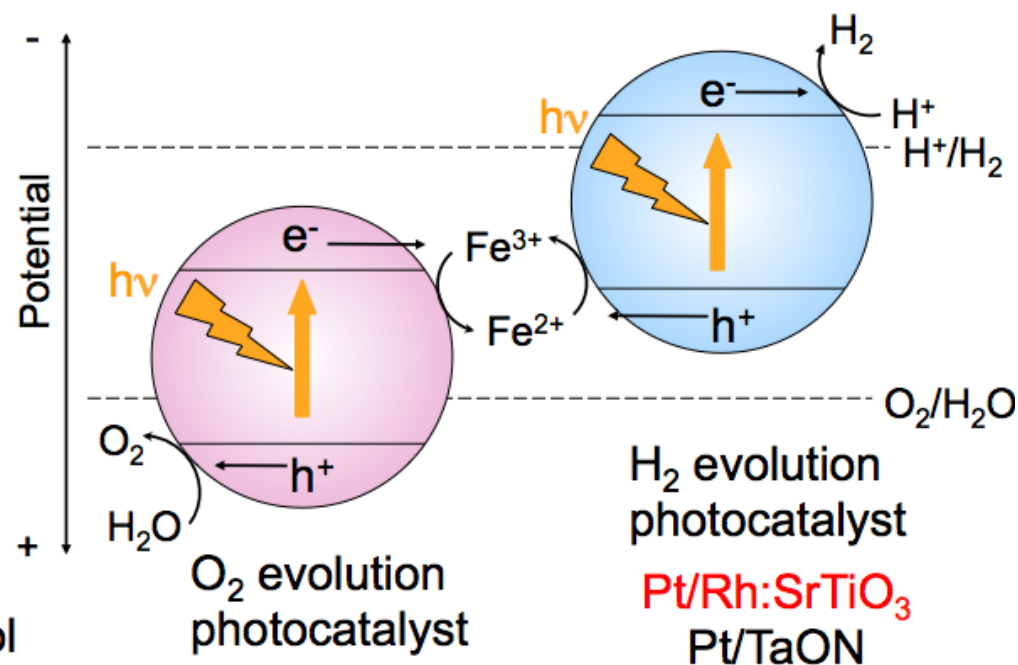
光エネルギーの  
化学エネルギーへの変換

# 可視光応答水分解光触媒

## Photocatalyst



## Z-scheme system (two-photon process)

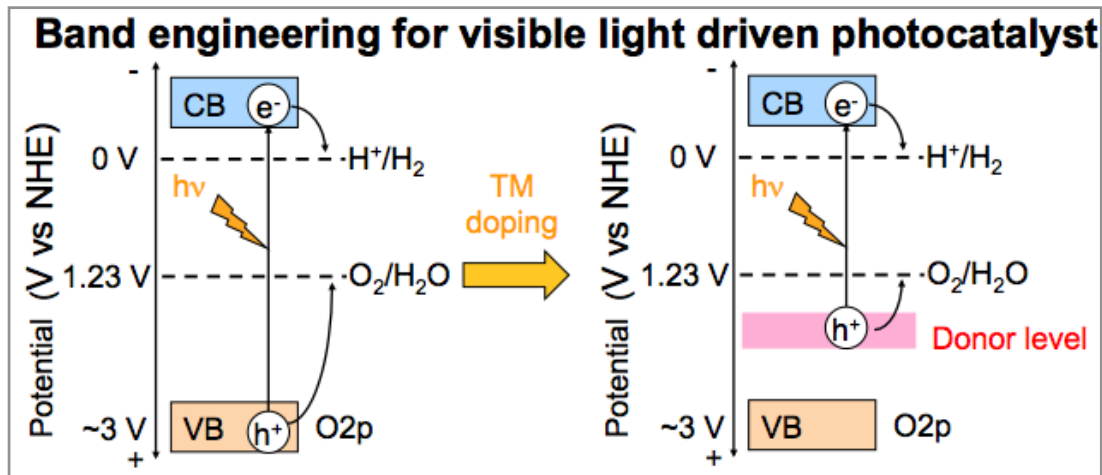


$\text{BiVO}_4$   
 $\text{WO}_3$   
 $\text{Bi}_2\text{MoO}_6$

$\text{Pt/Rh:SrTiO}_3$   
 $\text{Pt/TaON}$

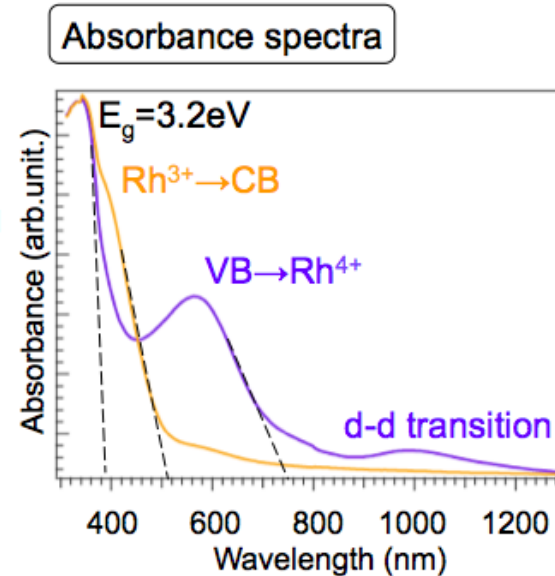
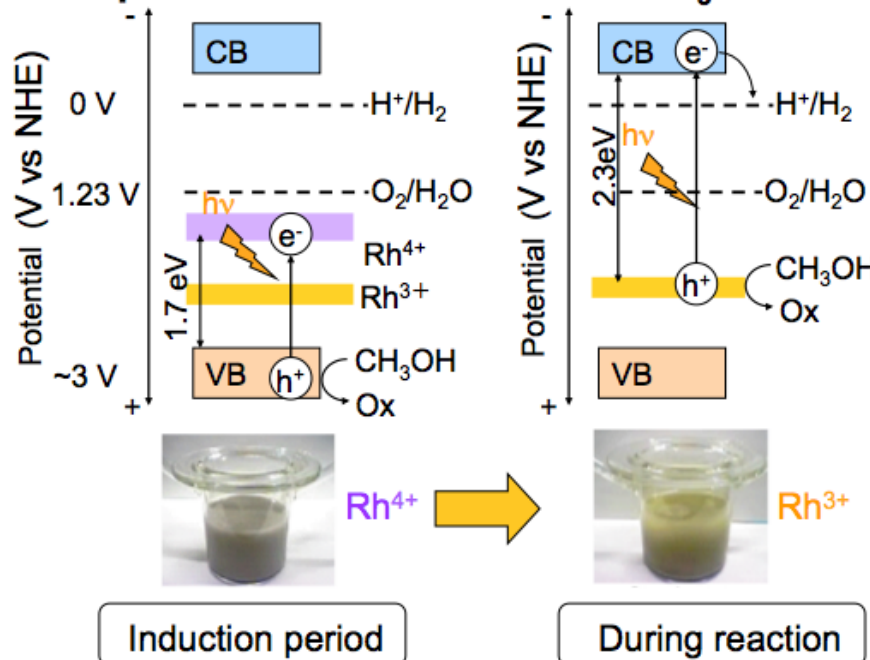
A.Kudo and Y.Miseki, *Chem. Soc. Rev.* **38**, 253 (2009).

# 可視光応答への戦略：遷移金属ドーピング

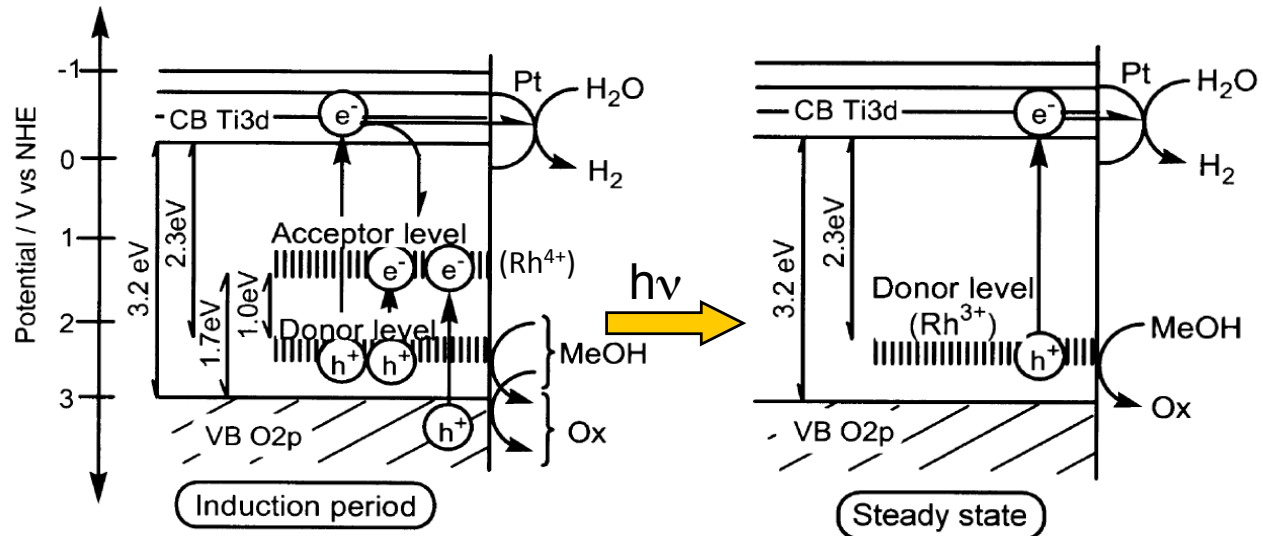


$\text{SrTiO}_3$      $\text{Rh:SrTiO}_3$   
 $E_g=3.2\text{eV}$      $E_g=2.3\text{eV}$   
                           $Q.Y.=5.2\%$   
                          at 420nm

## Unique characteristic of Rh:SrTiO<sub>3</sub>

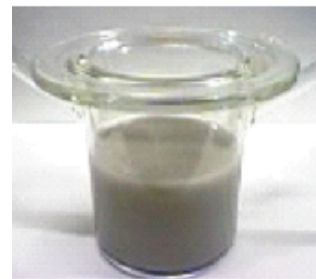
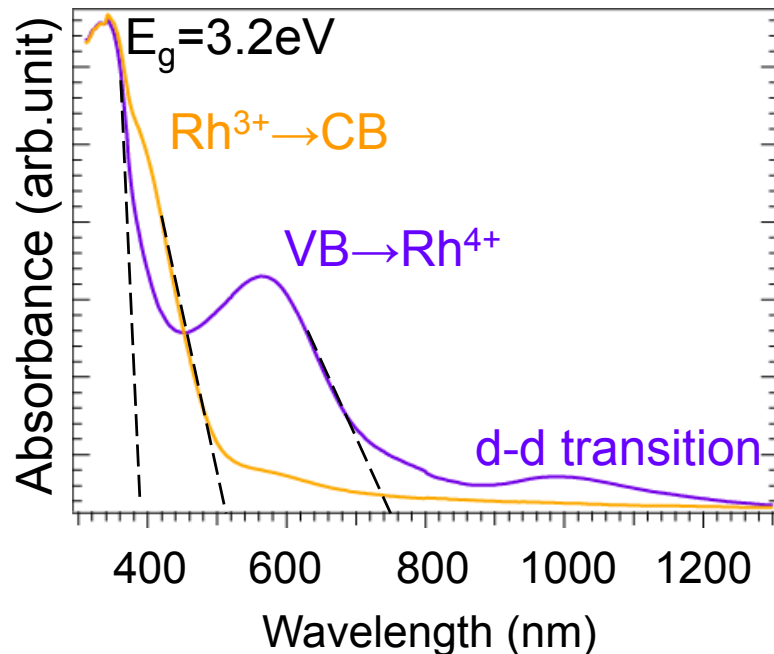


# Previous study on Rh:SrTiO<sub>3</sub> photocatalyst

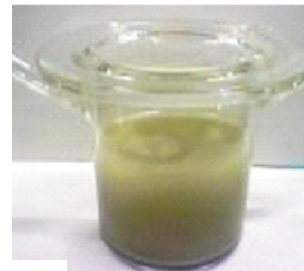


Rh valence: an important factor

Absorbance spectra



Rh<sup>4+</sup>  
dominant



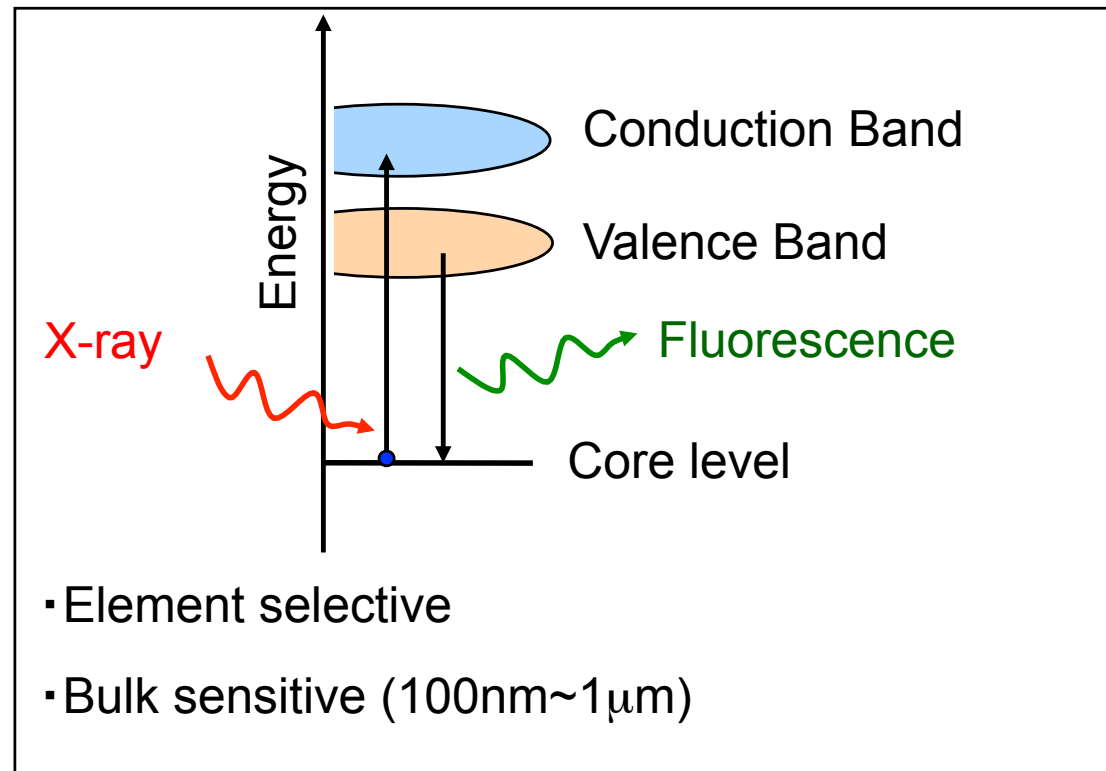
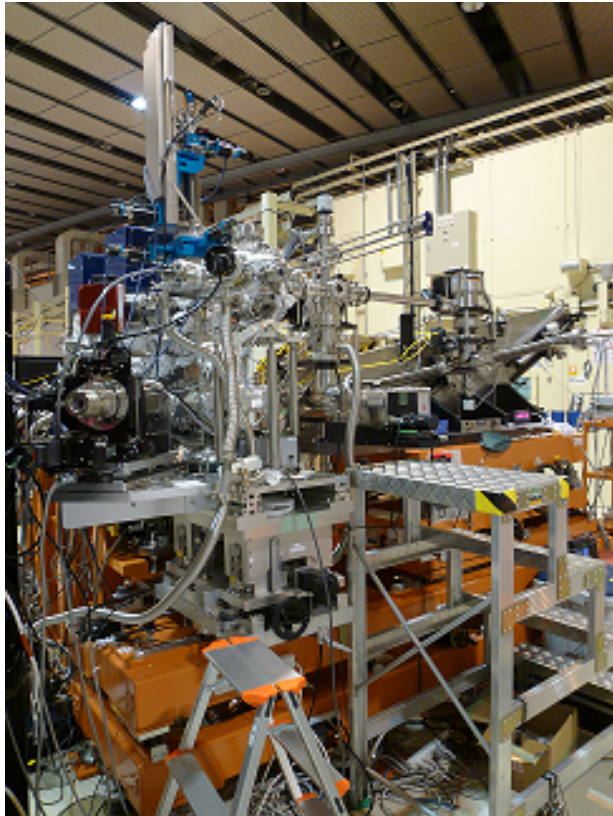
Rh<sup>3+</sup>  
dominant  
active

However, the detailed electronic state has not been known yet.

R.Konta, T.Ishii, H.Kato, and A.Kudo, *J. Phys. Chem. B* **108**, 8992 (2004)

# XAS & XES experiments @ SPring-8

BL07LSU@SPring-8



High Resolution XAS & XES

BL07LSU of SPring-8.  $E/\Delta E \doteq 3600$ .

# Samples for XAS & XES @ SPring-8

## Sample (Sintered pellet)

$\text{Rh}^{4+}:\text{SrTiO}_3$



Rh5%



Rh3%



Rh1%

$\text{Rh}^{3+}:\text{SrTiO}_3$



Rh5%

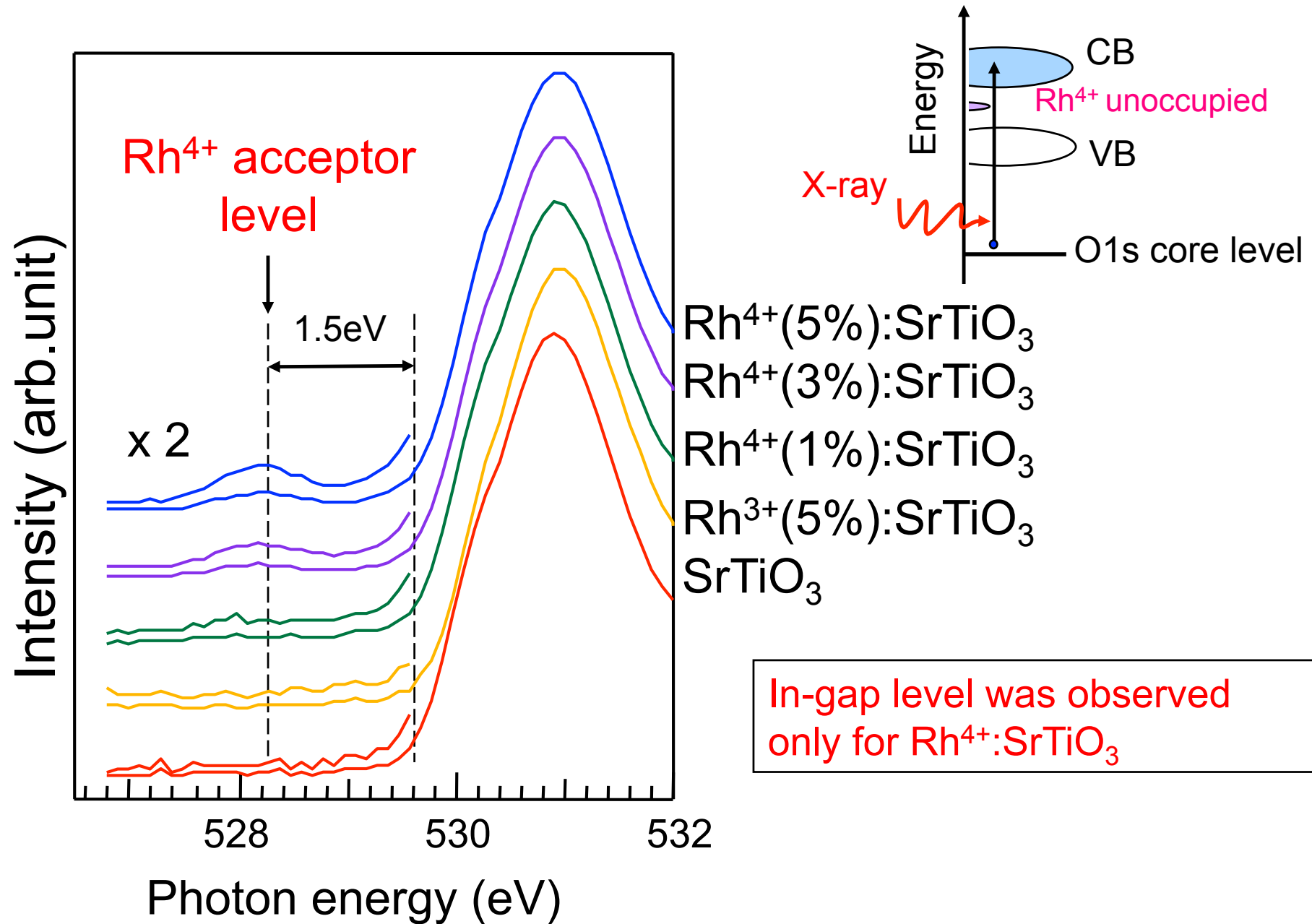
$\text{SrTiO}_3$



Non-doped

Annealed in  $\text{H}_2$   
@300°C, 2h

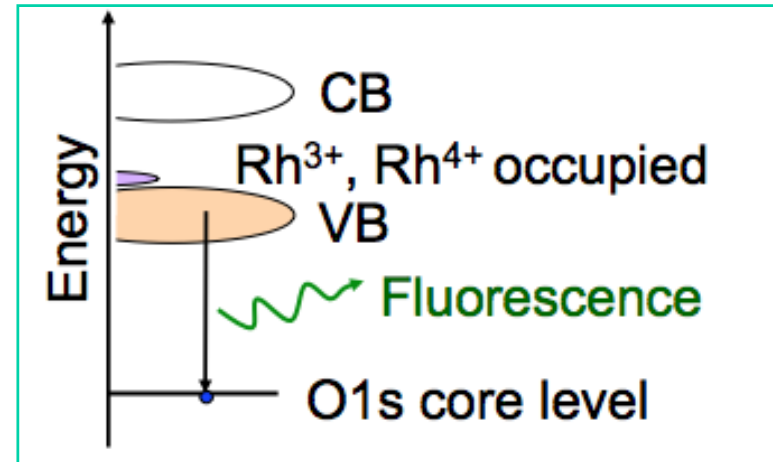
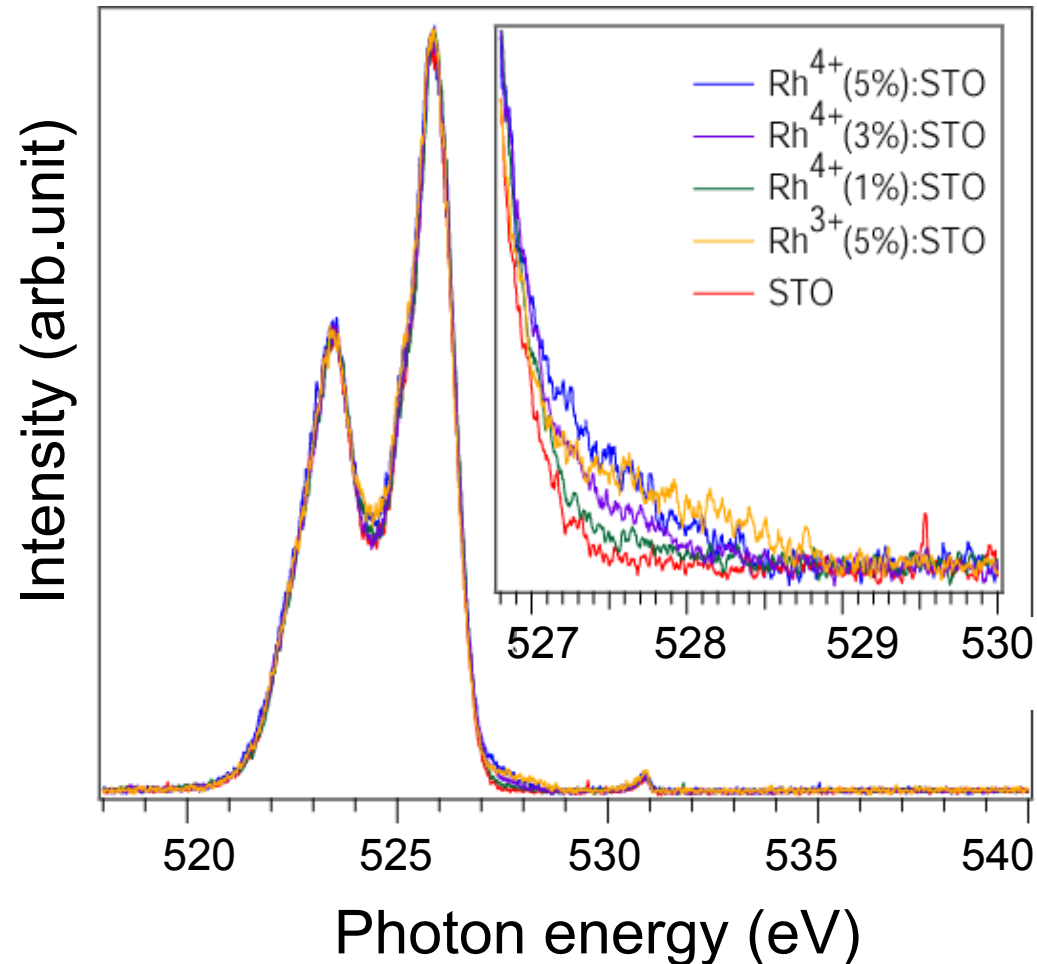
# O 1s XAS @ SPring-8 BL07LSU





# O 1s XES @ SPring-8 BL07LSU

O 1s XES  $h\nu = 530.9$  eV



1. Rh-induced states were observed just above the valence band top of SrTiO<sub>3</sub>.
2. In the case of the Rh<sup>3+</sup> STO sample, the induced state is observed at ~528 eV, which is slightly above that of Rh<sup>4+</sup>.

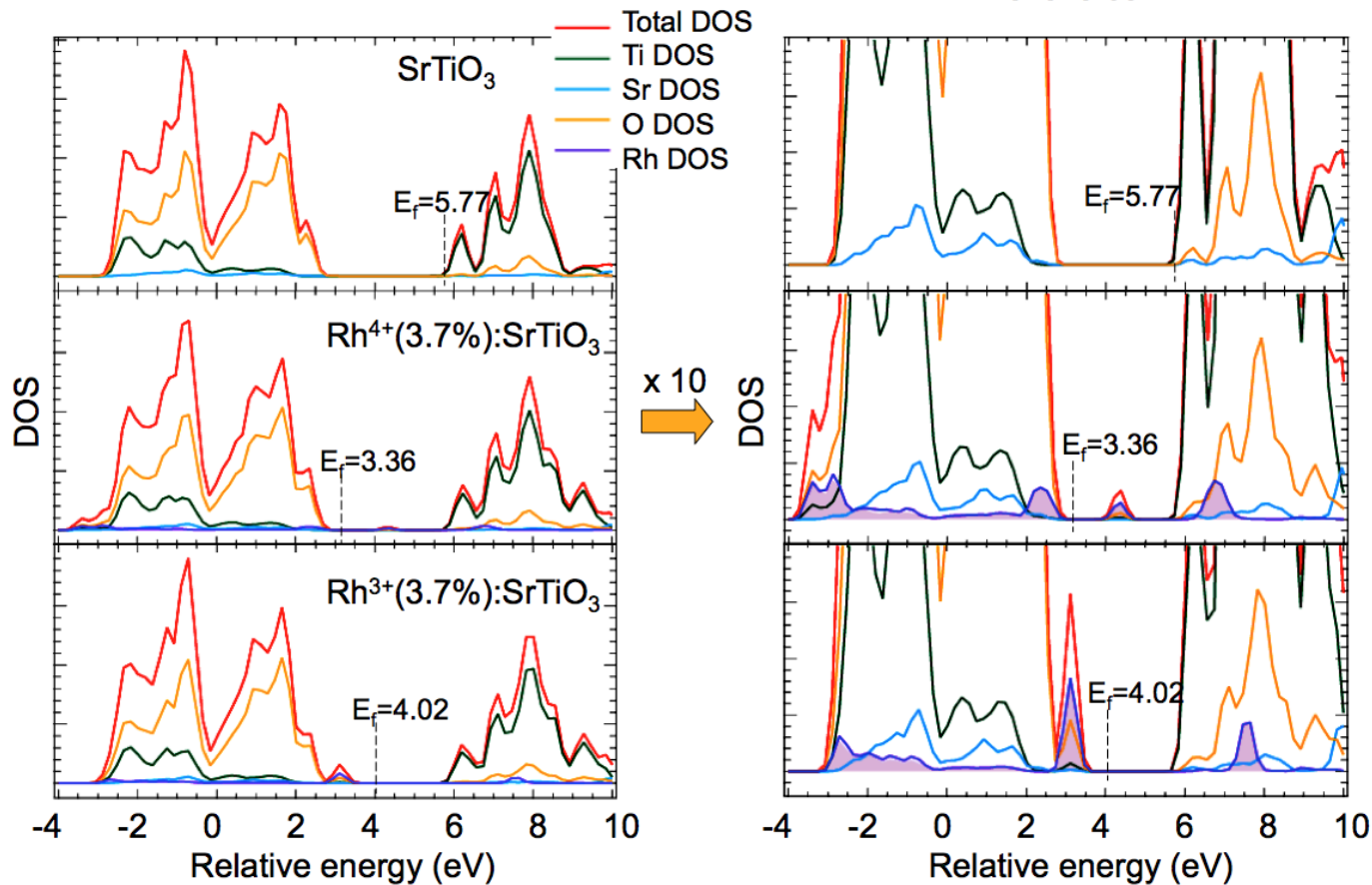
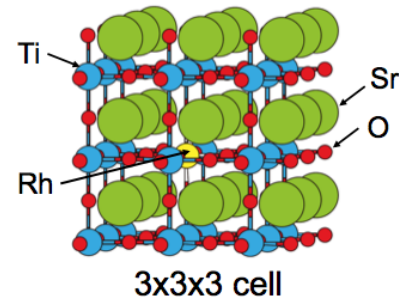
# First principles calculations by Prof. Akagi

## First-principles calculation

Density of states (DOS) calculated VASP using HSE functional for  $3 \times 3 \times 3$   $\text{SrTiO}_3$

For  $\text{Rh}^{4+}:\text{SrTiO}_3$ , a Rh atom was substituted at a Ti site

For  $\text{Rh}^{3+}:\text{SrTiO}_3$ , an additional  $e^-$  was inserted into the  $\text{Rh}^{4+}:\text{SrTiO}_3$  cell

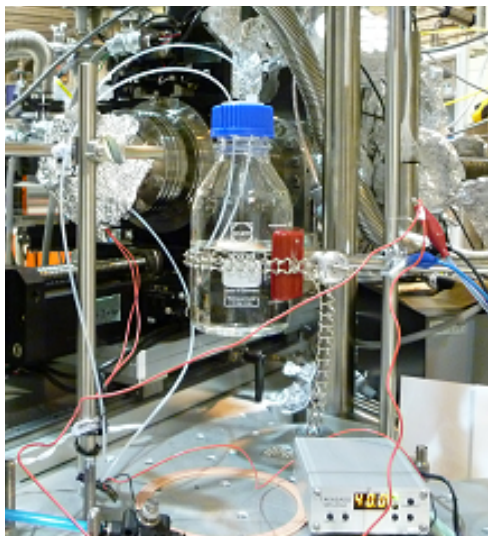


1. Positions of  $\text{Rh}^{3+}$  and  $\text{Rh}^{4+}$  in-gap levels were estimated.
2. Hybridization between  $\text{O}2p$  and  $\text{Rh}4d$  was found at the top of the valence band for both  $\text{Rh}^{4+}:\text{SrTiO}_3$  and  $\text{Rh}^{3+}:\text{SrTiO}_3$
3. The position of  $E_f$  is changed with Rh doping in  $\text{SrTiO}_3$

The calculation results are consistent with the present XAS/XES results.

# In-situ XAS/XES measurement

Pure-H<sub>2</sub>O



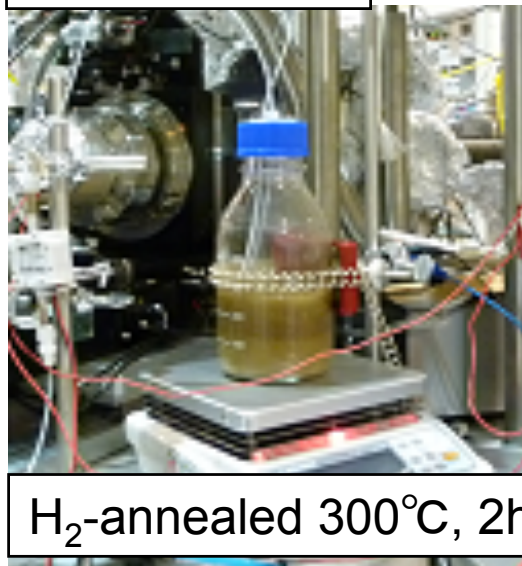
STO



Rh<sup>4+</sup>(5%):STO



Rh<sup>3+</sup>(5%):STO



H<sub>2</sub>-annealed 300°C, 2h

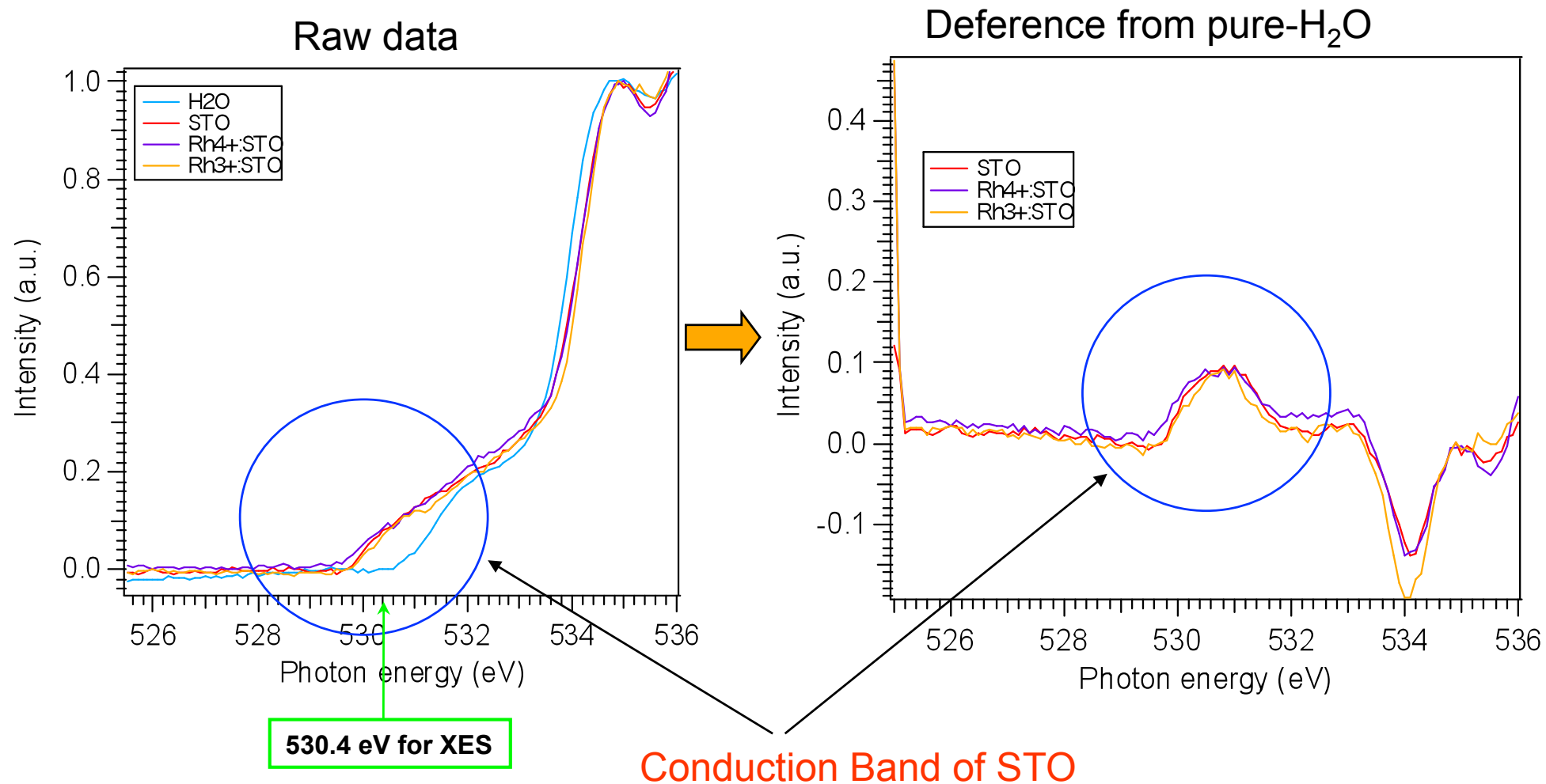
## Suspension

0.8g(powder)/300ml(H<sub>2</sub>O)  
r.t., 500rpm,  
circulation cell

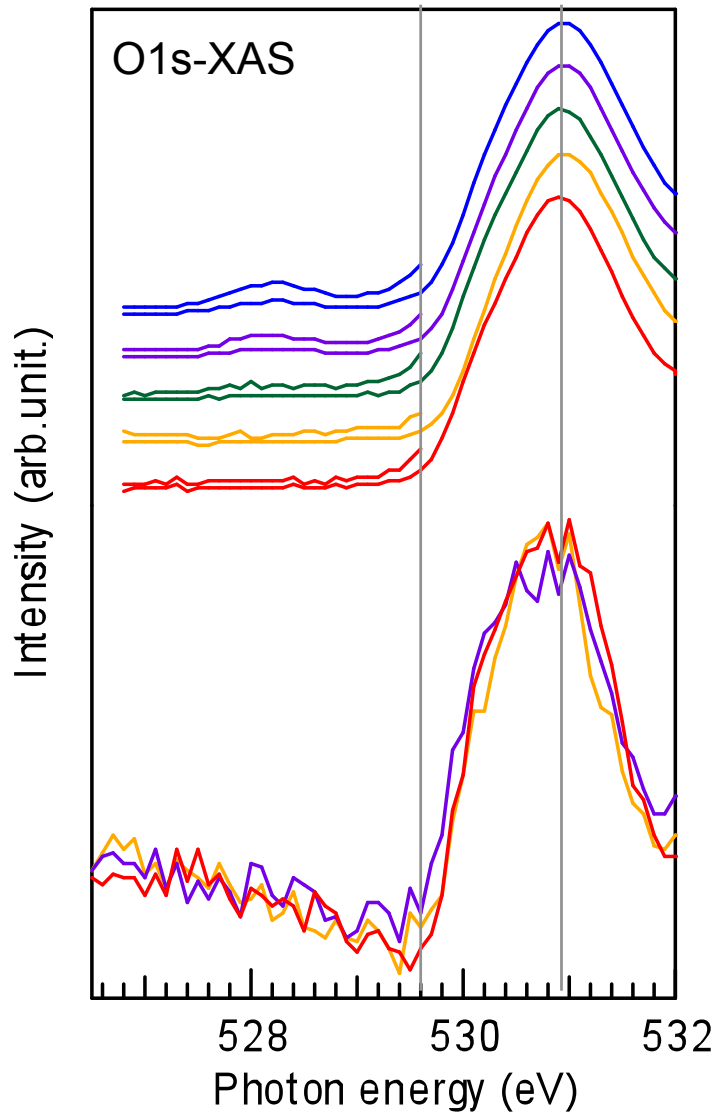
## Measurement

XAS & XES

# In-situ XAS of Rh-SrTiO<sub>3</sub> @ SPring-8: raw data



# In-situ XAS of Rh-SrTiO<sub>3</sub> @ SPring-8



Pellet

Rh<sup>4+</sup>(5%):STO

Rh<sup>4+</sup>(3%):STO

Rh<sup>4+</sup>(1%):STO

Rh<sup>3+</sup>(5%):STO

STO

Suspension

Rh<sup>4+</sup>(5%):STO

Rh<sup>3+</sup>(5%):STO

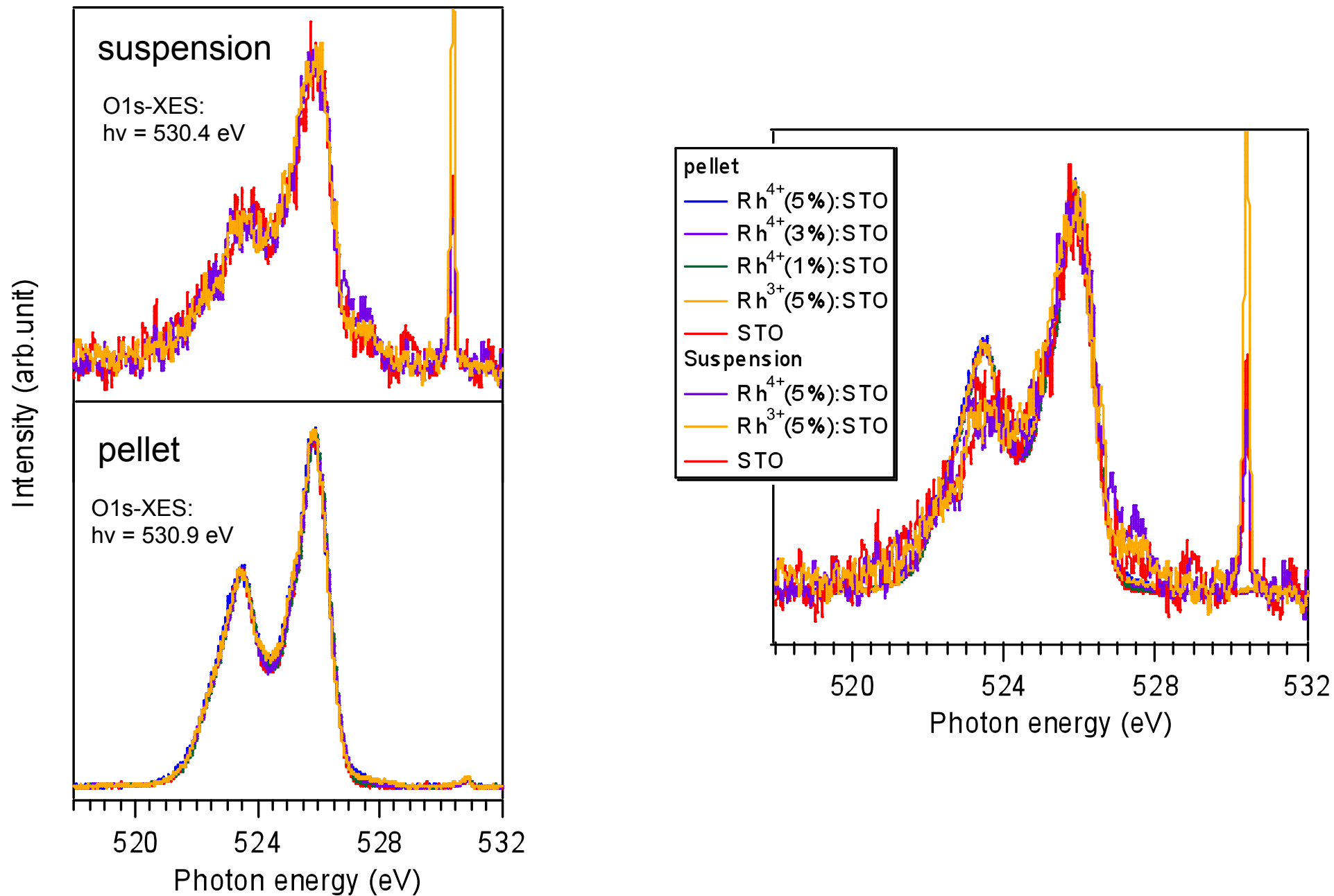
STO

懸濁液でもSTO由来の  
XASスペクトルを抽出できる

↓

ペレットと大体一致

# In-situ XES Rh-SrTiO<sub>3</sub> @ SPring-8



# Summary

- ◆ 可視光応答光触媒Rh:SrTiO<sub>3</sub>(ペレット)の電子状態をO1s-XES/XASにより測定し、Rhのドーピング量、価数状態の違いにより、SrTiO<sub>3</sub>のin-gapに存在するピークを観測した.
- ◆ 第一原理計算の結果と比較することにより、これらはRhドーピングにより誘起された状態と考え、以下のように帰属した.
  - XASで観測されたピーク: Rh<sup>4+</sup>によるアクセプター準位.
  - XESによる価電子帯上端のショルダー: O2pとRh4dの軌道の混成状態
- ◆ 水中に分散させたRh:SrTiO<sub>3</sub>(粉体)のin-situ XAS/XES測定を行った.
  - ペレットで観測されたピークとだいたい一致したが、ピーク幅や強度比などにわずかな違いが見られた.
- ◆ In-situ(水中)さらにオペランド観測(光触媒反応中)を行い、定量的議論をするためには、シグナル強度の増大や光照射のためのセル開発が必要である.