SPring-8 グリーンサスティナブル
ケミストリー研究会
平成27年12月8日（品川）

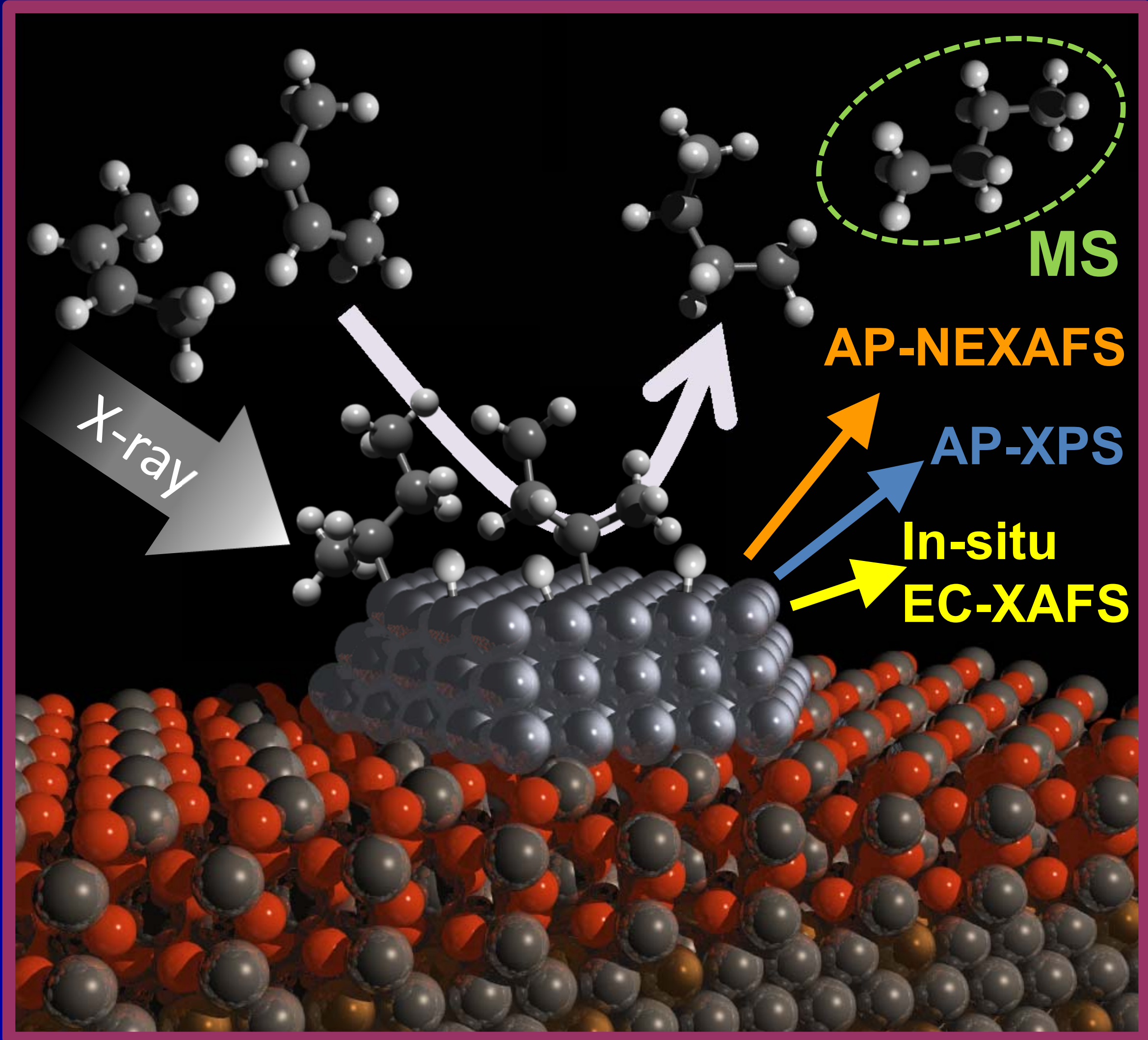
機能する触媒を観る
ー軟X線オペランド分光によるアプローチー

近藤　寛

慶應義塾大学

SPring-8 グリーンサスティナブル
ケミストリー研究会
平成27年12月8日（品川）

触媒表面で進む化学反応をX線で捉える（X線オペランド観測）



アウトライン

背景

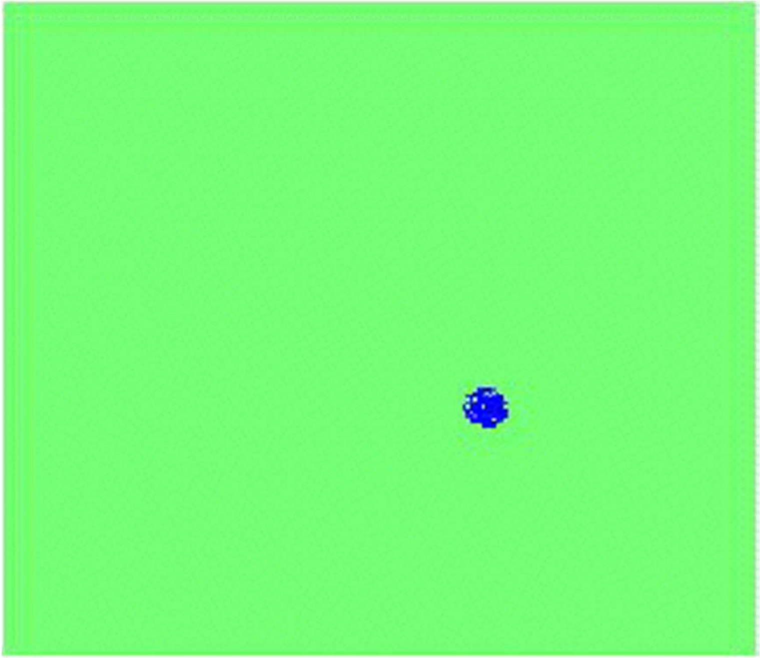
軟X線オペランド観測手法

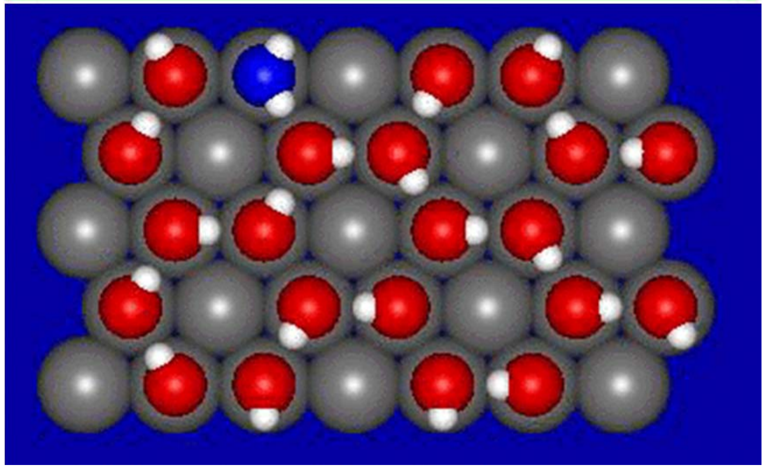
触媒が活性になったときに見えるもの

NAP-XPSによる排気ガス浄化触媒
電気化学XAFSによる水分解触媒

Catalytic Surface Reactions

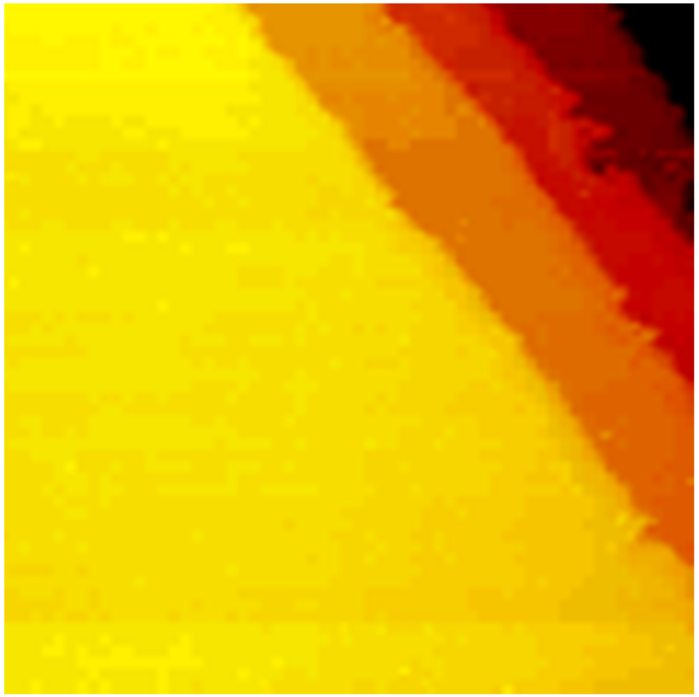
Water formation on Pt(111)





Nagasaka et al. (Univ. Tokyo)

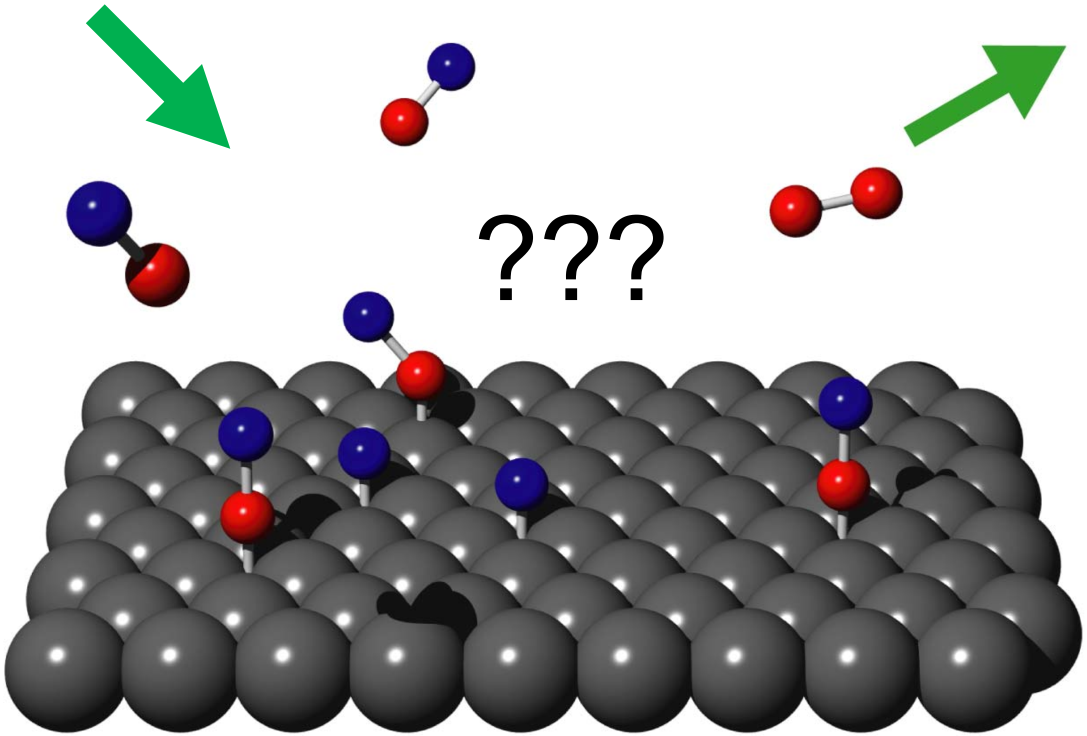
Carbonyl formation on NiAu



Besenbacher et al. (Aarhus Univ.)

attractive but not simple phenomena…..

Catalytic Surface Reaction



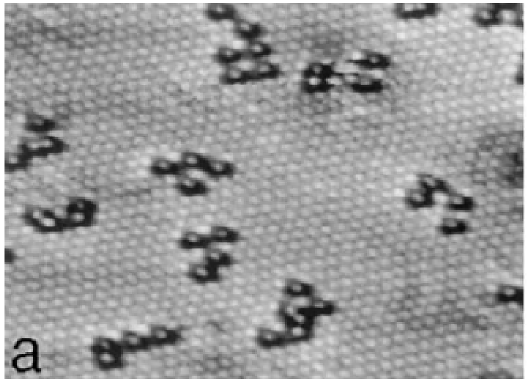
Elementary Step

- Adsorption
- Diffusion
- Reaction
- Desorption

:

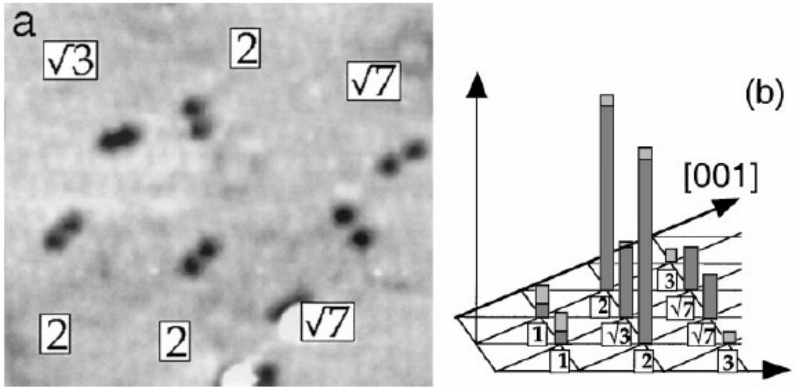
Surface science analysis of each elementary step

Adsorption



Precursor-mediated adsorption
for O_2/Pt(111)

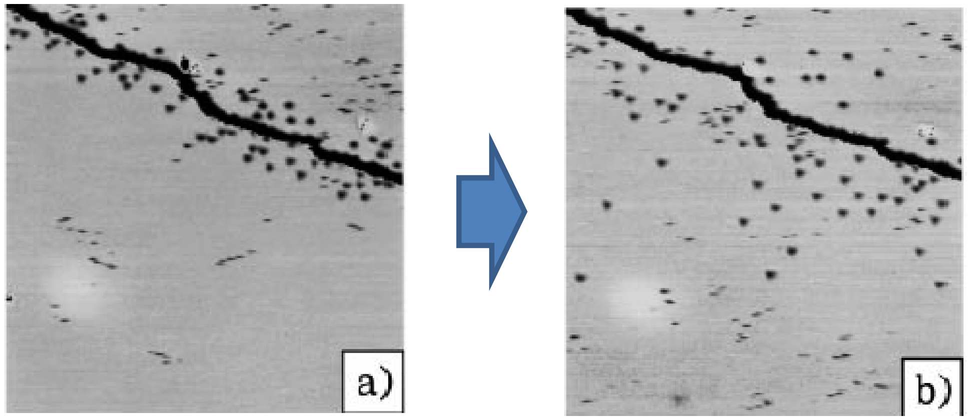
T. Zambelli et al. *Nature* **390,** 495 (1997).



Hot-atom formation on adsorption
for O_2/Pt(111)

J. Wintterlin et al. *Phys. Rev. Lett.* **77,** 123 (1996).

Surface diffusion

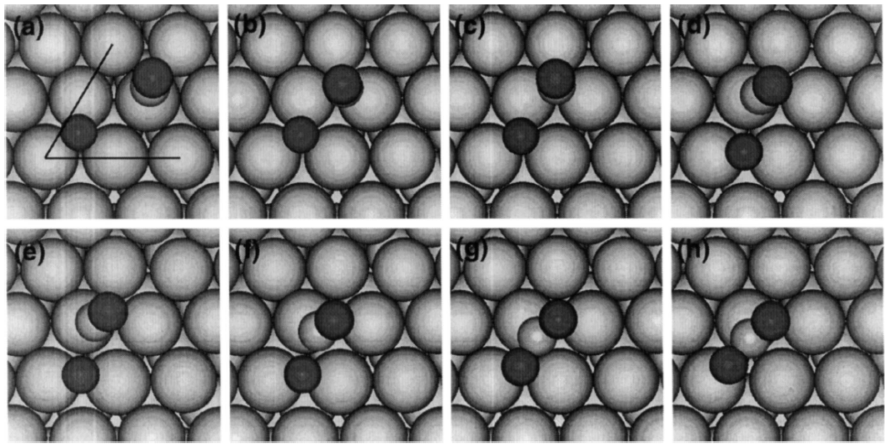


Surface diffusion of atomic N
from a step on Ru(0001)

T. Zambelli et al.
Phys. Rev. Lett. **76,** 795 (1996).

Surface science analysis of each elementary step

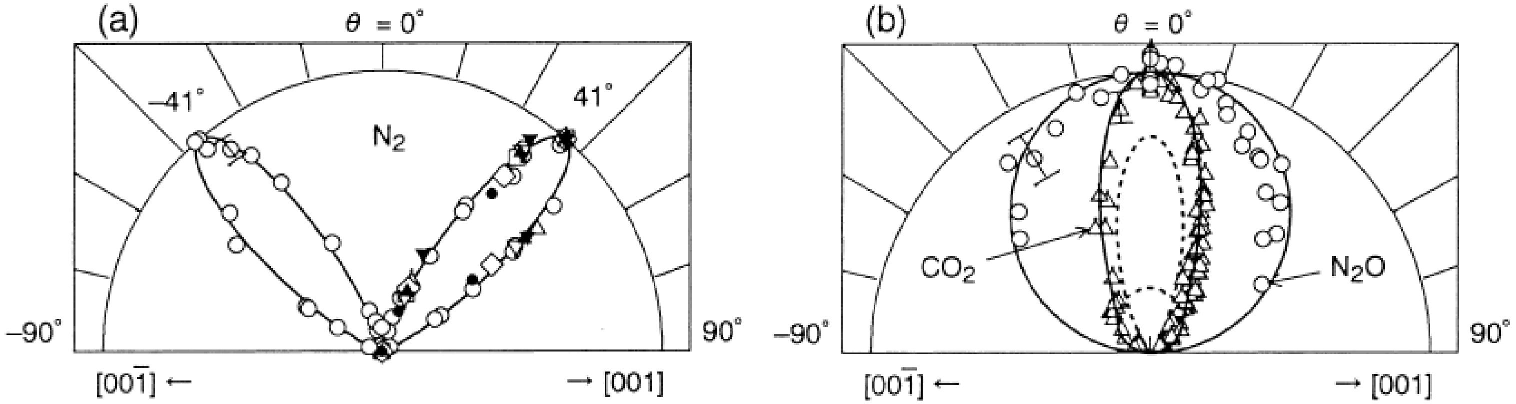
Reaction



Reaction pathway of CO oxidation on Pt(111) deduced from DFT calculations

A. Alavi et al.
Phys. Rev. Lett. **80,** 3650 (1998).

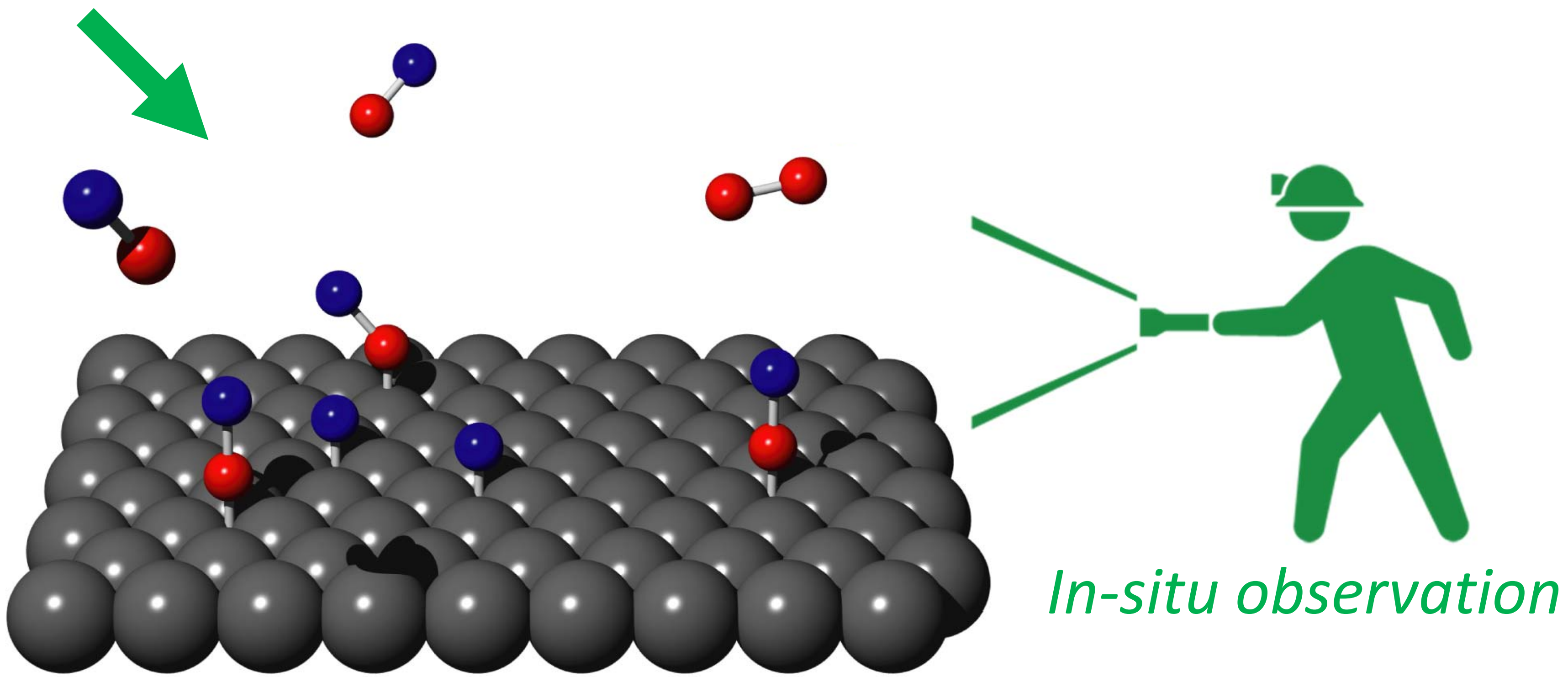
Desorption



Angular distribution of desorption species via CO+NO reaction on Pd(110)

T. Matsushima, *Surf. Sci. Rep.* **22**, 127 (1995).

Catalytic Surface Reaction



Elementary Step
- Adsorption
- Diffusion
- Reaction
- Desorption
- :

mutually correlating

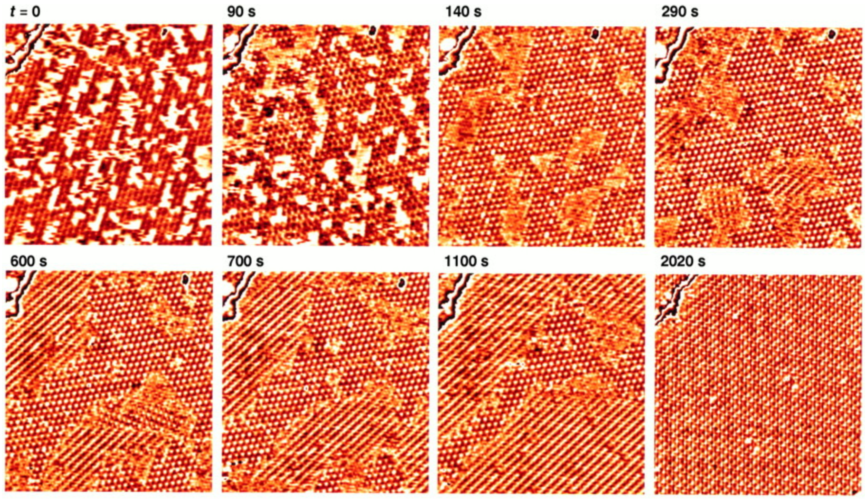
In-situ observation with microscopy

PEEM

Spatiotemporal evolution of chemical waves of CO oxidation on Pt(110)

S. Nettesheim, A. von Oertzen, H. H. Rotermund and G. Ertl, *J. Chem. Phys.* **98,** 9977 (1993).

STM

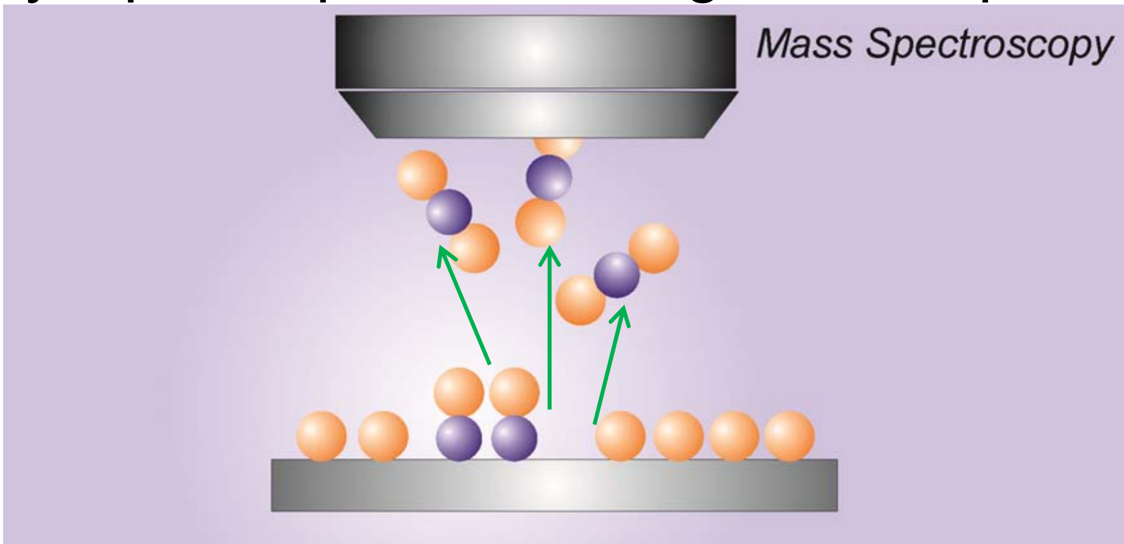


Site specific reaction of CO oxidation on Pt(111)

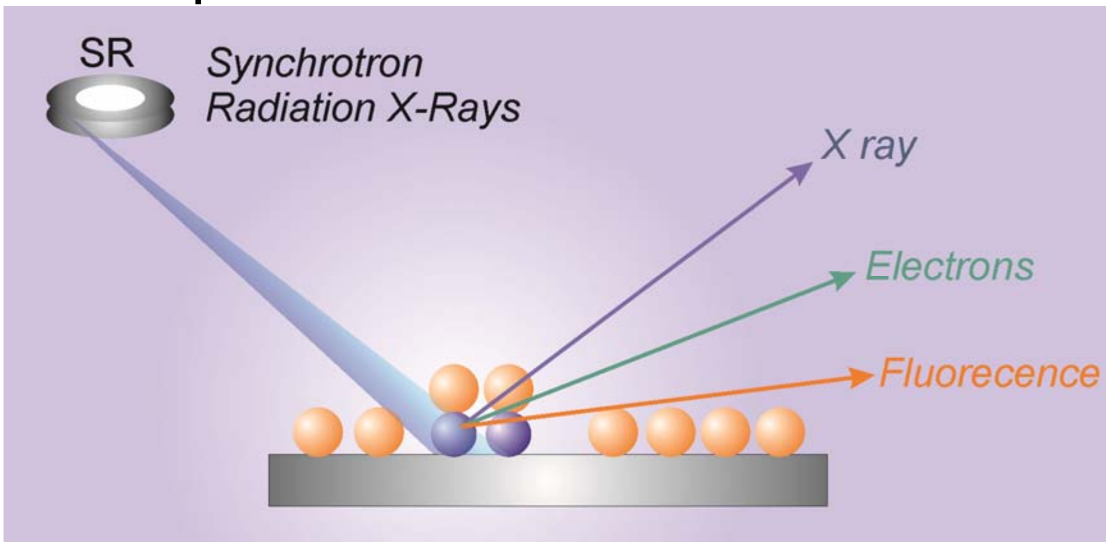
J. Wintterlin, S. Völkening, T. V. W. Janssens, T. Zmbelli and G. Ertl, *Science* **278,** 1931 (1997).

In-situ observation with spectroscopy

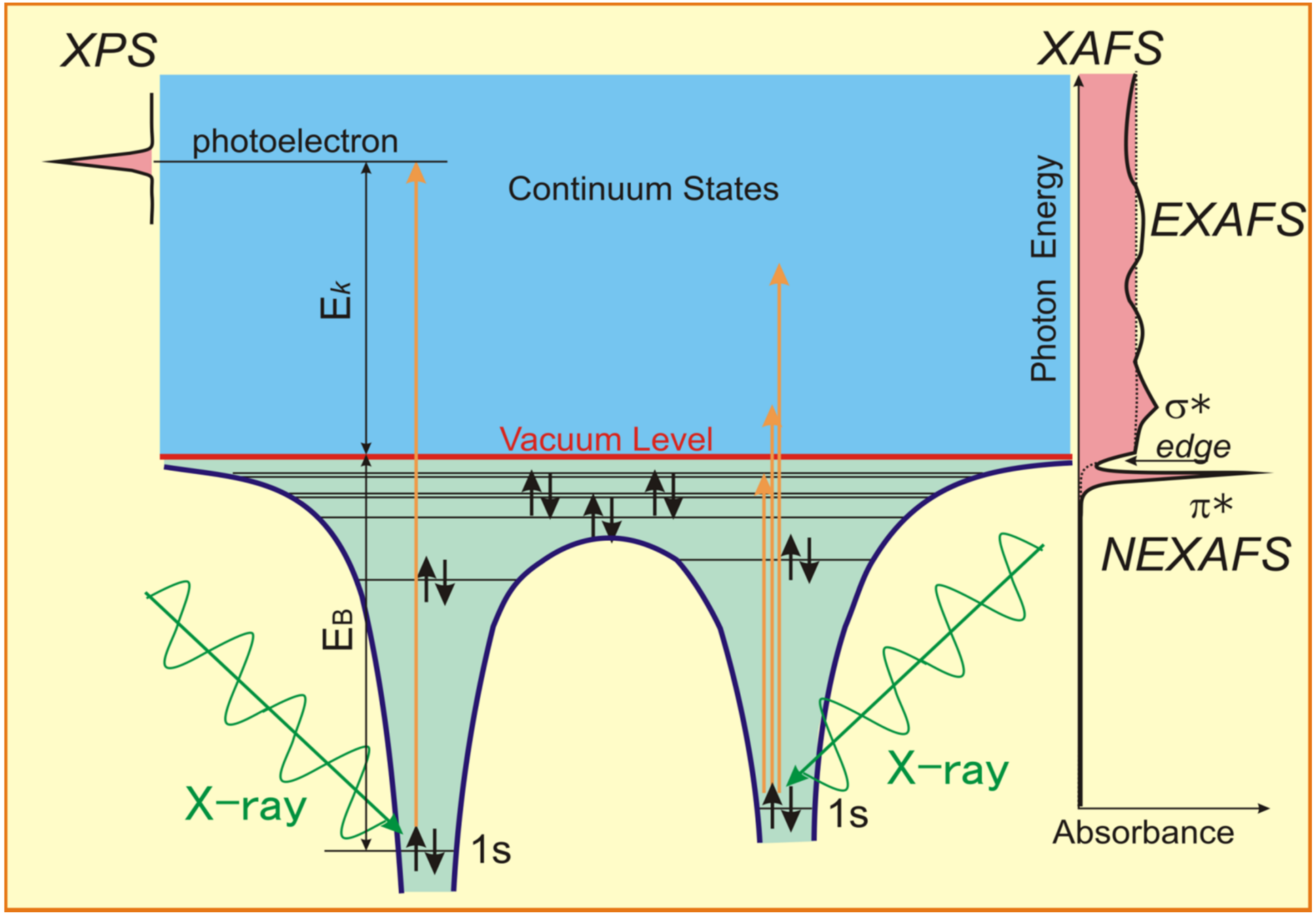
- From the early days, partial pressures of gaseous species were monitored



- Observation of surface species with SR-based core-level spectroscopy



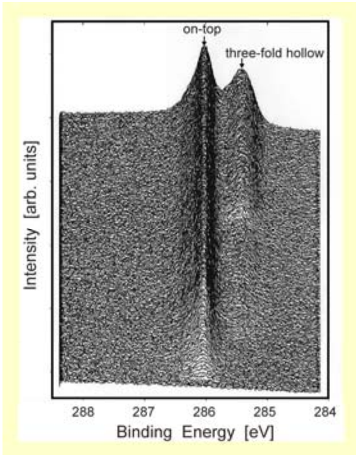
SR-based X-ray spectroscopy (XPS & XAFS)

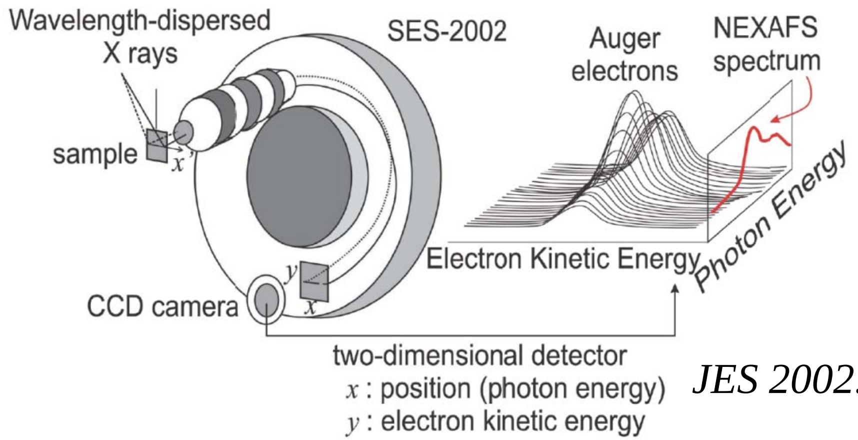


- *Chemical states for substrate and adsorbate*
- *Geometric and electronic structures*

SR-based electron-detecting techniques for in-situ monitoring under UHV conditions

- *Fast-XPS*
- *Fast-NEXAFS*
- *Micro-XPS*

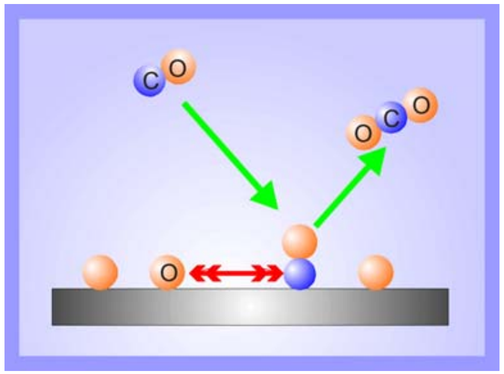




JES 2002.

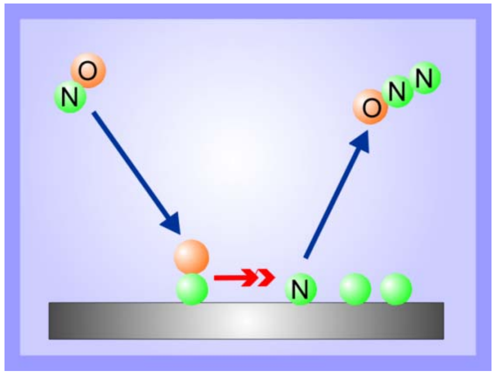
Previous our studies…

CO oxidation



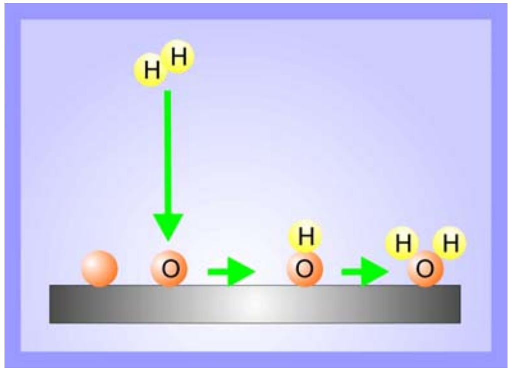
J. Chem. Phys. **122,** 134709 (2005).
J. Chem. Phys. **124,** 224712 (2006).
J. Chem. Phys. **126,** 044704 (2007).
Appl. Phys. Lett. **99,** 074104 (2011)

NO reduction



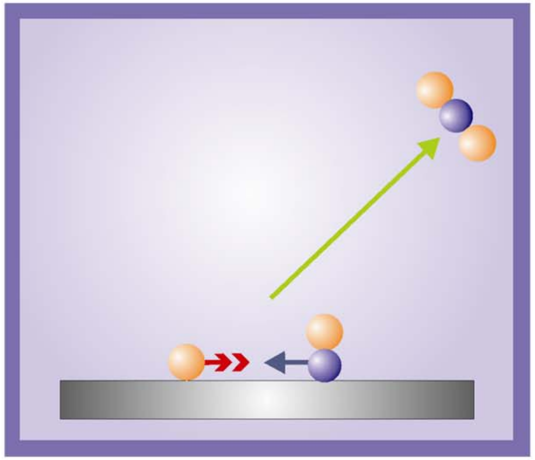
J. Phys. Chem. B **110,** 25578 (2006).
J. Chem. Phys. **127,** 024701 (2007).
J. Phys. Chem. C **113,** 13257 (2009).

H_2O formation



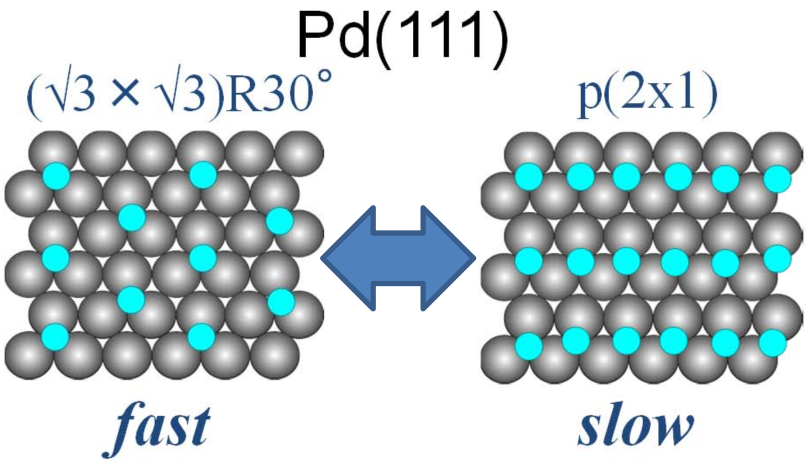
J. Chem. Phys. **119,** 9233 (2003).
J. Chem. Phys. **122,** 204704 (2005).
Phys. Rev. Lett. **100,** 106101 (2008)

In-situ observations under UHV conditions

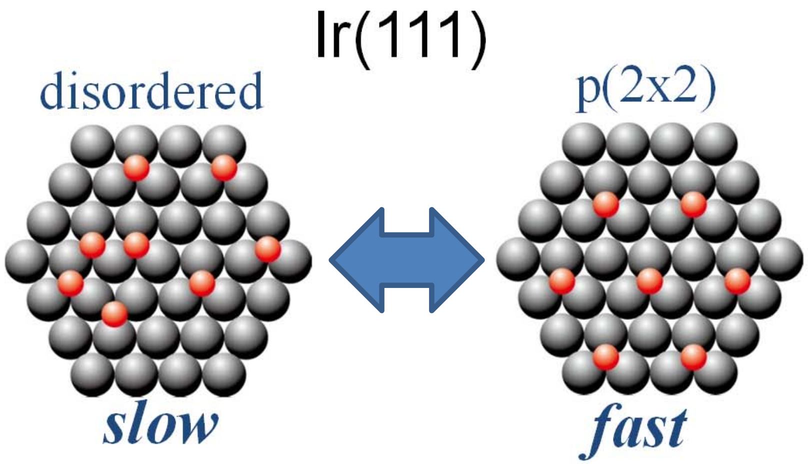


Langmuir-Hinshelwood mechanism
both for Pd and Ir under UHV

Phase-dependent reactivity both for Pd and Ir under UHV



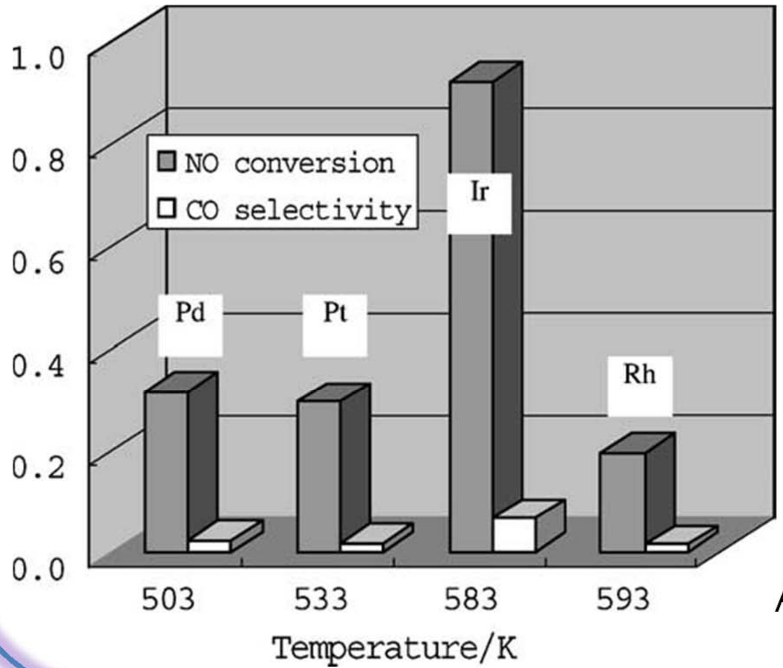
J. Chem. Phys. **124**, 224712 (2006).



Appl. Phys. Lett. **99**, 074104 (2011).

Practical catalytic reaction under ambient-pressure conditions

Activity of PGM catalysts for the NO reduction by CO under an ambient-pressure (AP) condition



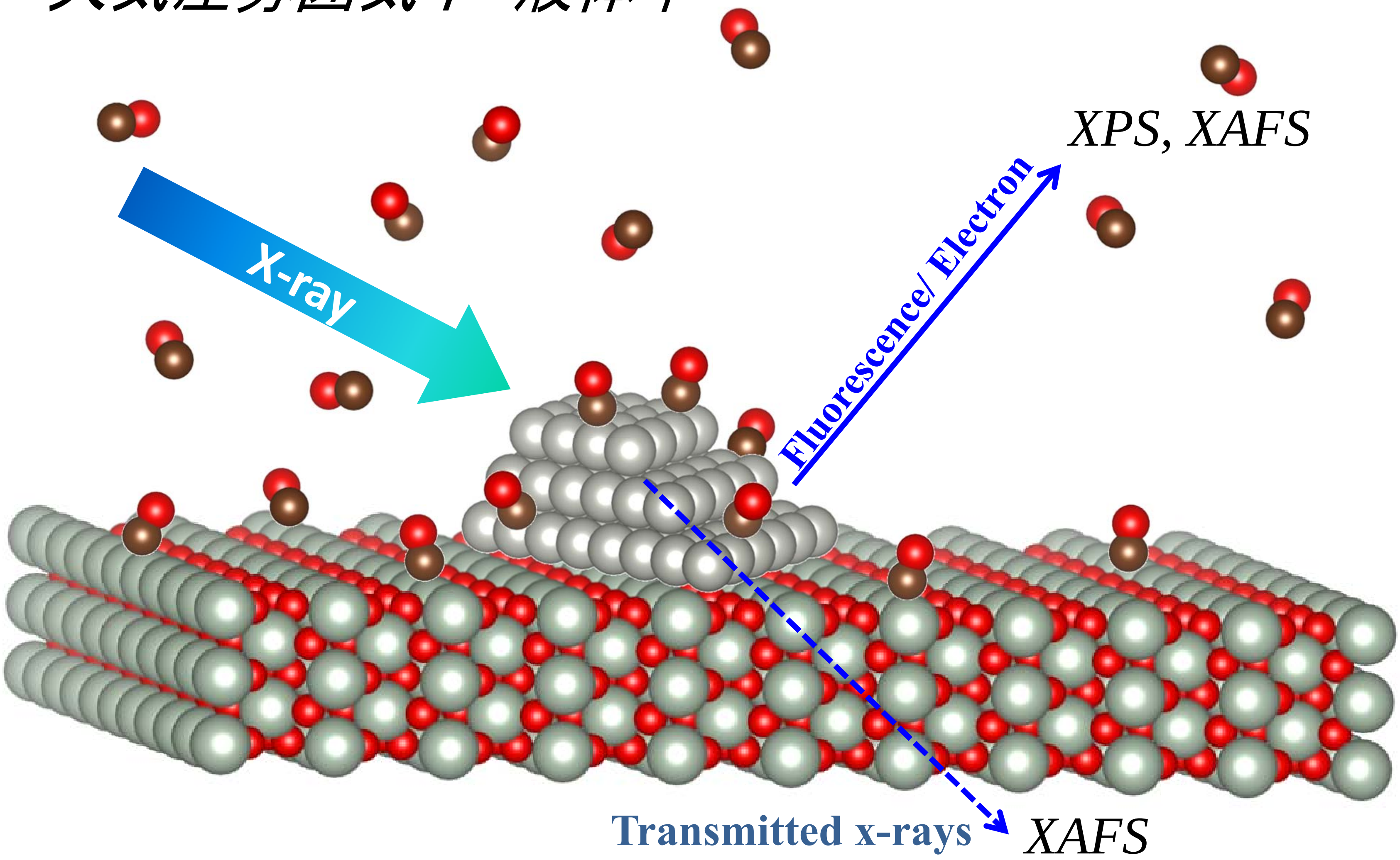
Pd and Ir catalysts :

Large difference in activity under AP condition

A. Wang et al. *Appl. Catal., B,* **40,** 319 (2003)

実作動条件下の触媒を直接見たい

大気圧雰囲気下･液体中



目次

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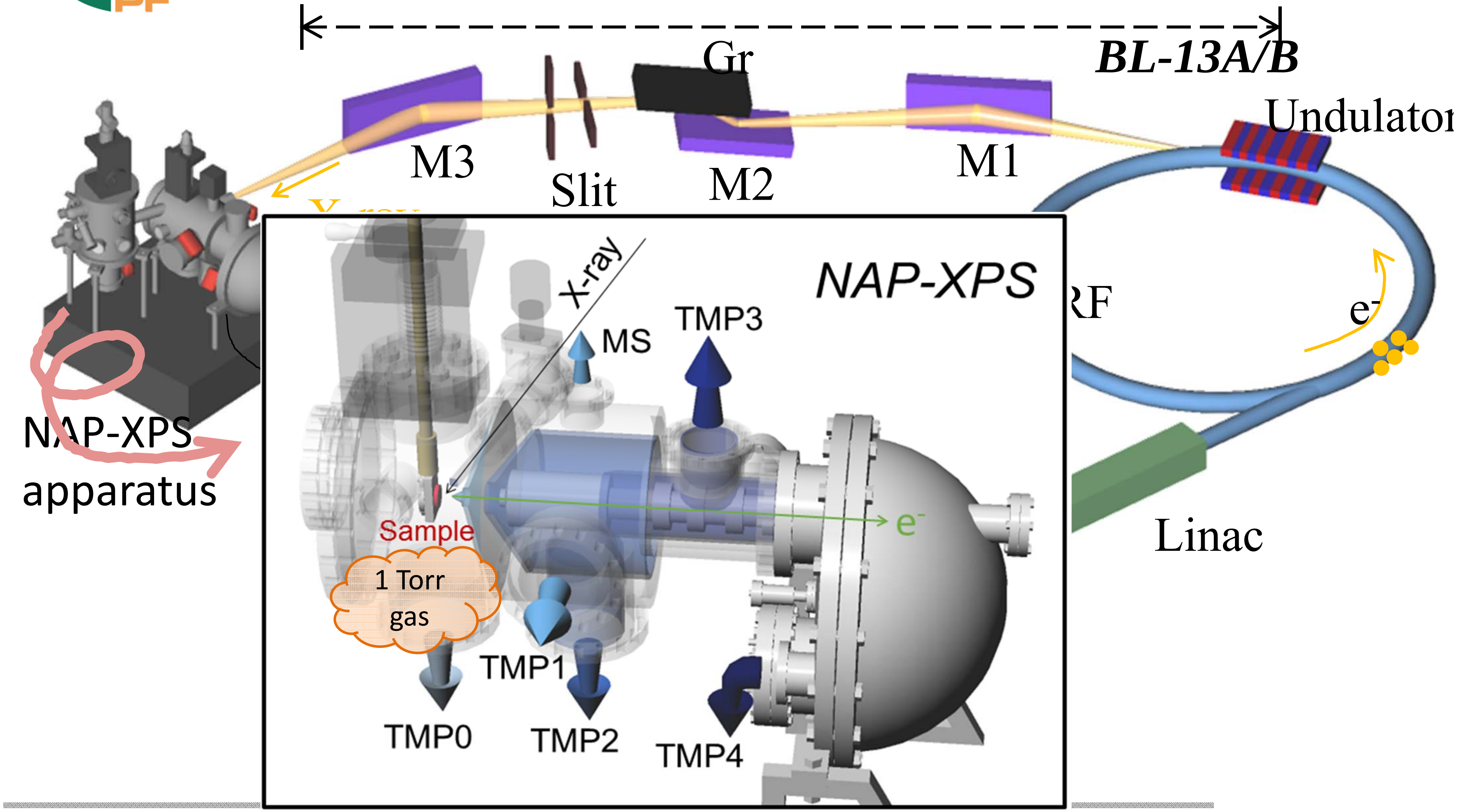
軟X線オペランド観測手法

触媒が活性になったときに見えるもの

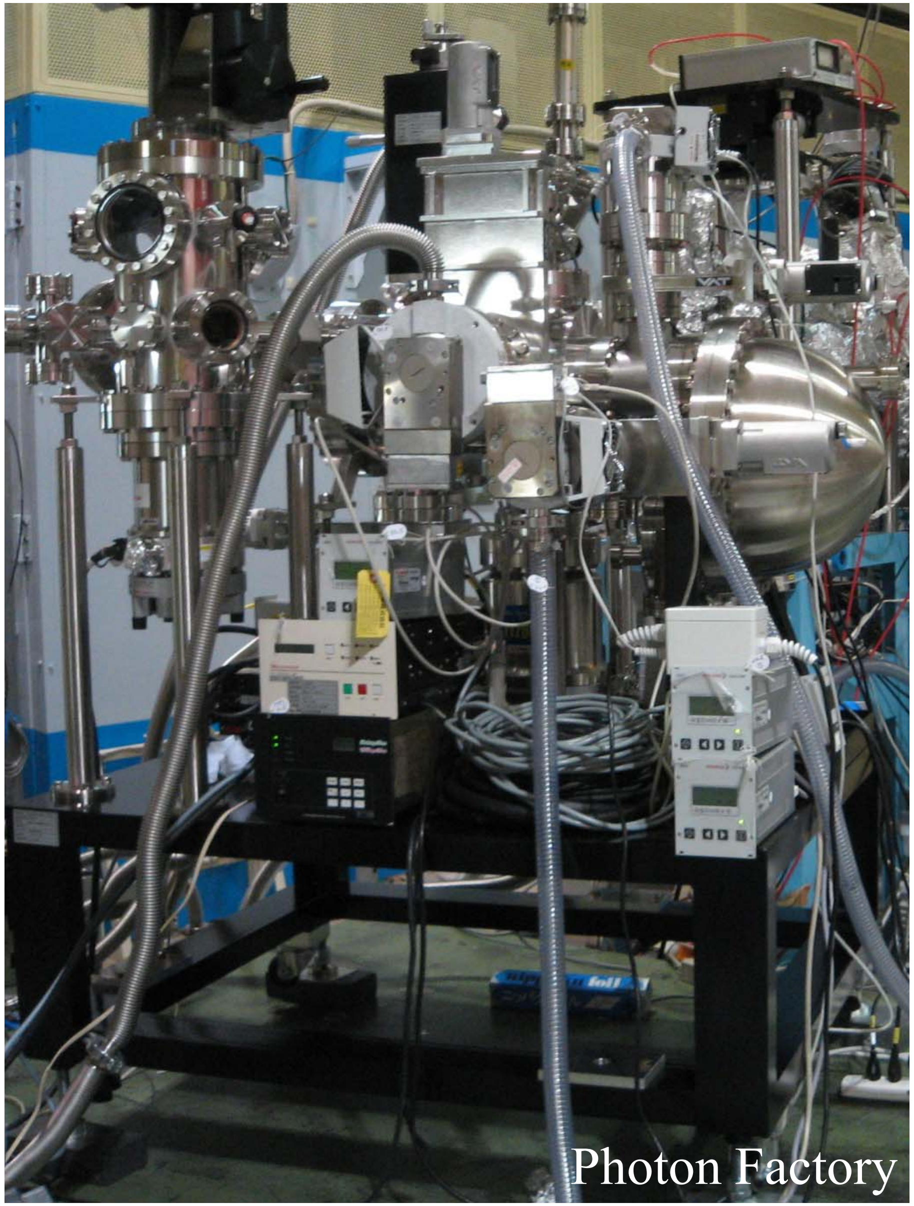
NAP-XPSによる排気ガス浄化触媒
電気化学XAFSによる水分解触媒

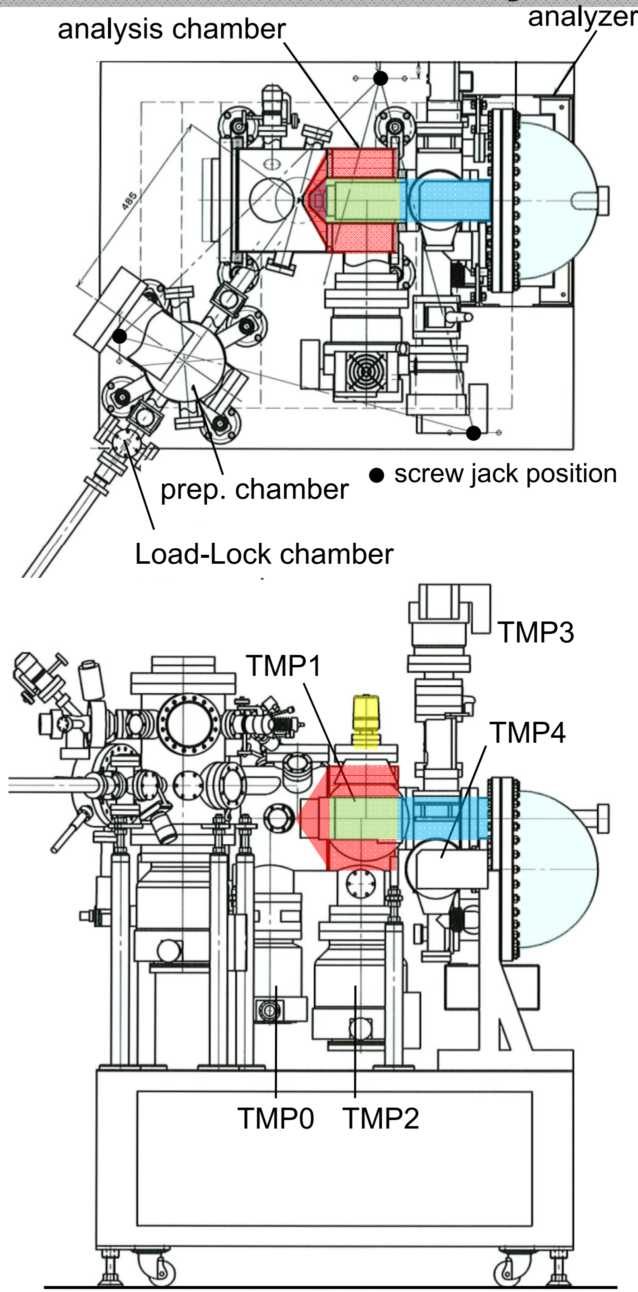
NAP-XPS at the Photon Factory

High Energy Accelerator Research organization Photon Factory (KEK-PF)

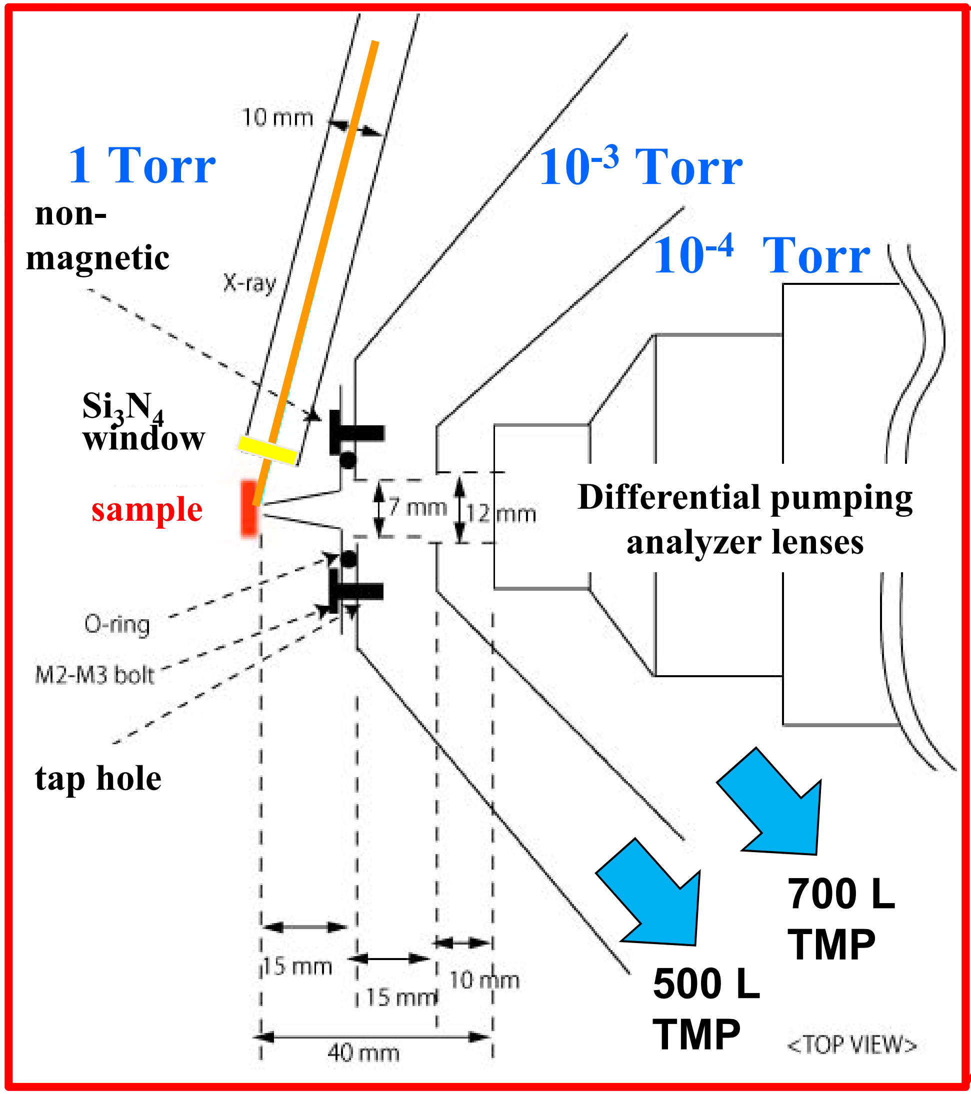


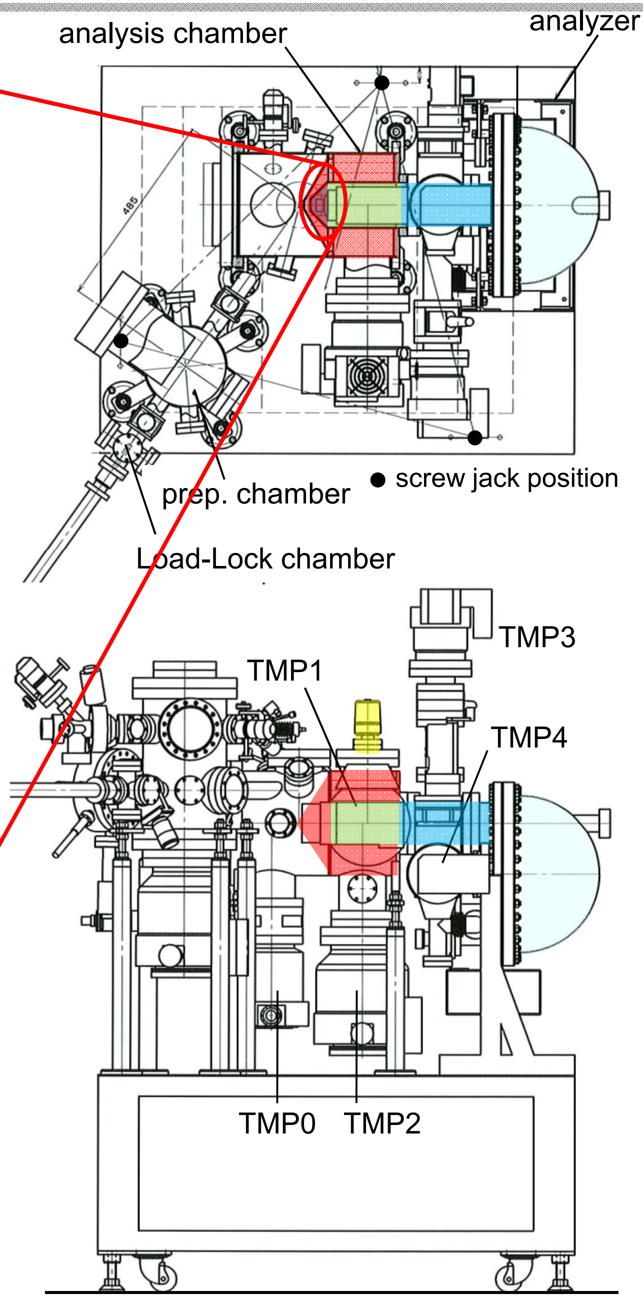
NAP-XPS at the Photon Factory





NAP-XPS at the Photon Factory

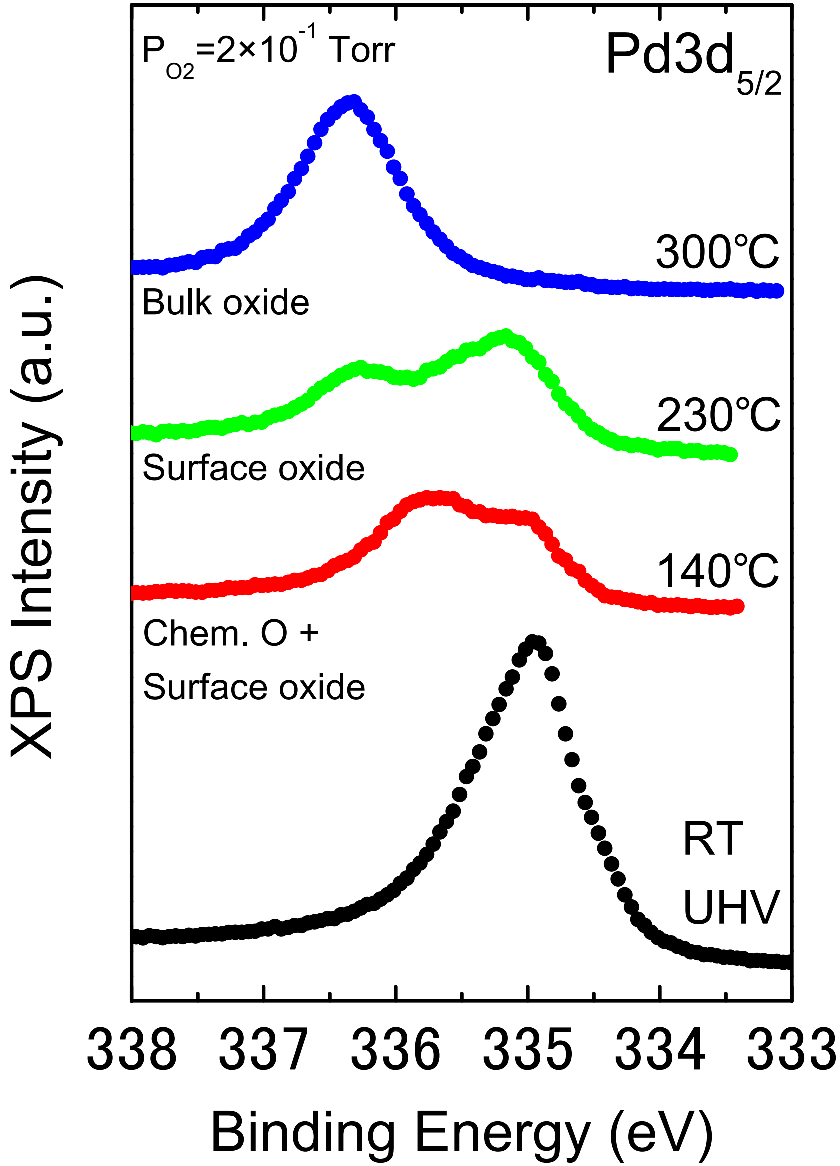


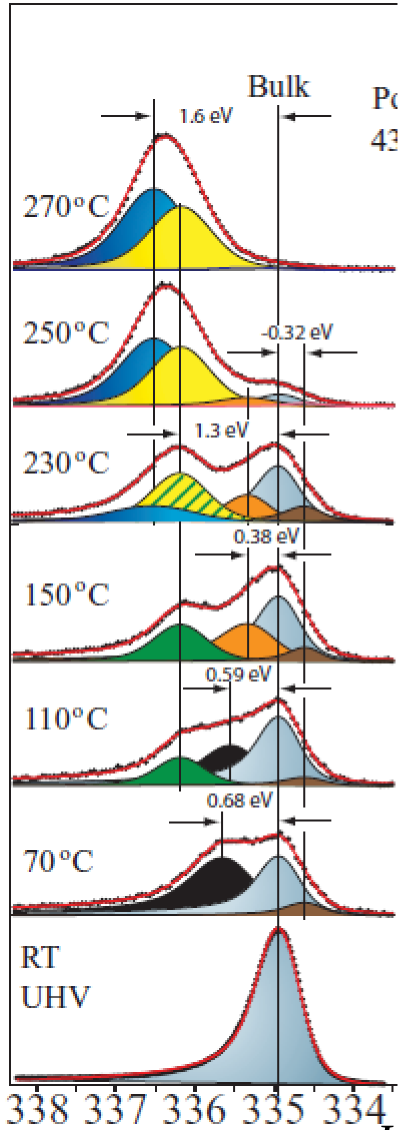


2-stage differential pumping for analyzer
2-stage differential pumping for chamber

NAP-XPS at the Photon Factory

Actual NAP-XP spectra taken at BL-13A with E_{kin} = 100 eV





Photon Energy = 435 eV

Sample: Pd(100)

Gas: O_2 0.2 Torr

Temperature Dependence

Good agreement with previous results obtained under a similar condition (*Gas*: O_2 0.5 mbar)

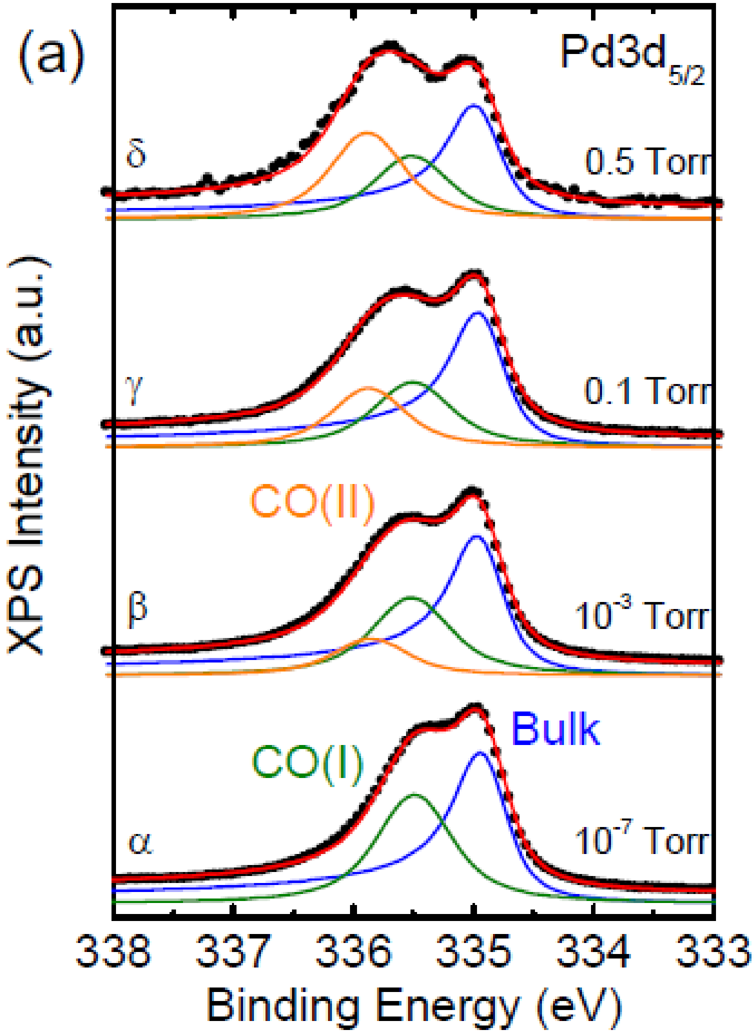
(PRB **83**, 115440 (2011))

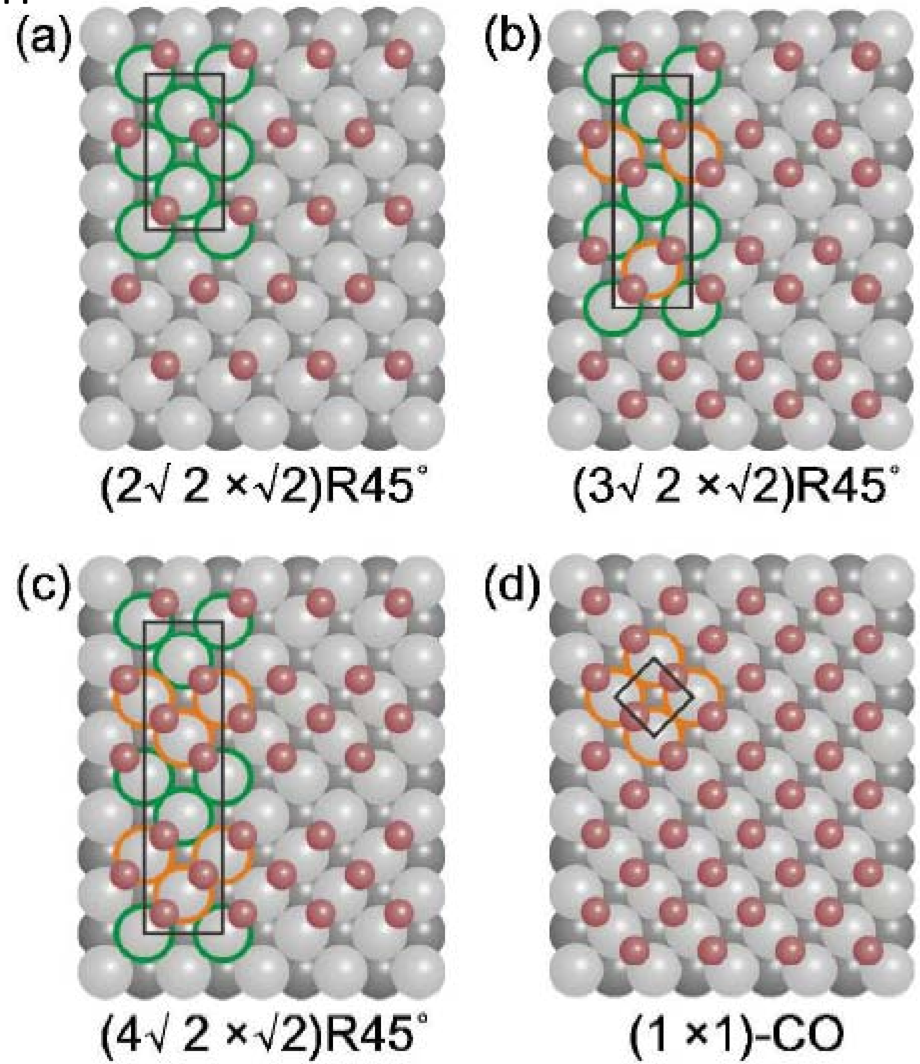
J. Phys. Chem. Lett. **3,** 3182 (2012).

NAP-XPS at the Photon Factory

Actual NAP-XP spectra taken at BL-13A with E_{kin} = 100 eV

Sample: Pd(100) *Gas*: up to CO 0.5 Torr





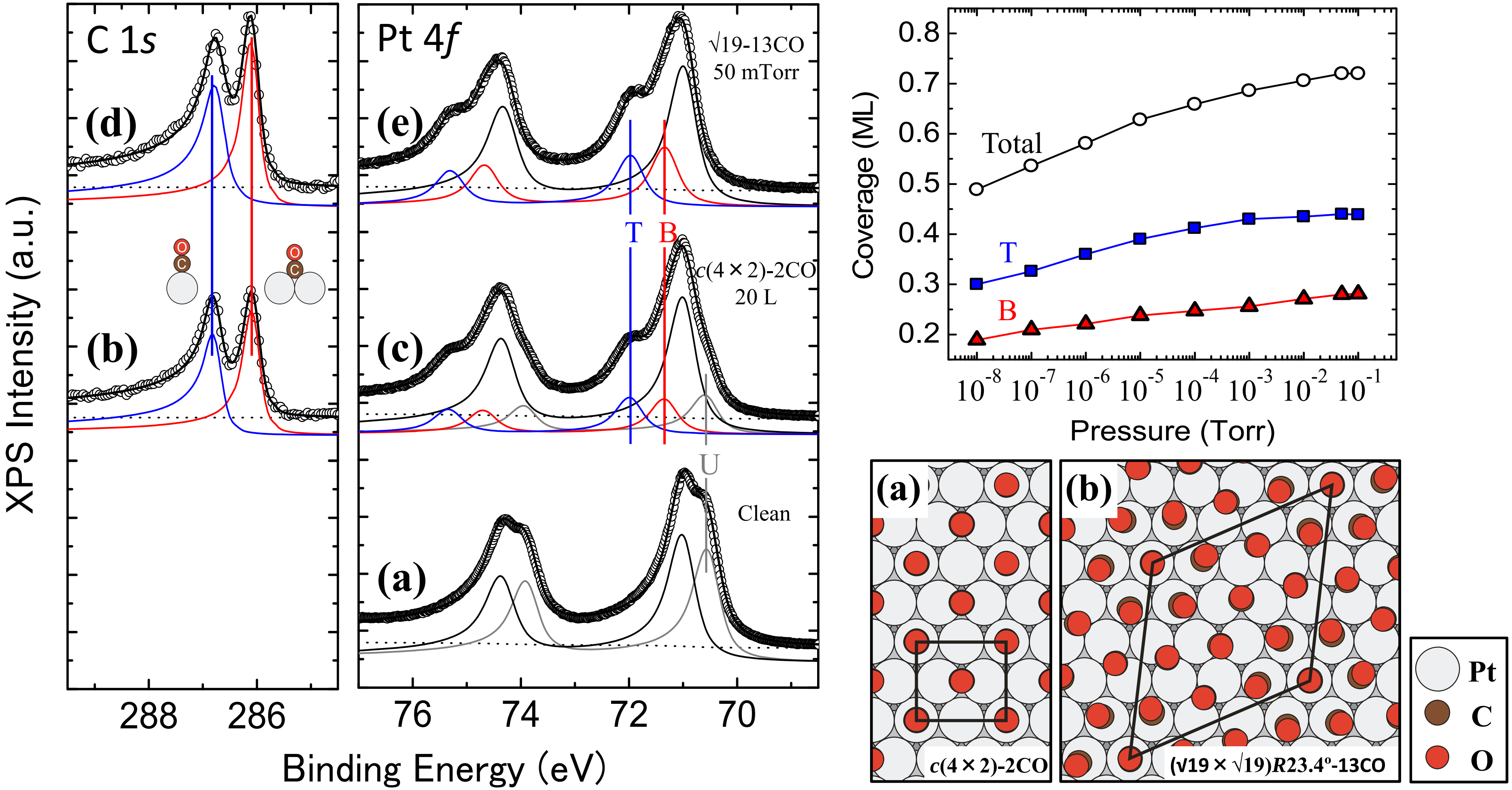
Formation of high-density phases

Surf. Sci.. **615,** 33 (2013).

NAP-XPS at the Photon Factory

Actual NAP-XP spectra taken at BL-13A with E_{kin} = 100 eV

Sample: Pt(111) *Gas*: CO 10^{-8} – 10^{-1} Torr

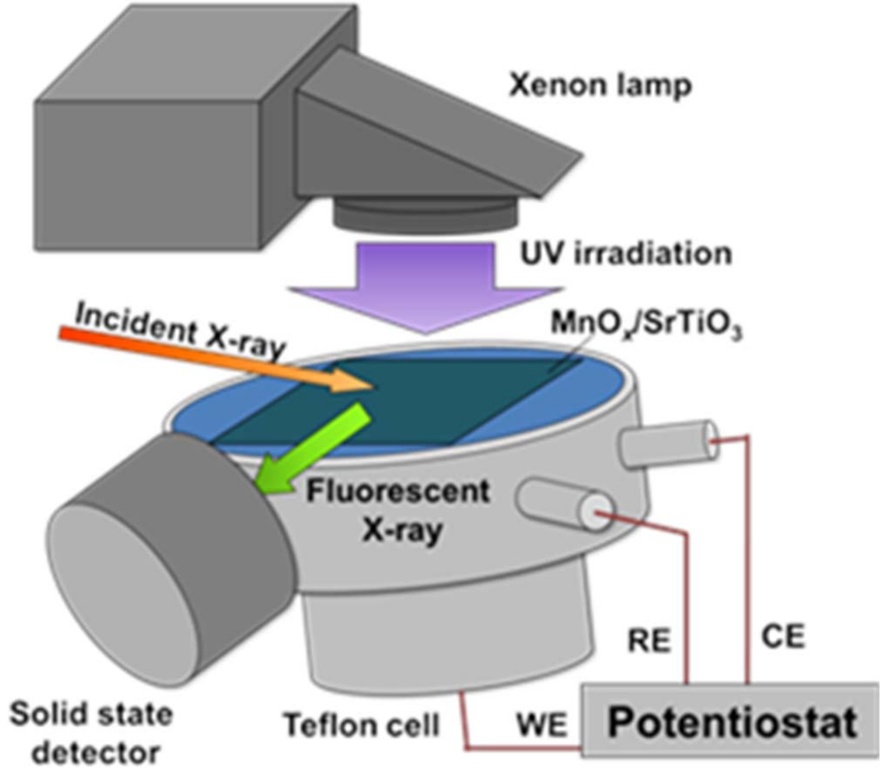


Formation of high-density phases

Phys. Chem. Chem. Phys. **16,** 23564 (2014).

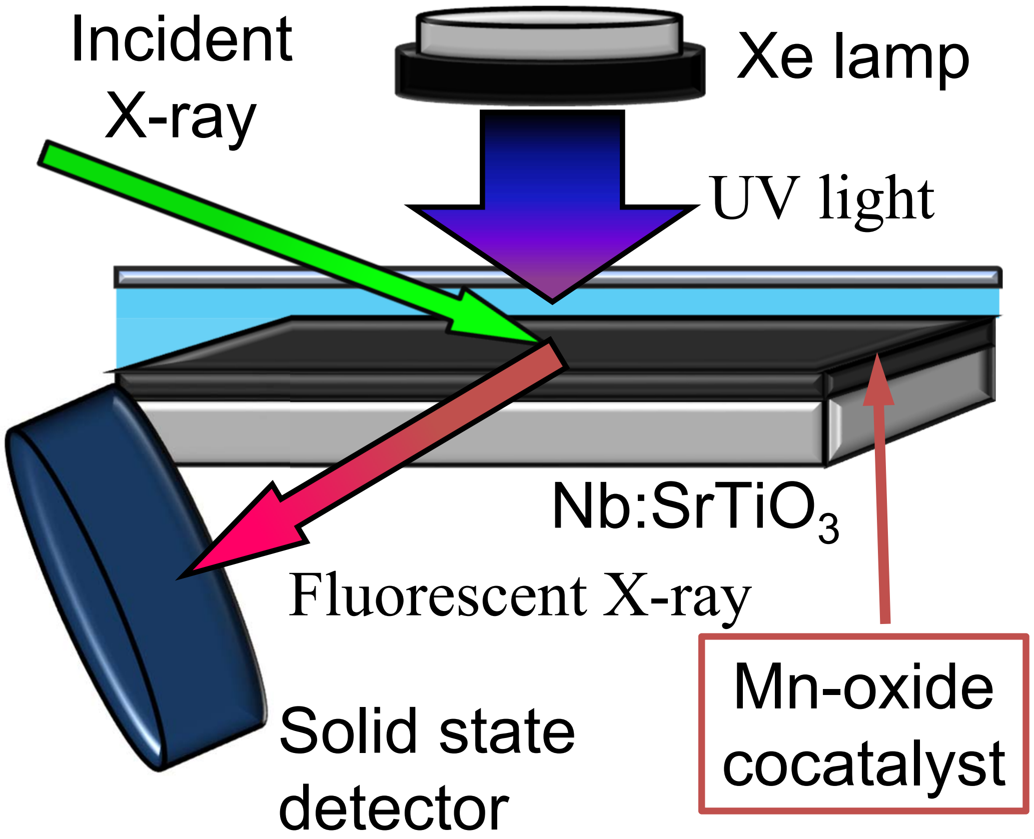
電気化学XAFS

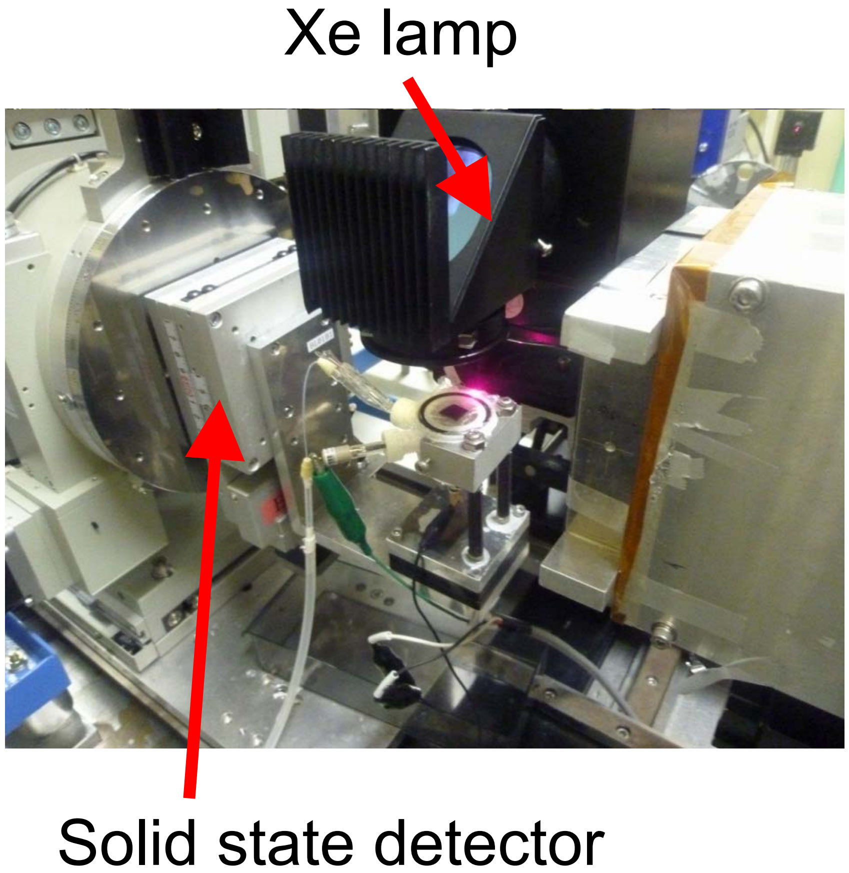
電気化学制御下の試料の蛍光XAFSを
水中の光電極のオペランド観測に応用



電気化学XAFS

電気化学制御下のセルに紫外光を照射

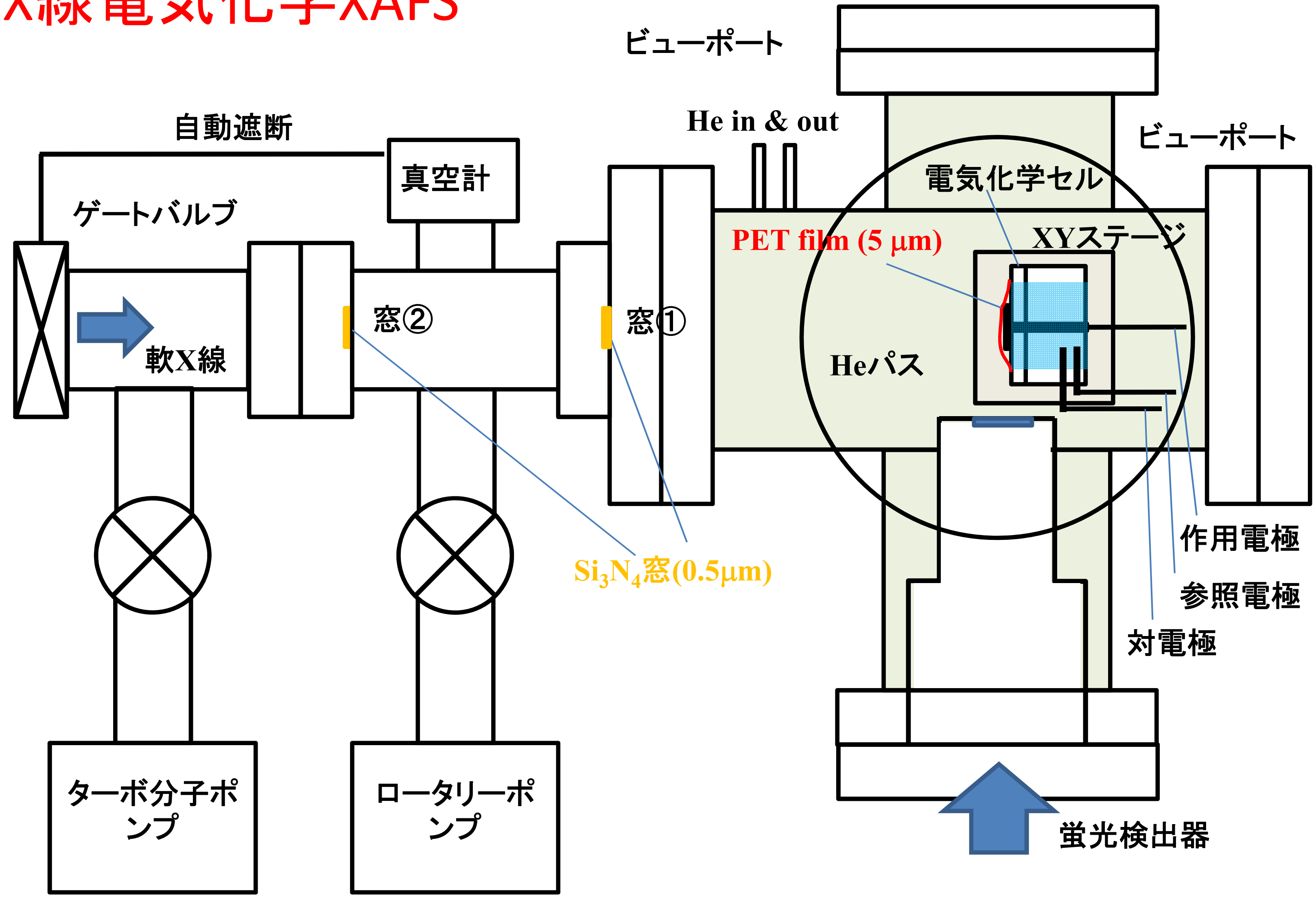




水分解反応時の助触媒の化学状態をその場観測

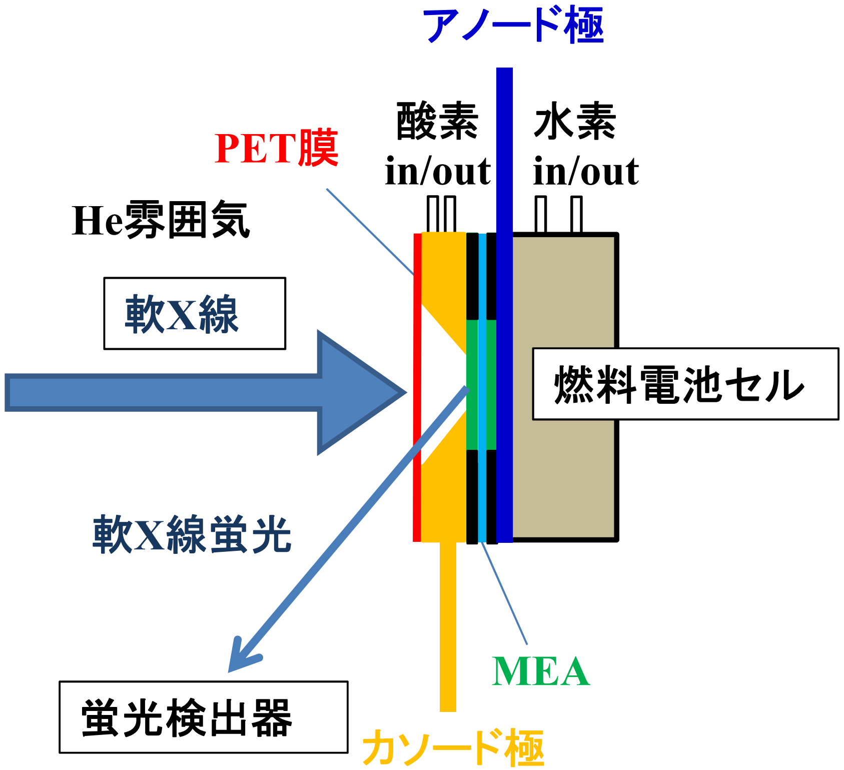
軟X線電気化学XAFS

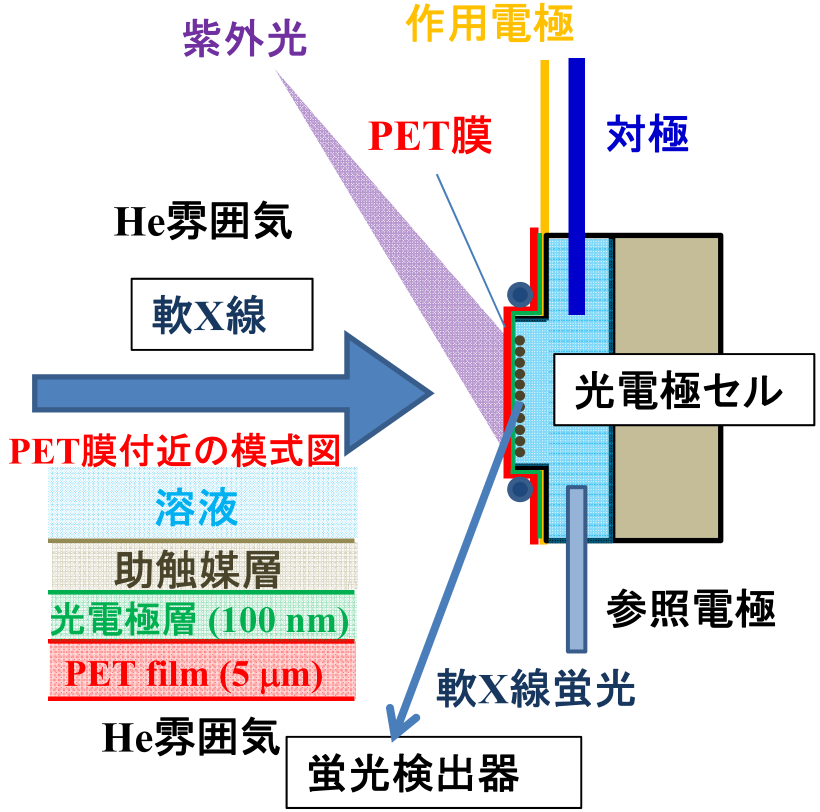
軟X線電気化学XAFS



軟X線電気化学XAFSによるオペランド観測

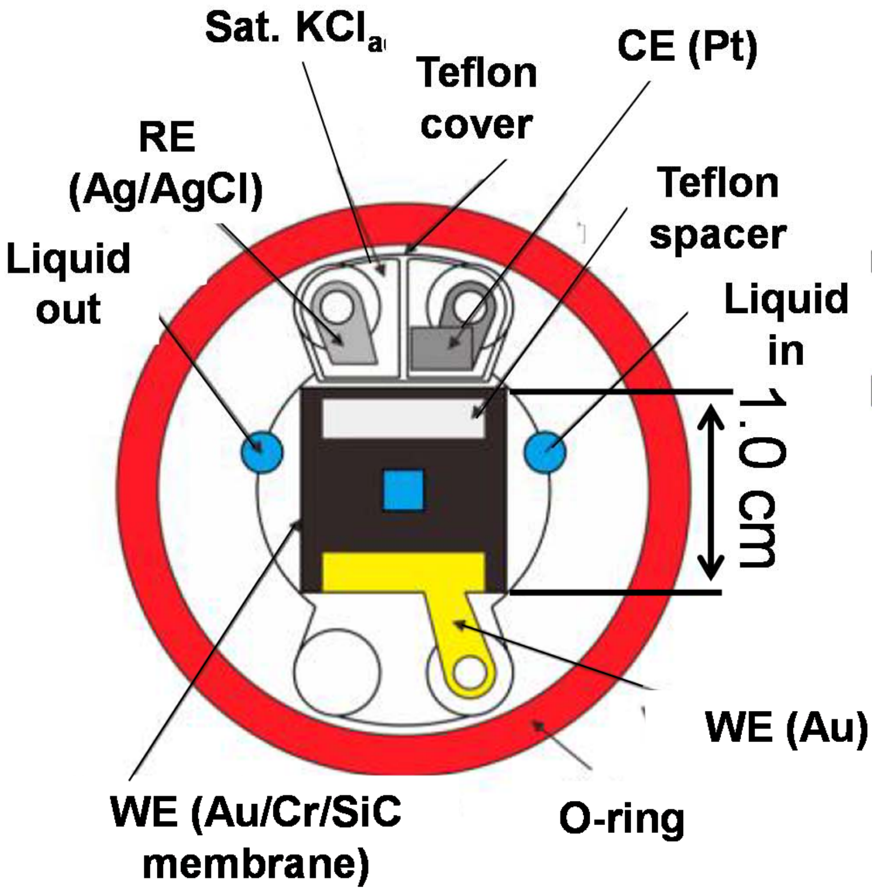
軟X線電気化学XAFSのセルと測定配置



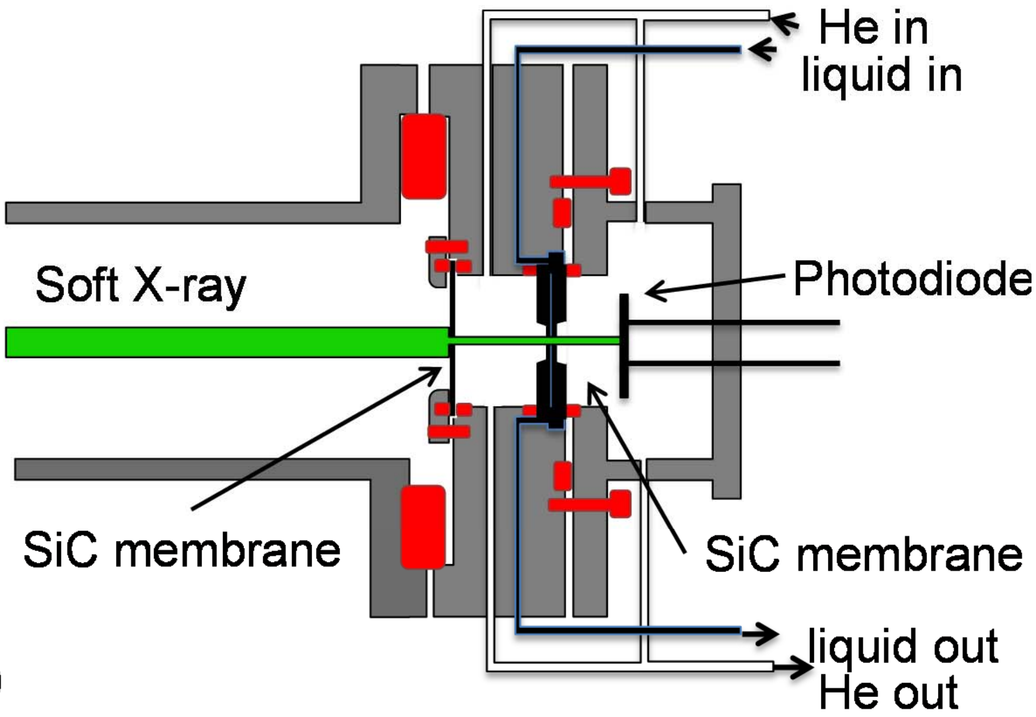


透過型軟X線電気化学XAFS

測定セルの内部



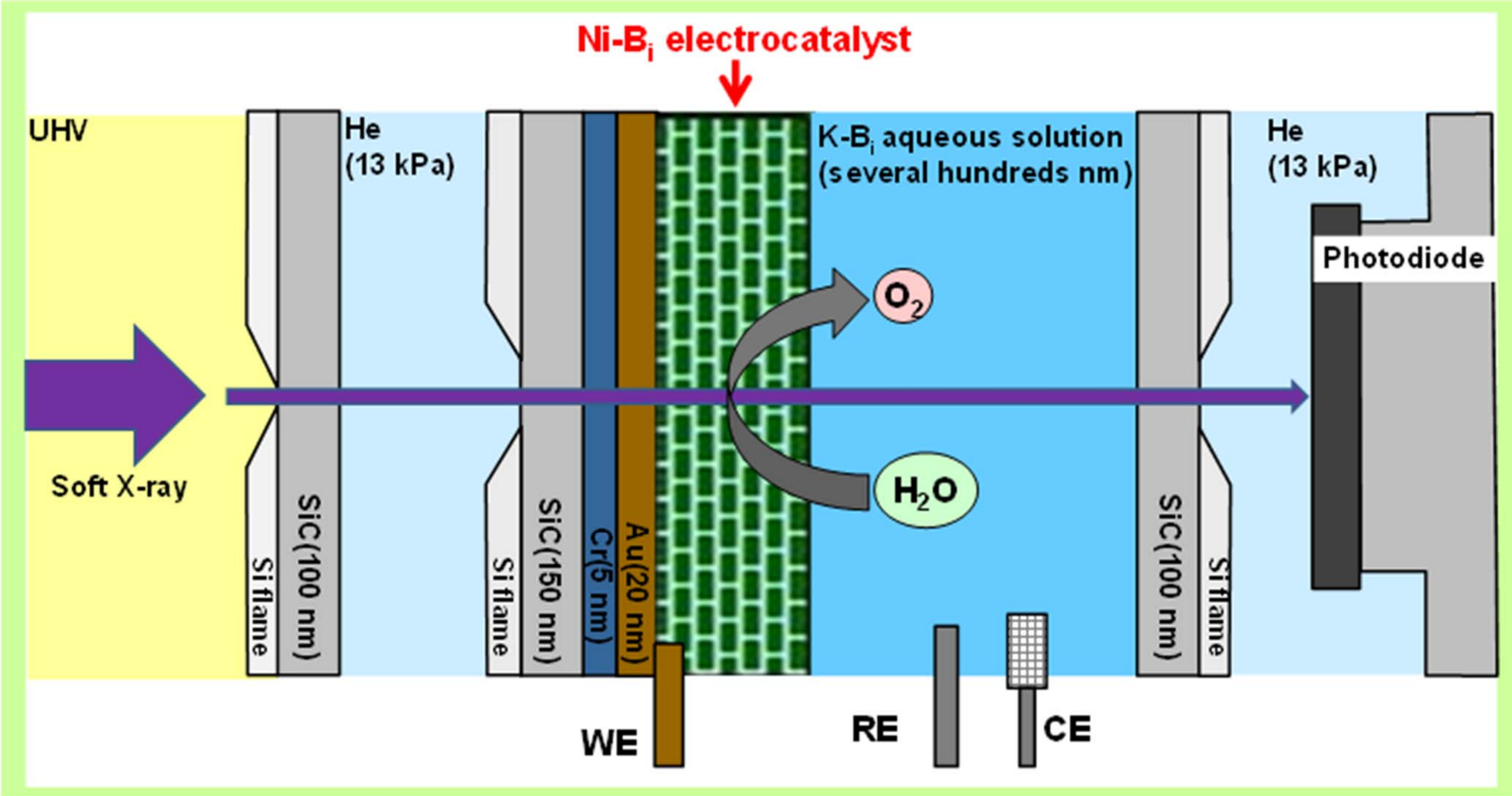
透過法によるXAFS測定



M. Nagasaka, *et al. J. Phys. Chem. C.*, **117**, 16343 (2013).

電析した触媒膜のC, N, O端XAFS測定が可能

透過型軟X線電気化学XAFSによるオペランド観測



*電極上触媒薄膜のオペランド*XAFS測定が可能

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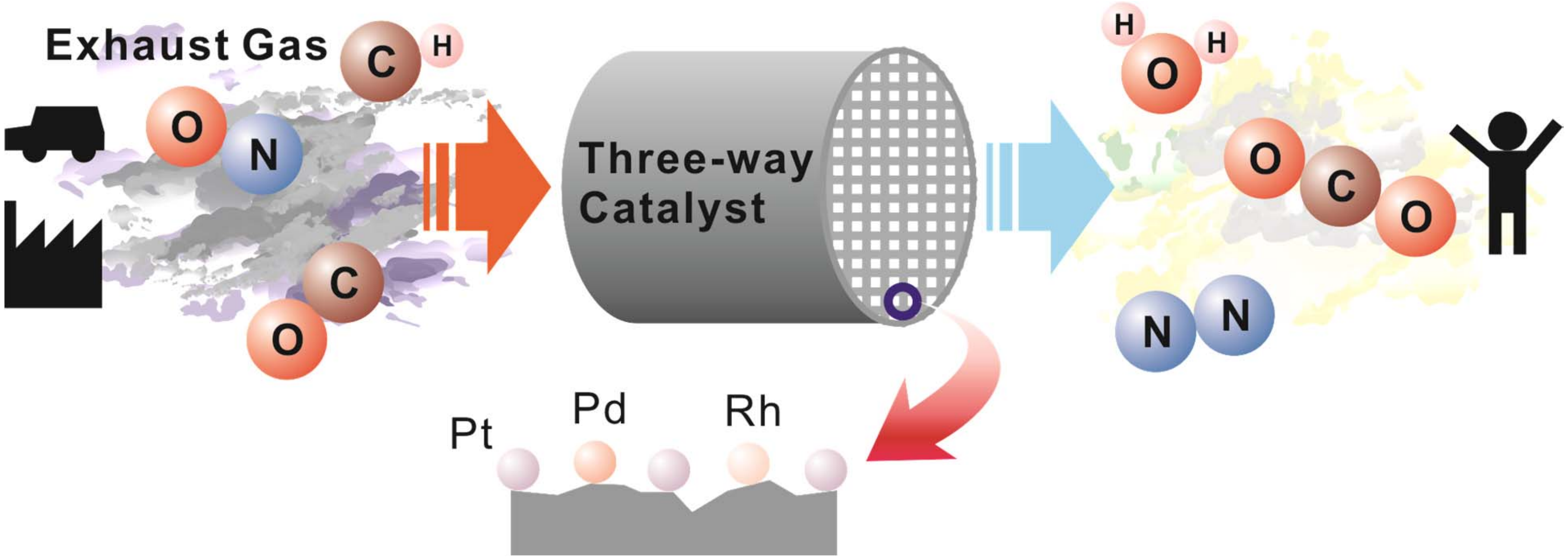
CO oxidation on Pt-group metal surfaces



$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

Ru 44	Rh 45	Pd 46
Os 76	Ir 77	Pt 78

Active Surface for CO oxidation on Pd

Previous results for Pd surfaces

Ultra High Vacuum; 10^{-9} Torr
Near Ambient Pressure; >10^{-2} Torr

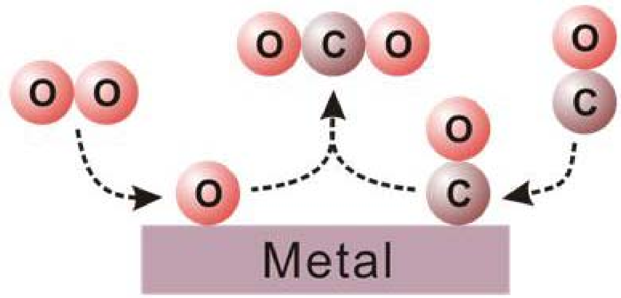
① Chemisorbed O/Metal

MB Ertl *et al.*, *J. Chem. Phys.* **1978**, *69*, 1267.

XPS Nakai *et al.*, *J. Chem. Phys.* **2006**, *124*, 224712.

AP-Mass Chen *et al.*, *Surf. Sci.* **2007** *601*, 5326.

PM-IRAS Gao *et al.*, *Surf. Sci.* **2009**, *603*, 65.



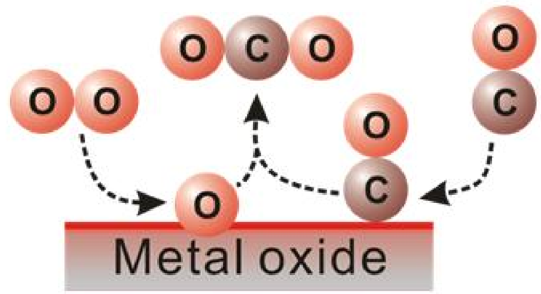
Langmuir-Hinshelwood

② Surface Oxide

SXRD van Rijn *et al.*, *Phys. Chem. Chem. Phys.* **2011**, *13*, 13167.

SXRD Gustafson *et al.*, *Phys. Rev. B* **2008**, *78*, 045423.

HP-STM Hendriksen *et al.*, *Surf. Sci.* **2004**, *552*, 229.



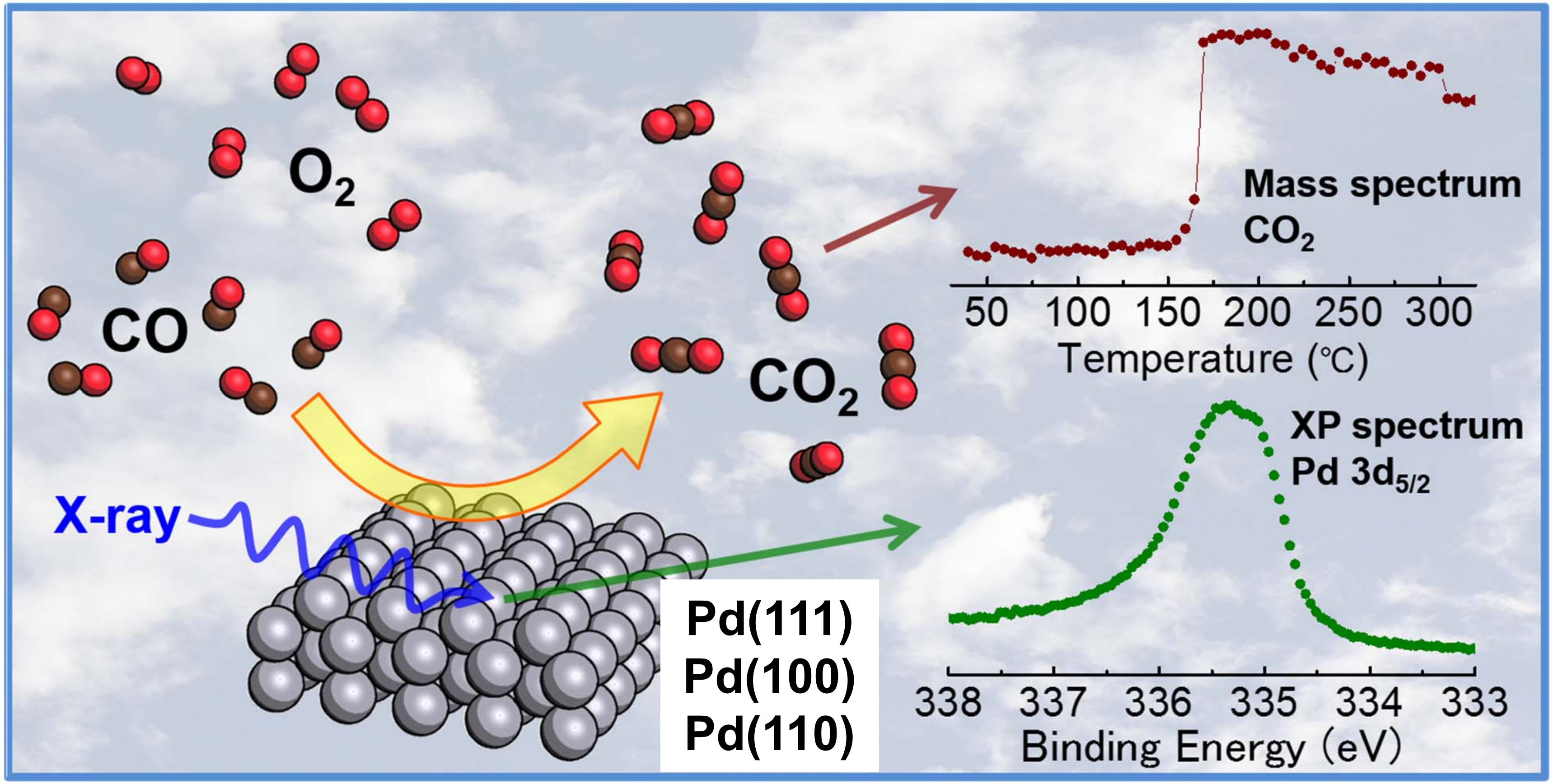
Mars-van Krevelen

In-situ observation using NAP-XPS

Active phase for CO oxidation on three Pd surfaces?

Oxygen-rich condition

P_{O2} = 2 × 10^{-1} Torr
P_{CO} = 2 × 10^{-2} Torr



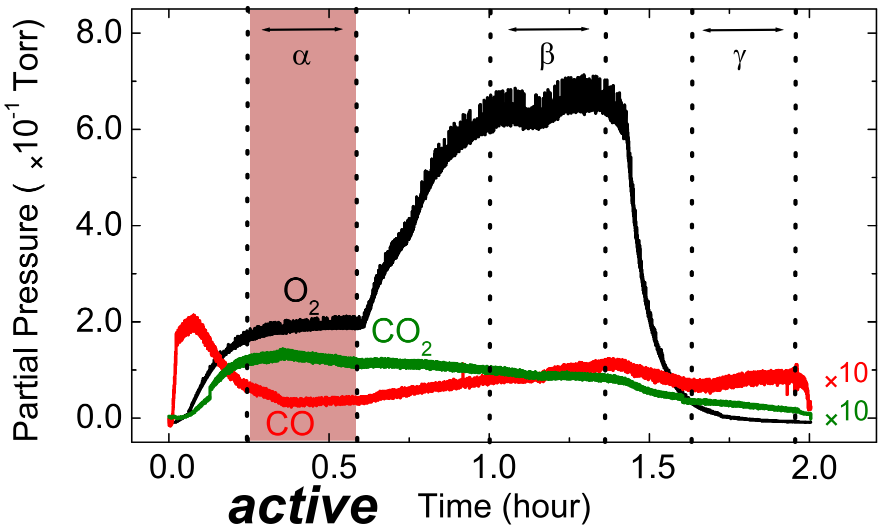
CO oxidation on Pd(111)

Oxygen-rich condition

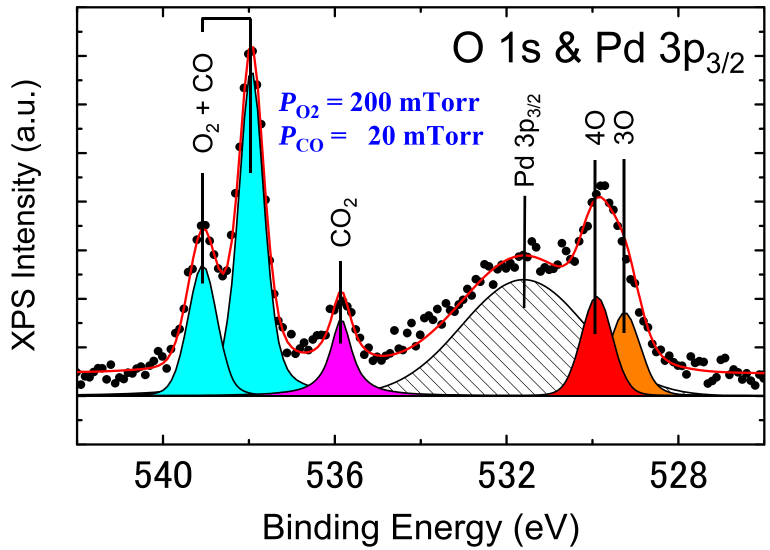
$P_{O2} = 2 \times 10^{-1}$ Torr
$P_{CO} = 2 \times 10^{-2}$ Torr

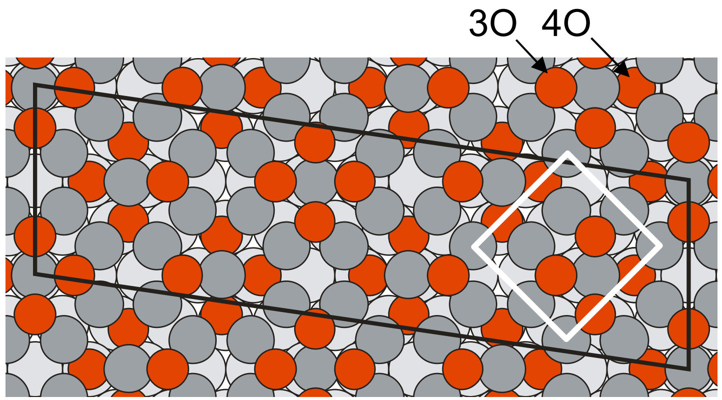
Temperature: 300℃

Partial Pressure



NAP-XPS

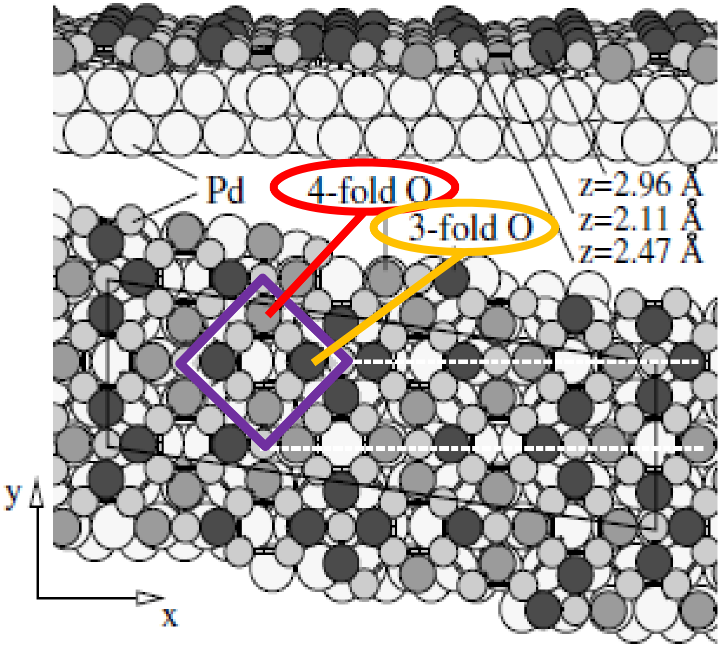


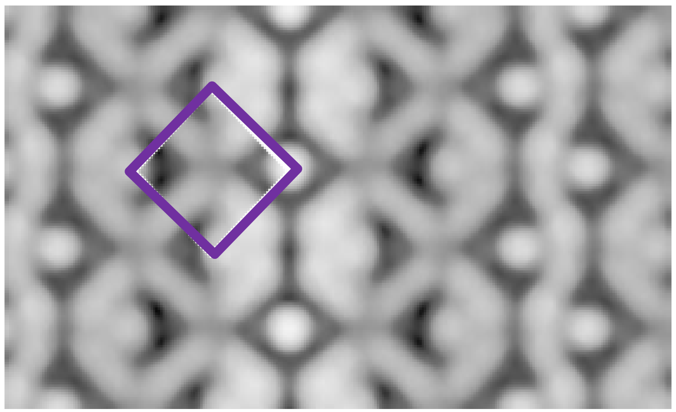


$(\sqrt{6} \times \sqrt{6})\ Pd_5O_4$

J. Phys. Chem. C **116**, 18691 (2012).

Structure of surface oxide on Pd(111)

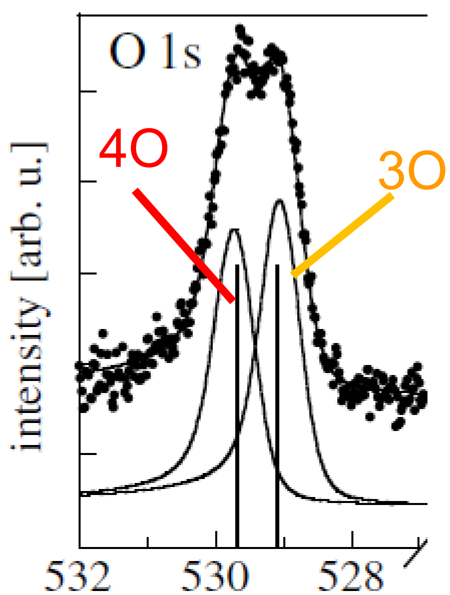




Surface oxide: (√6 x√6)Pd_5O_4

3O ⇒ 3-fold coordinated O

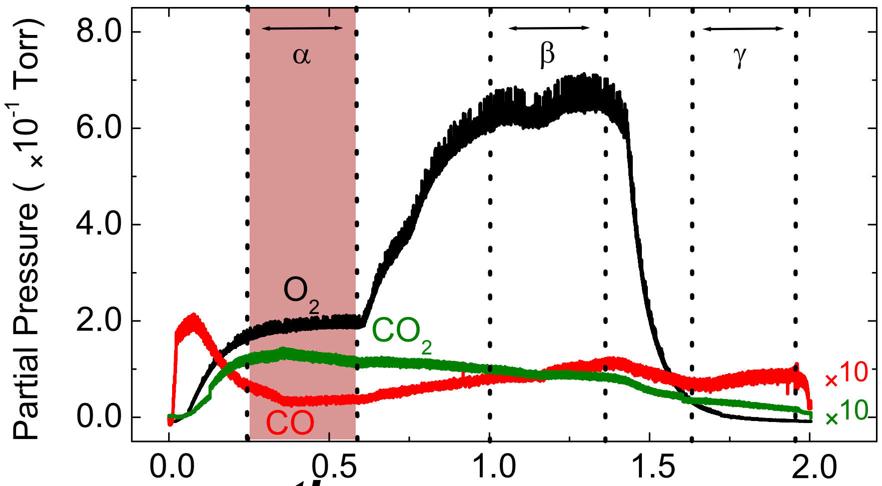
4O ⇒ 4-fold coordinated O



E. Lundgren et al., *Phys. Rev. Lett.*, **88**, 246103, (2002).

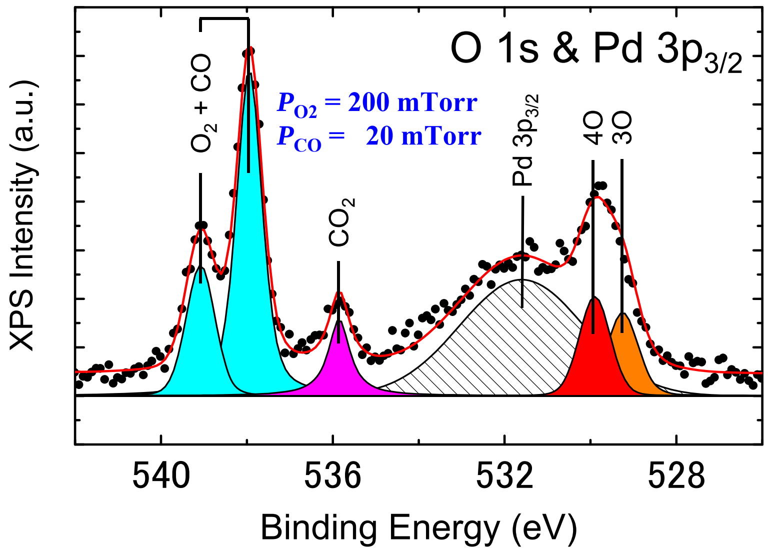
CO oxidation on Pd(111)

Partial Pressure



active

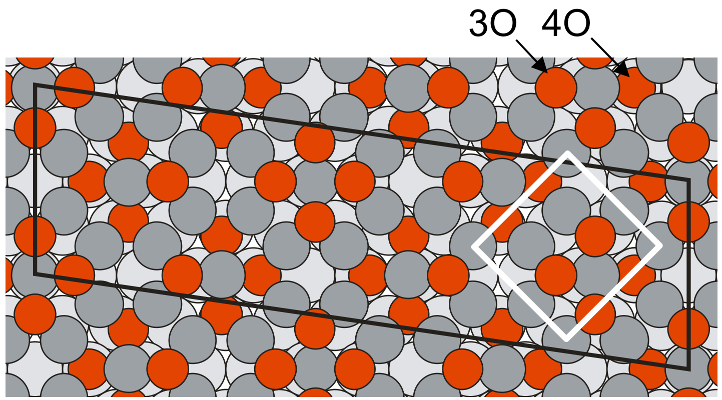
NAP-XPS



($\sqrt{6}$ x$\sqrt{6}$) Pd_5O_4 surface oxide

E. Lundgren et al., *Phys. Rev. Lett.*, **88**, 246103, (2002).

dominant phase



($\sqrt{6}$x$\sqrt{6}$) Pd_5O_4

J. Phys. Chem. C **116**, 18691 (2012).

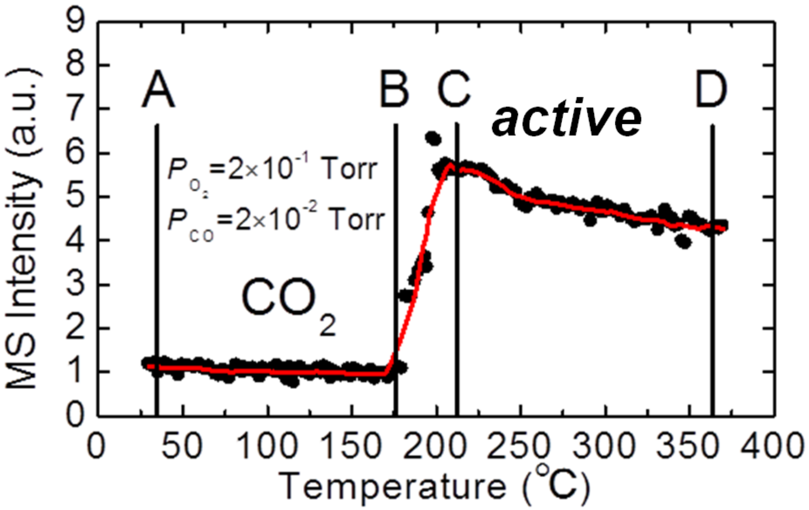
CO oxidation on Pd(100)

Oxygen-rich condition

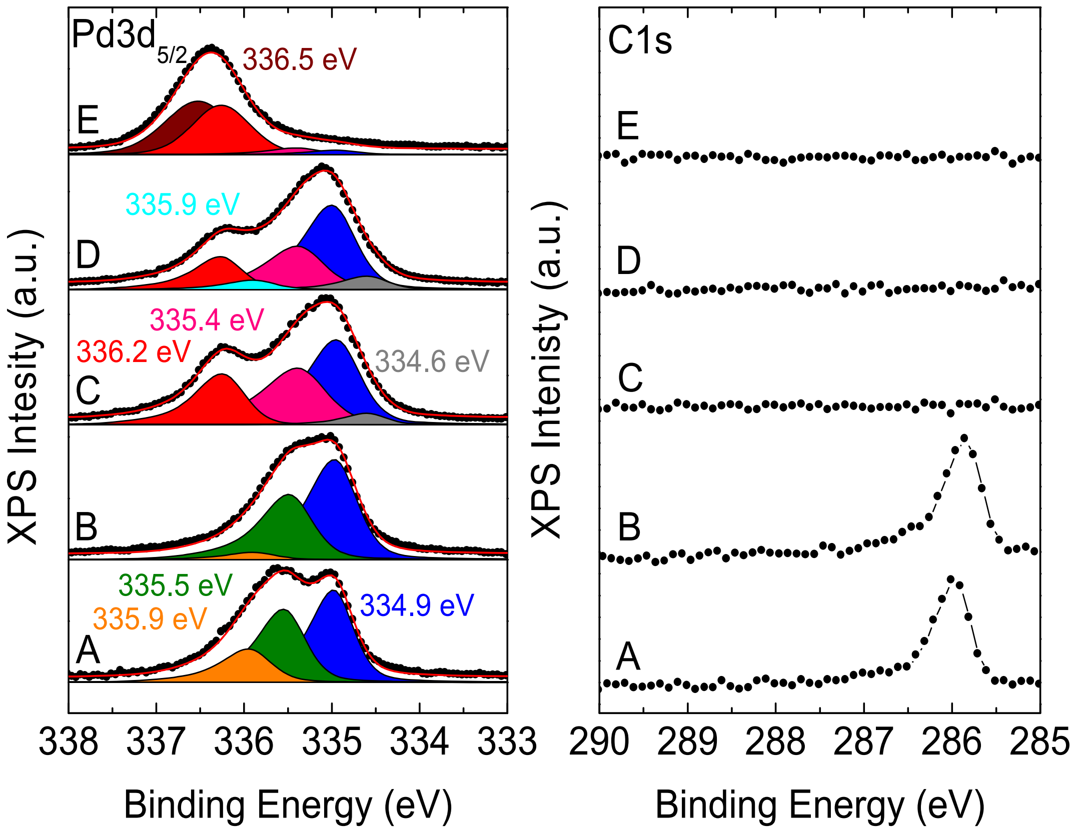
$P_{O2} = 2 \times 10^{-1}$ Torr
$P_{CO} = 2 \times 10^{-2}$ Torr

increasing temperature

CO_2 intensity



NAP-XPS



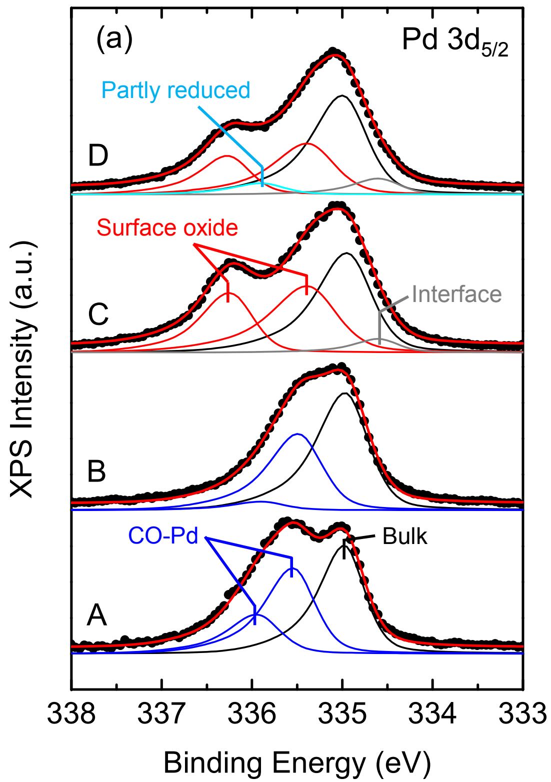
< 190℃
CO poisoning

> 190℃
surface oxide

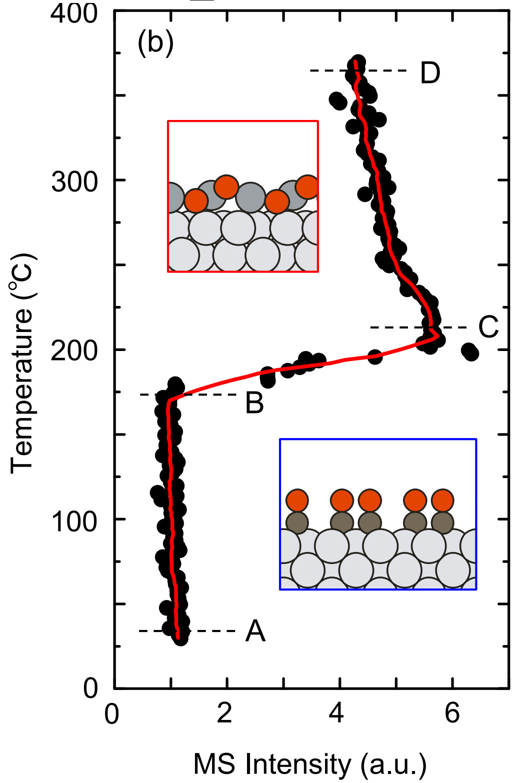
J. Phys. Chem. Lett. **3,** 3182 (2012).

CO oxidation on Pd(100)

NAP-XPS

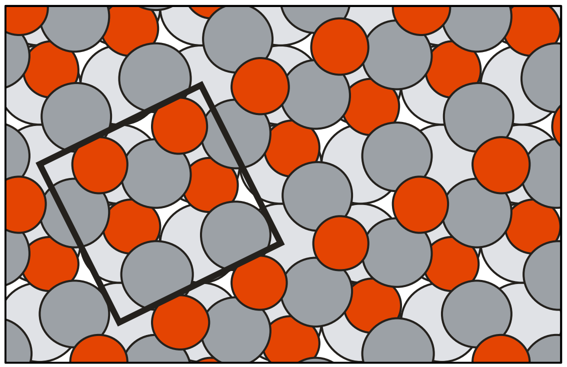


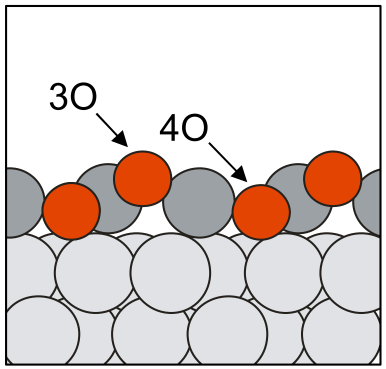
CO_2 intensity



> 190℃
surface oxide

< 190℃
CO poisoning



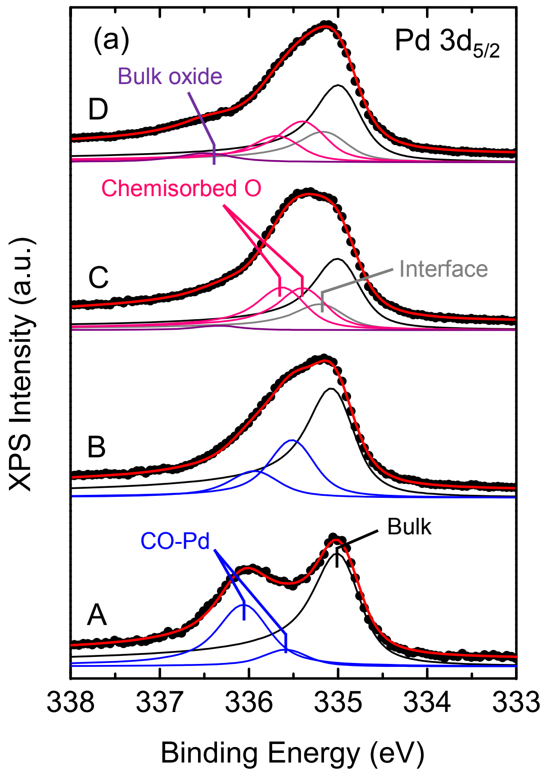


(√5 × √5)R27º
surface oxide

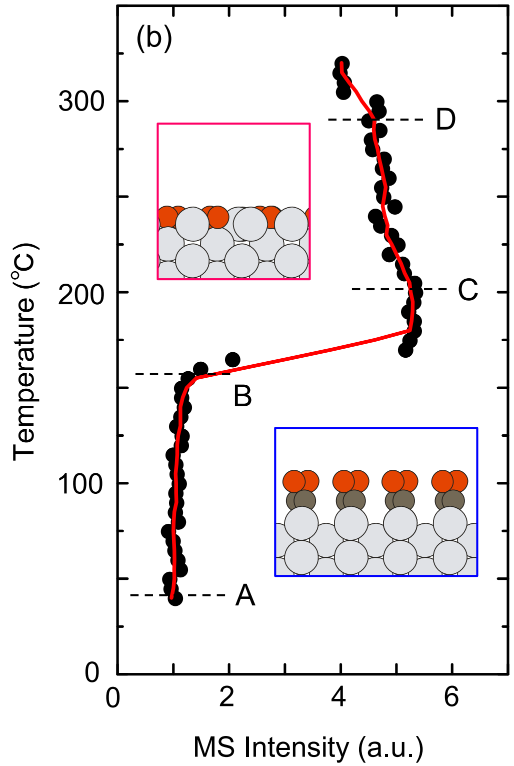
J. Phys. Chem. Lett. **3,** 3182 (2012).

CO oxidation on Pd(110)

NAP-XPS

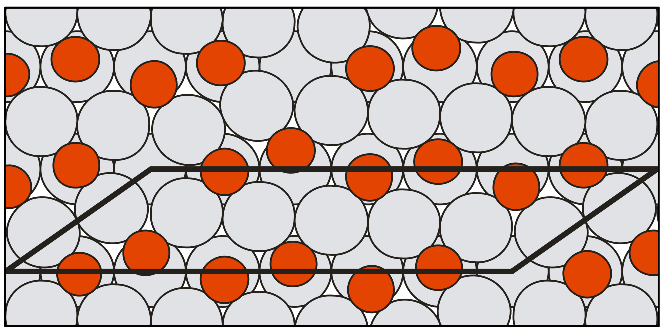


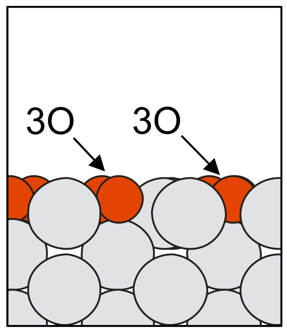
CO_2 intensity



> 165℃
Chemisorbed O

< 165℃
CO poisoning



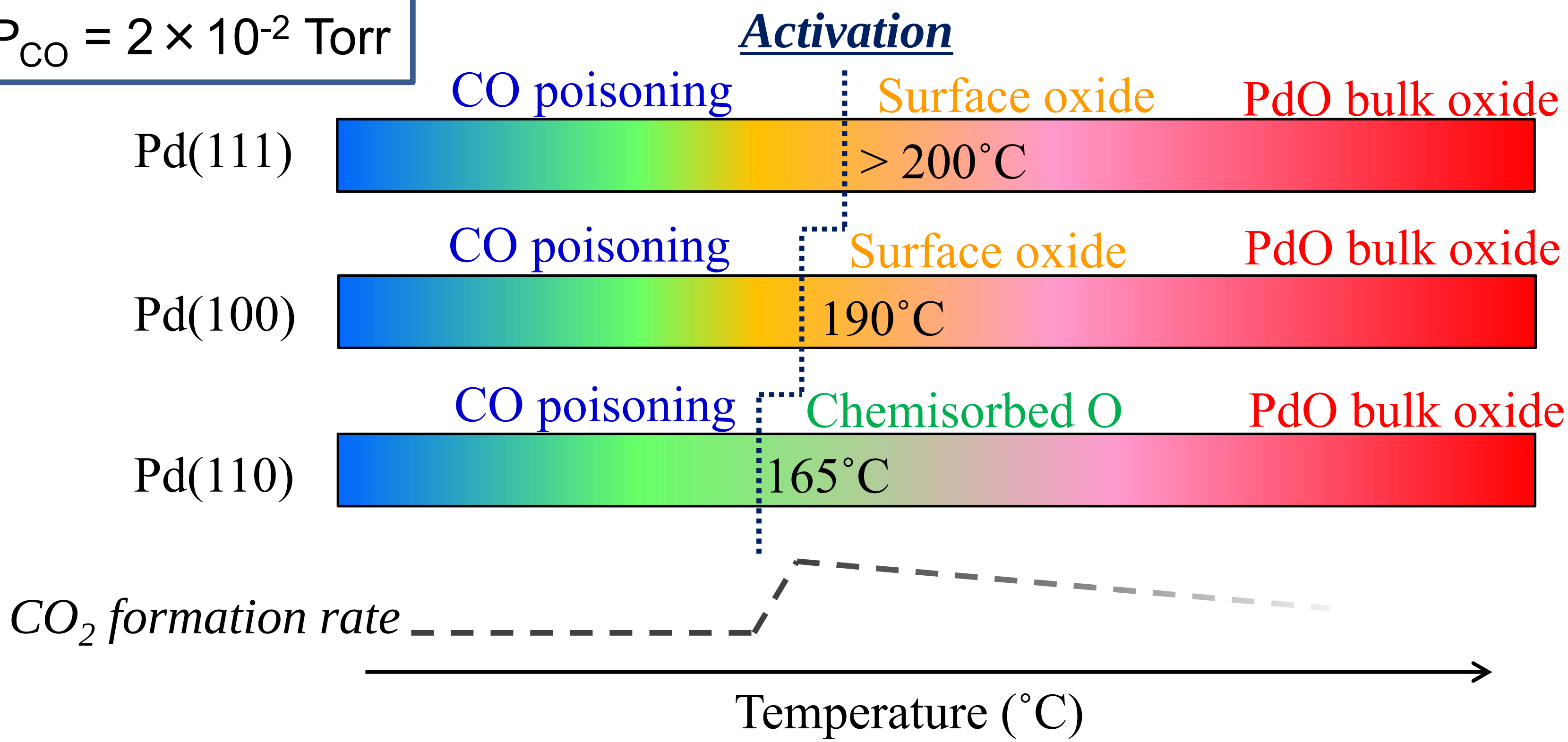


(7 × √3)
Chemisorbed O

J. Phys. Chem. C **117,** 20617 (2013).

CO oxidation on Pd surfaces

$P_{O2} = 2 \times 10^{-1}$ Torr
$P_{CO} = 2 \times 10^{-2}$ Torr



Active Phases for CO oxidation on Pd

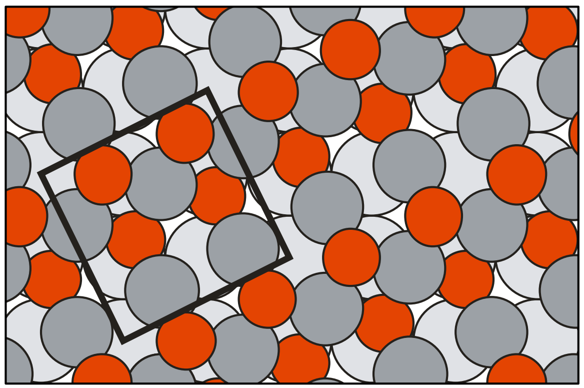
Both **Surface oxide** and **Chem-O** can be reactive depending on surface orientation.

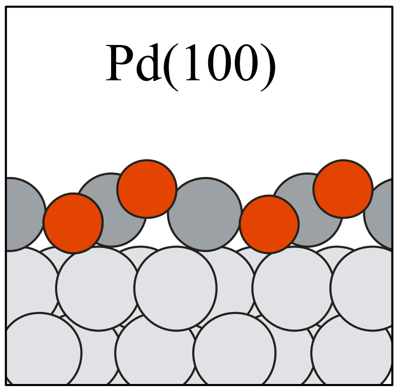
J. Phys. Chem. C **116**, 18691 (2012).
J. Phys. Chem. Lett. **3,** 3182 (2012).
J. Phys. Chem. C **117,** 20617 (2013).

Surface oxide and Chem-O

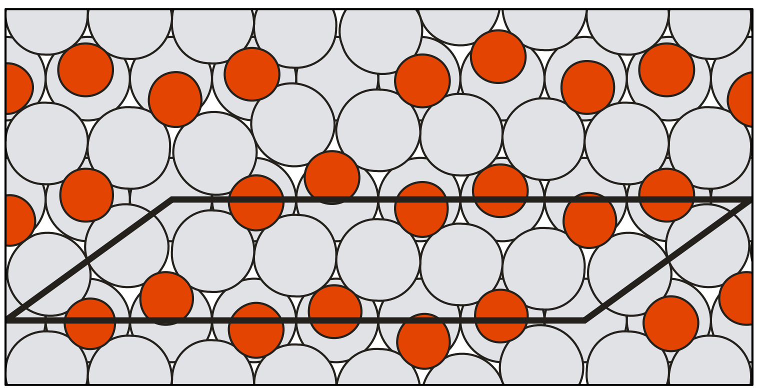
High-density oxygen are accommodated in the active phases in common:

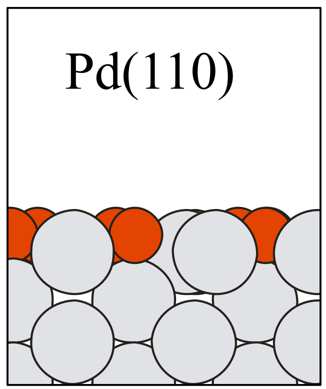
0.8 ML	√6 surface oxide/Pd(111)
1.0 ML	√5 surface oxide/Pd(100)
0.86–0.89 ML	Chemisorbed-O/Pd(110)





<u>Surface oxide</u>
O-M-O tri-layer



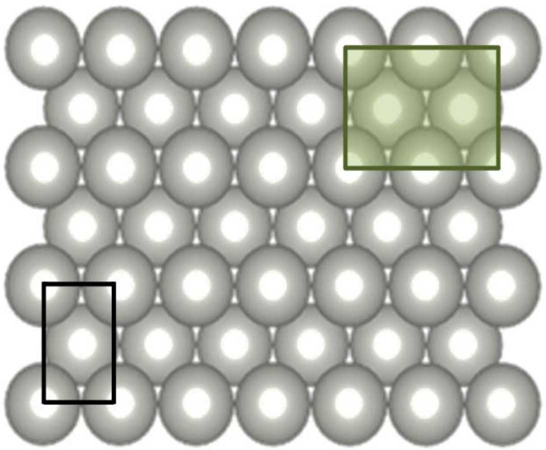


<u>Chemisorbed-O</u>
O-M-O planer layer

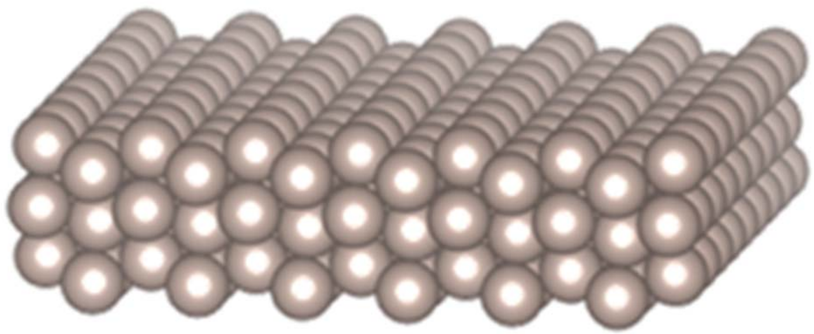
In-situ Observation using AP-XPS

CO oxidation on Ru(10$\bar{1}$0)
under near AP conditions

Ru 44	**Rh 45**	**Pd 46**
Os 76	**Ir 77**	**Pt 78**



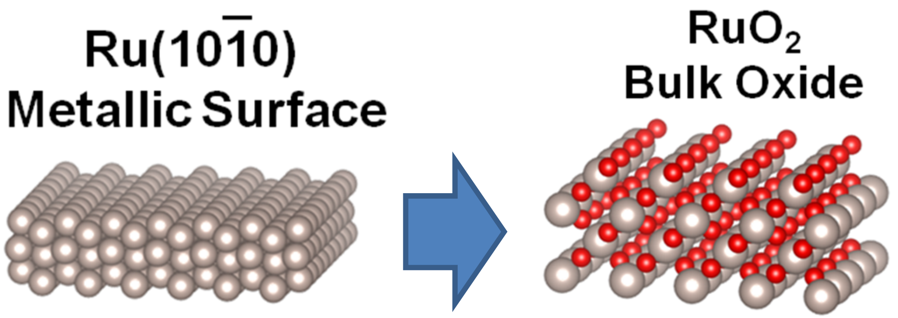
Pd(110)

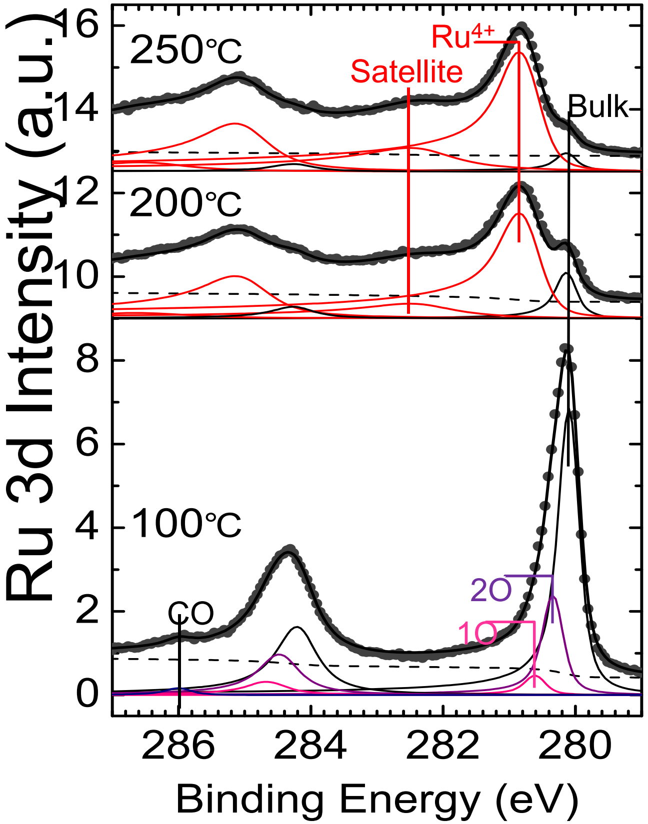


Ru(10$\bar{1}$0)

Similar ridge & trough surface structure

CO oxidation on Ru(10$\bar{1}$0)



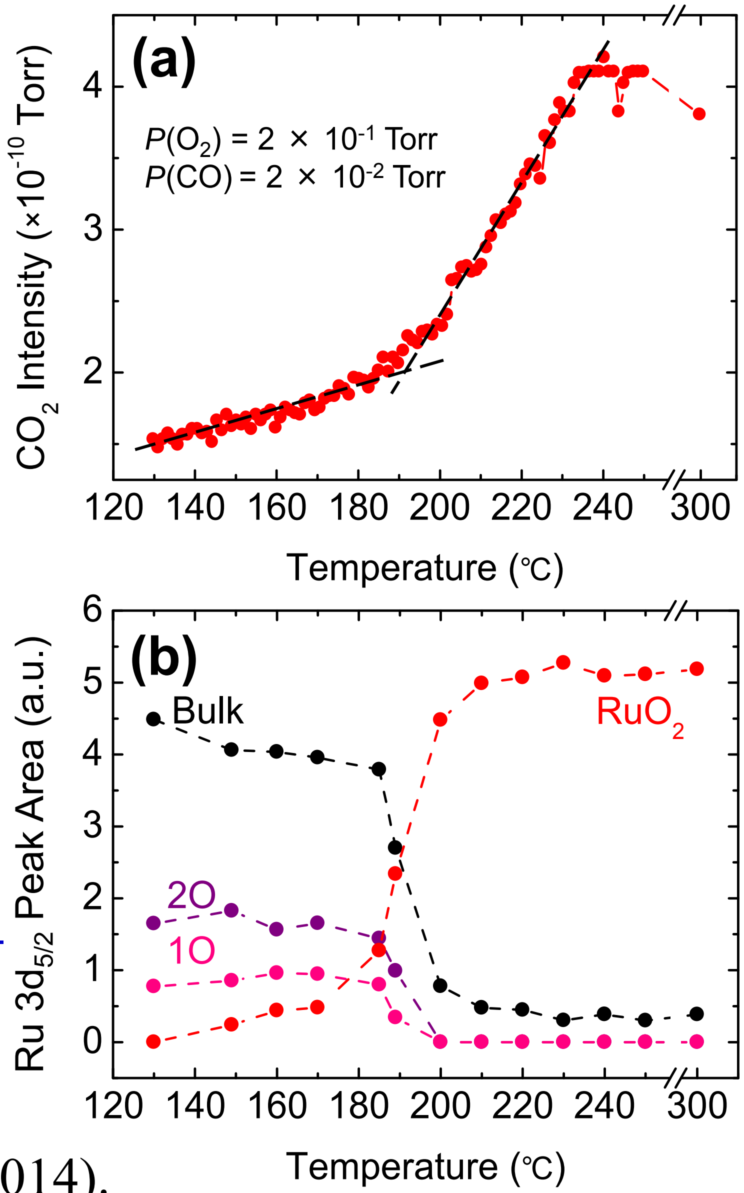


Active surface

RuO_2
bulk oxide

depends on
element of PGM

Surf. Sci. **621,** 128 (2014).



PGM上のCO酸化反応のまとめ

CO酸化反応に活性な触媒表面

- 酸化物
- 化学吸着酸素/金属
  の両方が活性に
  なりうる

- 高密度酸素相が重要

Pt-group metals (PGM)

oxide

Ru 44	Rh 45	Pd 46
Os 76	Ir 77	Pt 78

Chem-O/metal

Keio University

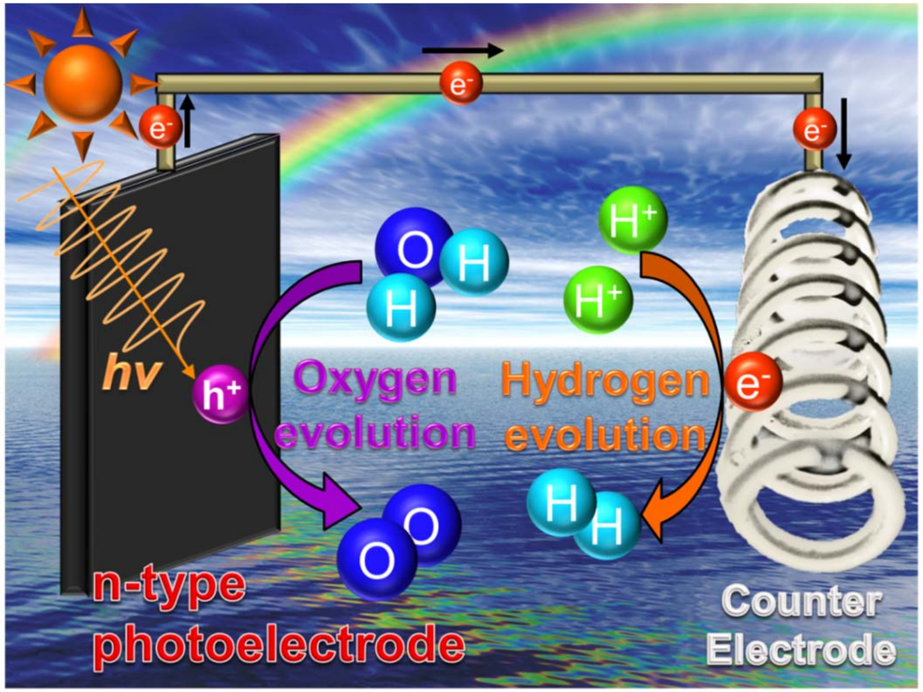
CALAMVS GLADIO FORTIOR 1858

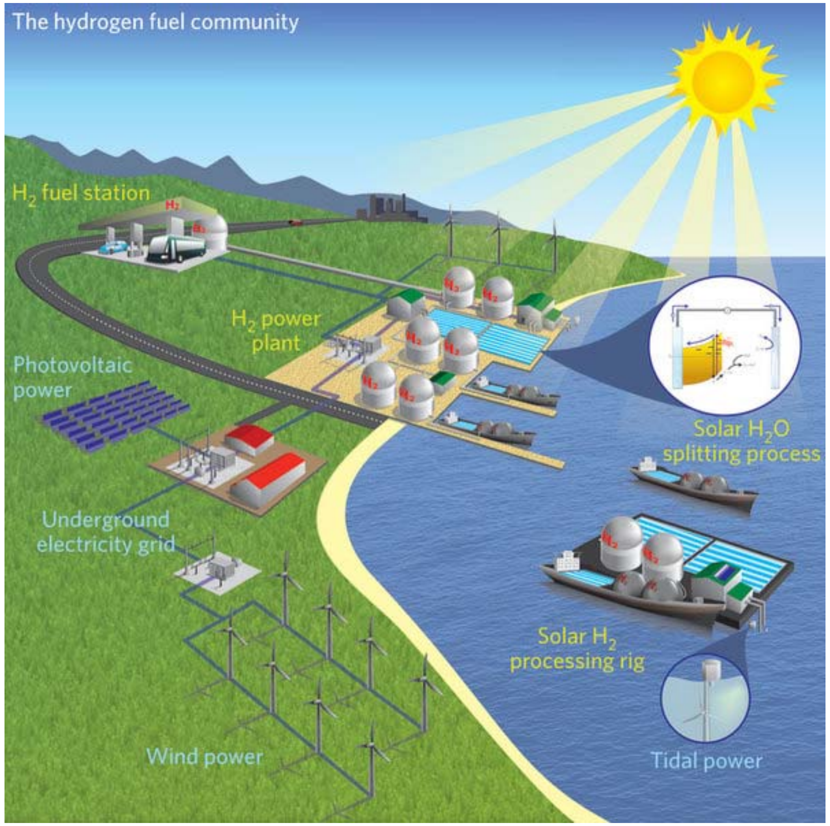
目次

水分解光電極

持続的エネルギー供給を実現するエネルギー変換

半導体を電極として使用





太陽光と水から水素を製造

A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37.

水素を燃料とした循環型社会

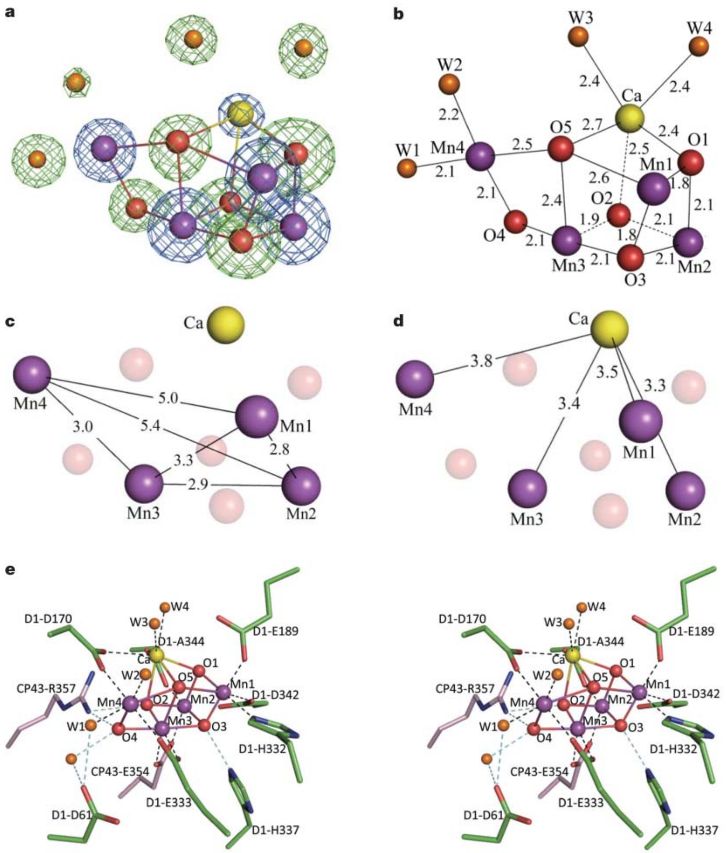
Y. Tachibana *et al.*, *Nat. photonics* **2012**, *6*, 511.

水分解の効率が低く，実用化のためにさらなる高効率化が必要

酸素生成触媒としてのマンガン酸化物

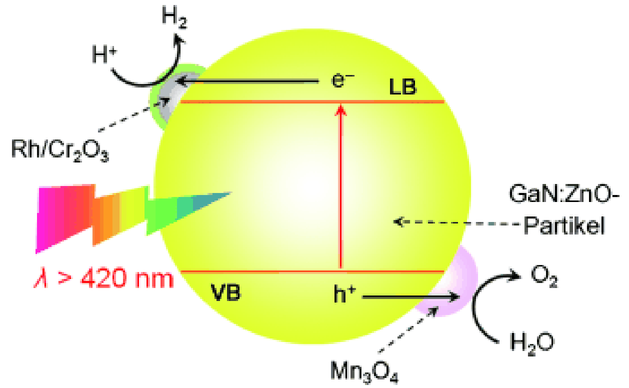
マンガン酸化物は酸素生成の触媒として機能

自然界における酸素生成中心

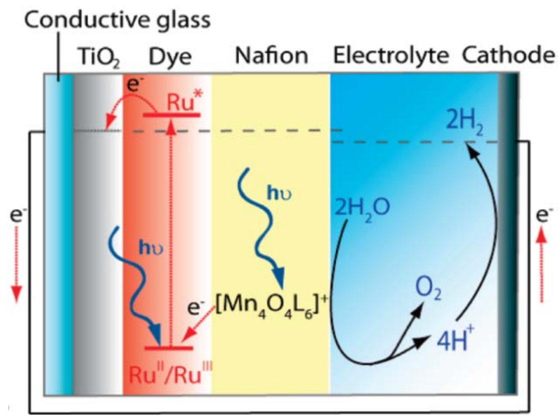


Y. Umeta *et al.*, *Nature* **2011**, *473*, 55.

光触媒や光電極系における酸素生成助触媒



K. Maeda *et al.*, *Angew. Chem. Int. Ed.* **2010**, *122*, 4190.

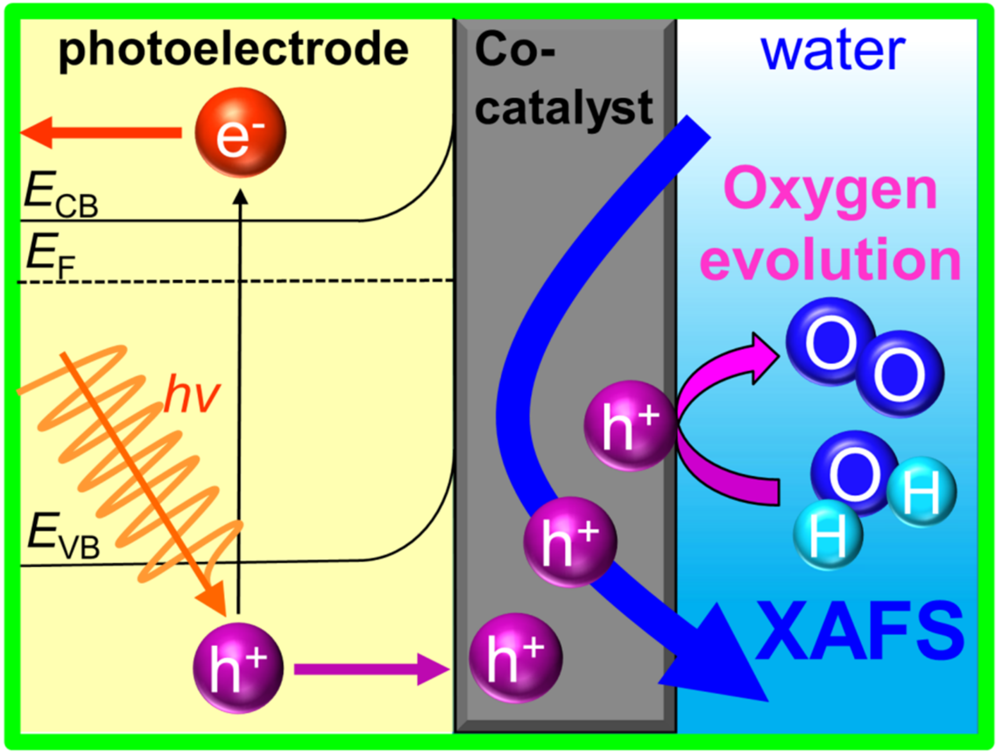


R. Brimblecombe *et al.*, *J. Am. Chem. Soc.* **2010**, *132*, 2892.

酸素生成触媒としてのマンガン酸化物

水分解反応時の光電極上の助触媒の化学状態を
in-situ電気化学XAFS法によって測定

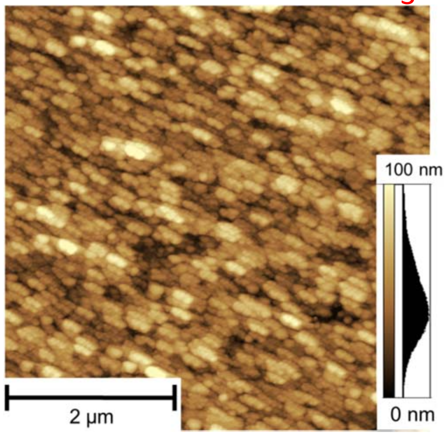
実作動条件下における助触媒の電子状態から
助触媒への励起ホール移動と光電極活性の相関



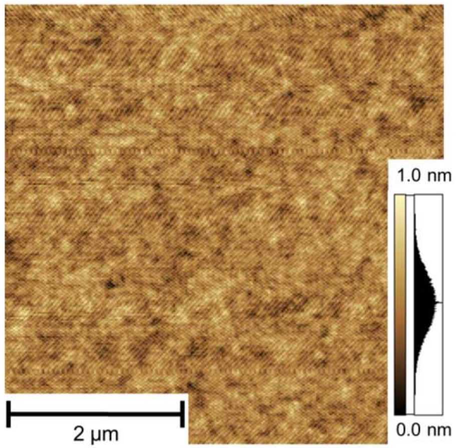
Mn-oxide/Nb:SrTiO$_3$光電極の電流-電位曲線

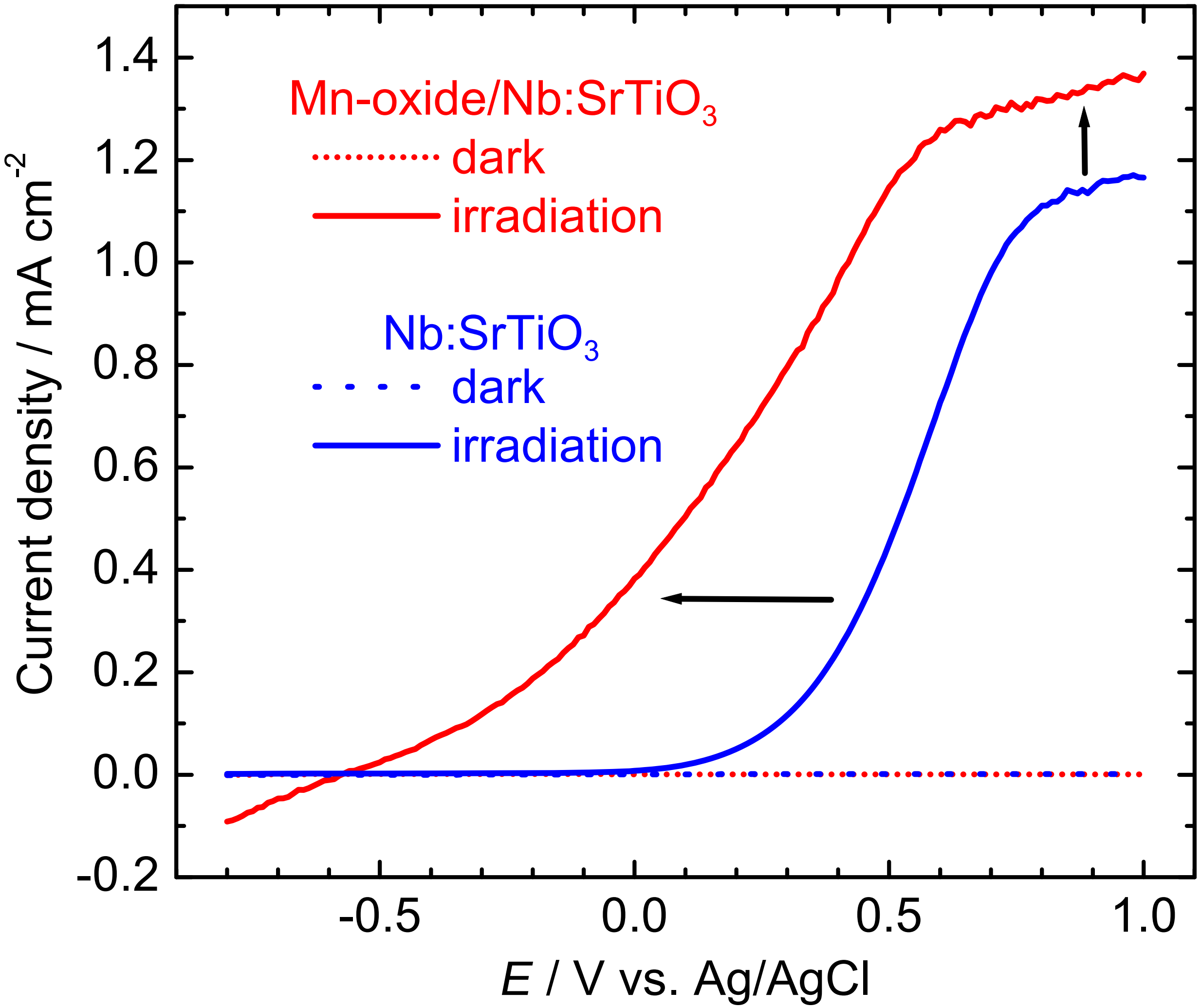
光電着前と光電着後のサンプルの光電極活性を比較

Mn-oxide/Nb:SrTiO$_3$



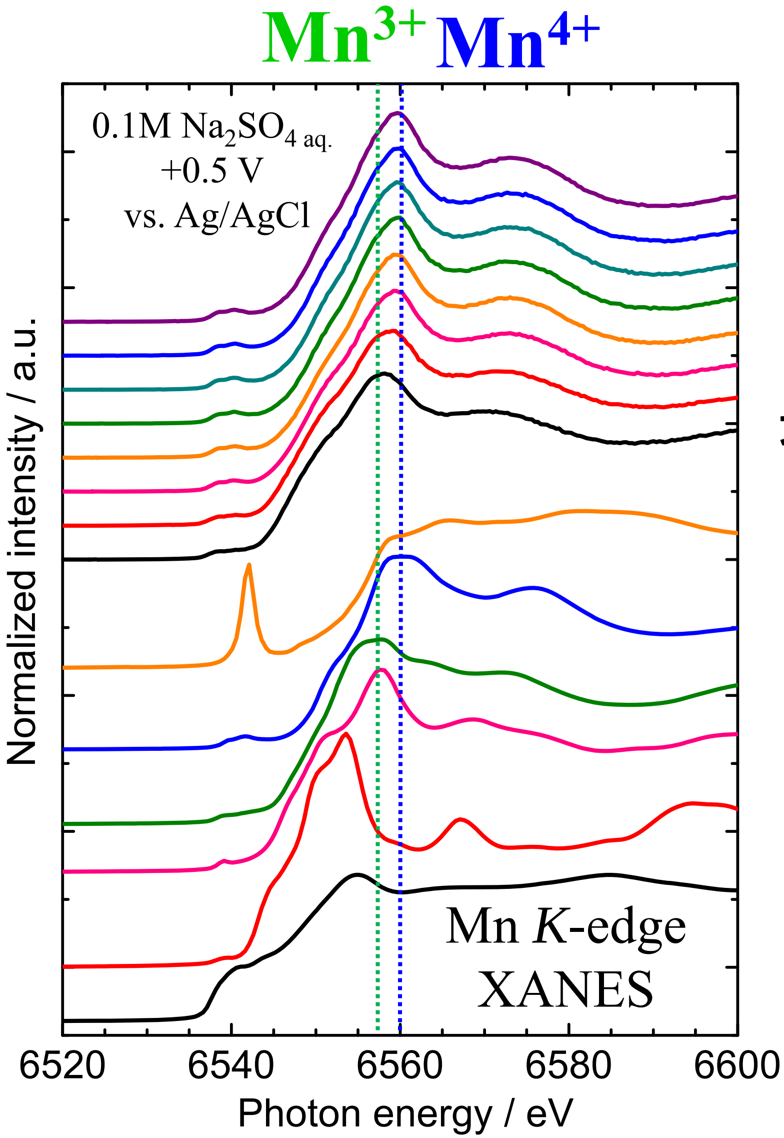
Nb:SrTiO$_3$

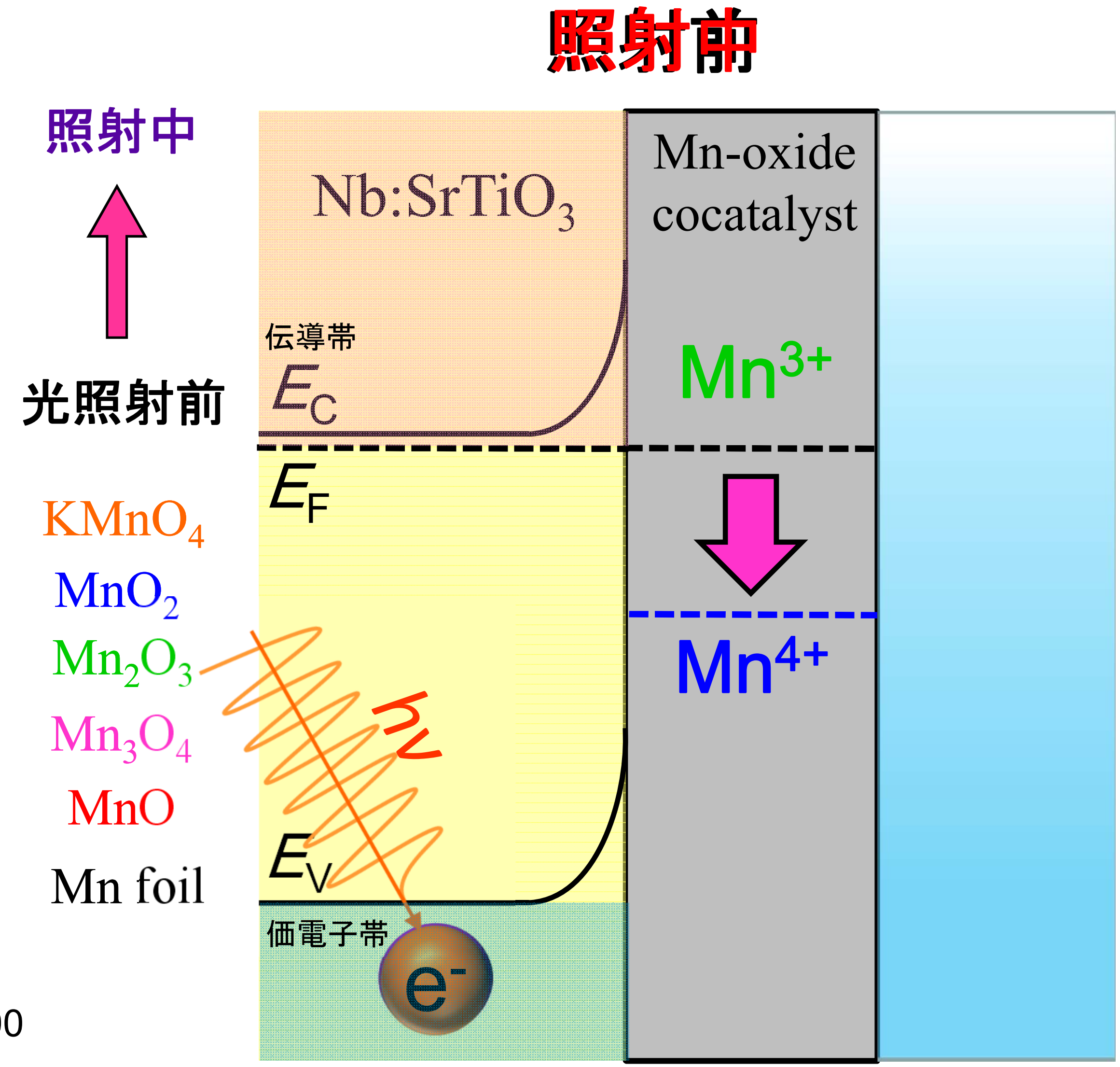




マンガン酸化物の担持による効率的な水分解を確認

光照射下でのMn-*K*端XANESスペクトルの変化

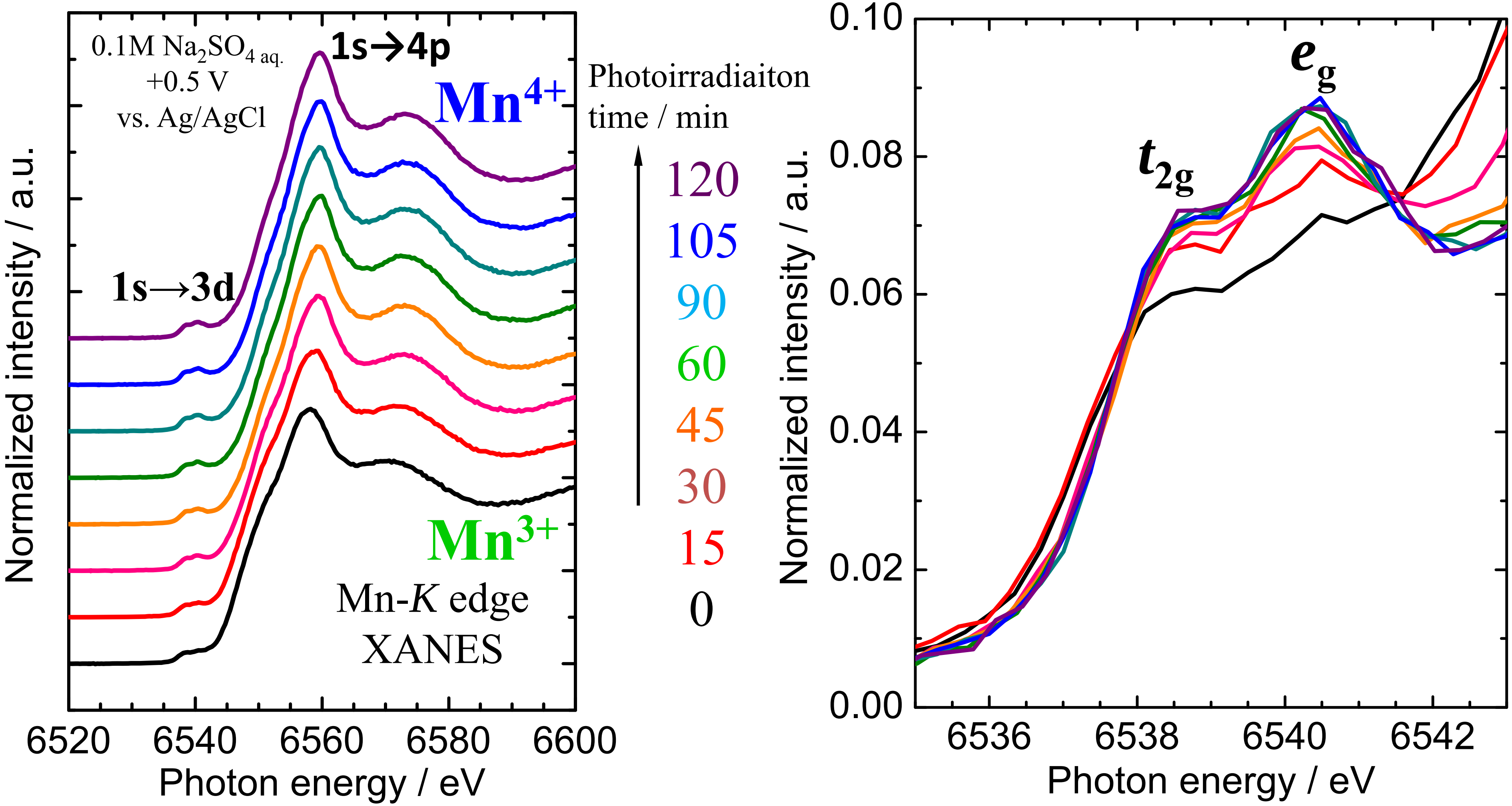




励起ホールによるマンガン酸化物の酸化を観測

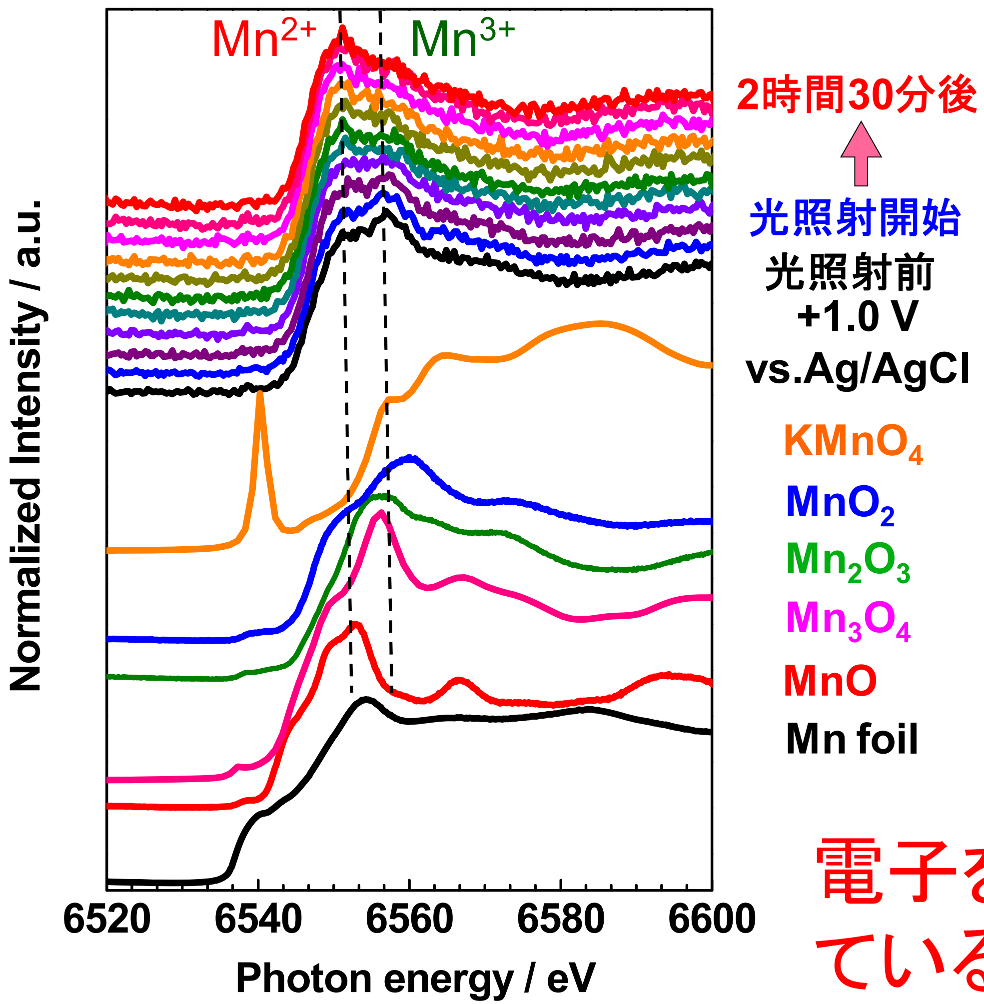
光照射に伴うMn 1s-3d遷移の変化

光照射時間が増えるに従い，1s-3d遷移の強度が増加

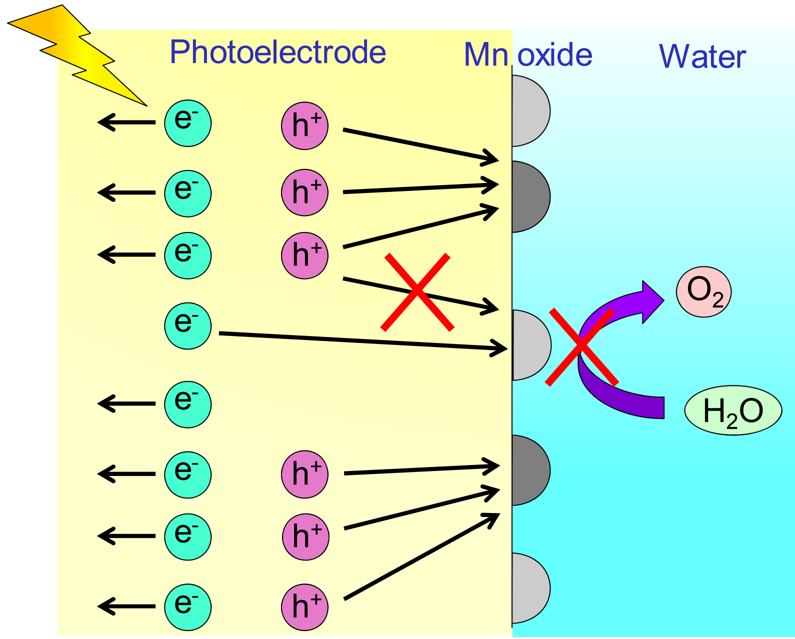


1s-3d遷移から、Mnのe_g軌道にホールが入る様子が分かる

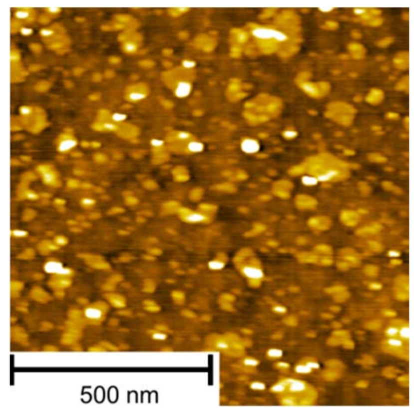
助触媒粒子が表面に分散している場合



一部の酸化マンガン粒子には逆のキャリアである励起電子が移動

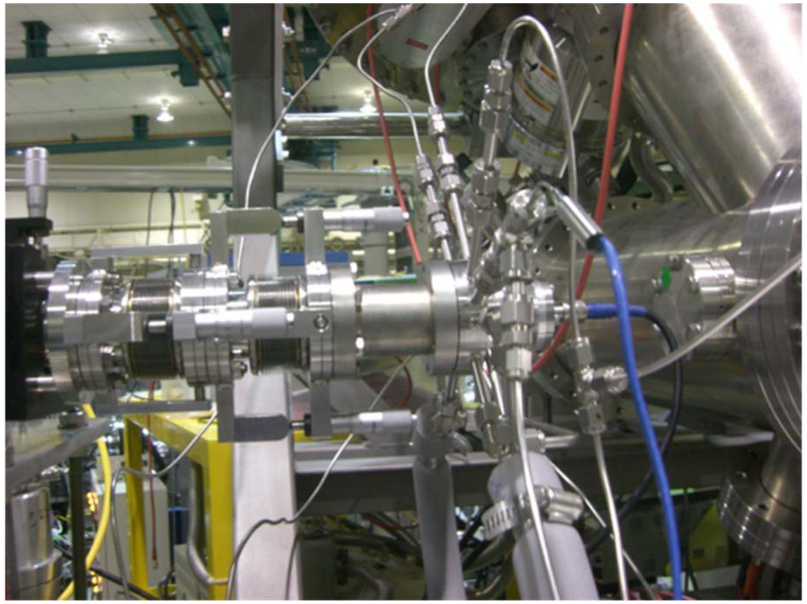


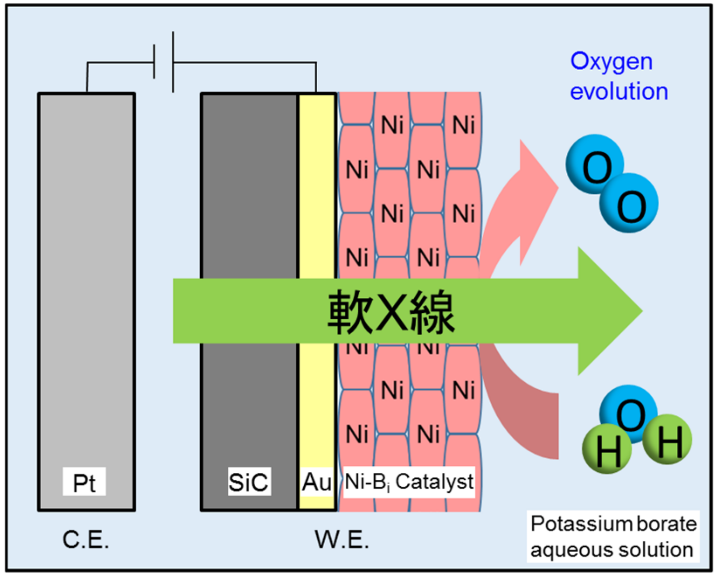
電子を受取っている助触媒粒子がある!!

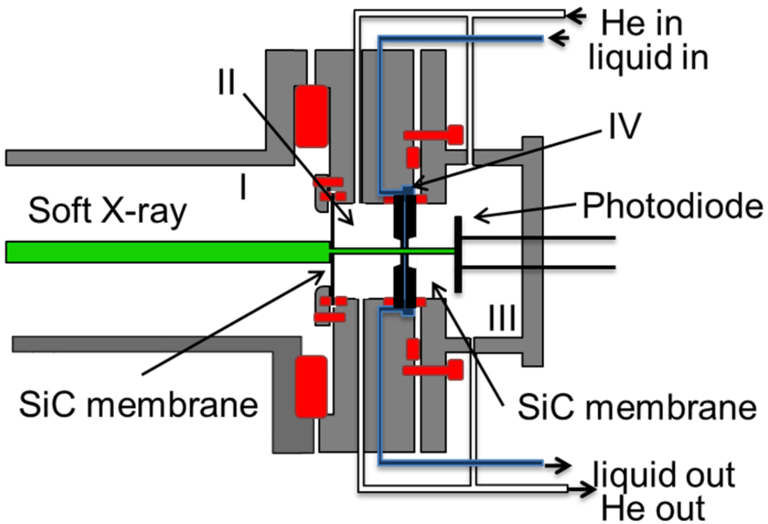


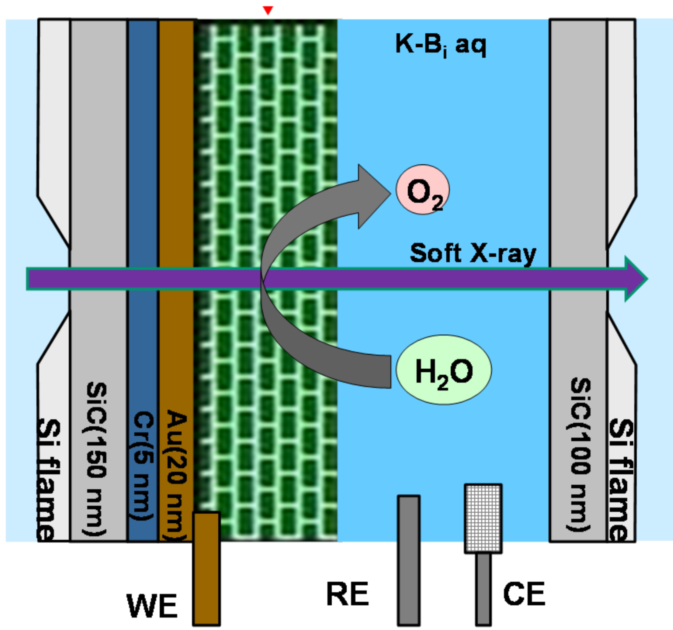
M. Yoshida, *et al.*, *Chem. Commun.* **49,** 7848 (2013).

透過型軟X線電気化学XAFSによる酸素発生触媒のその場観測



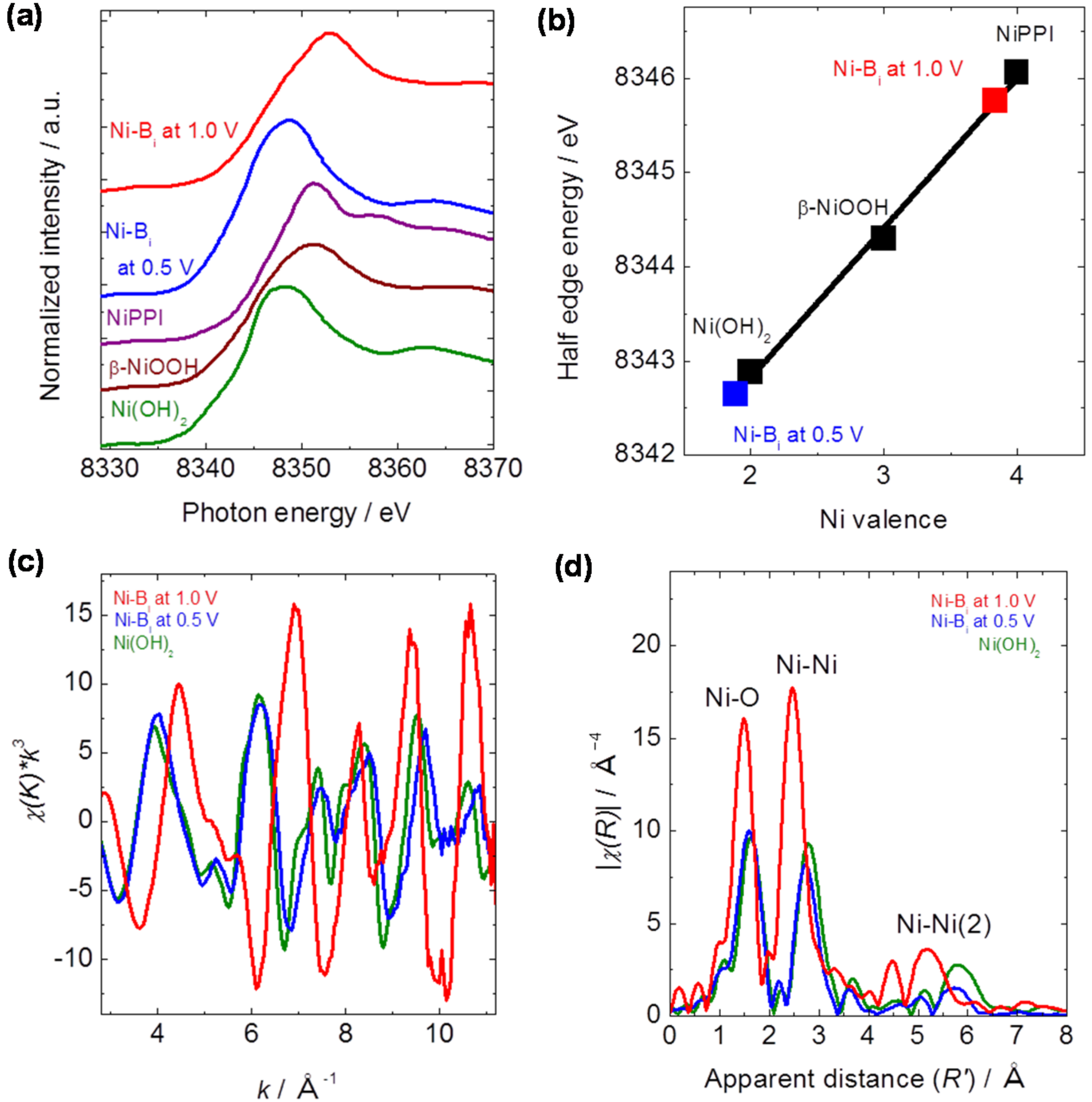




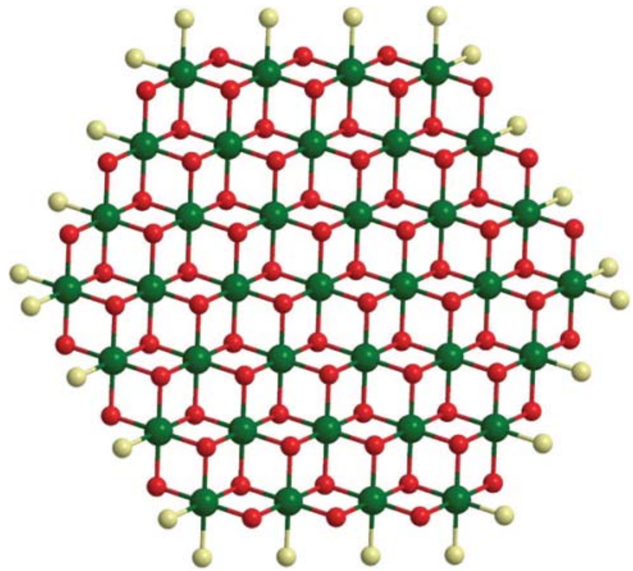


ホウ酸ニッケル(Ni-B_i)電極触媒

水分解時の酸素生成触媒を電気化学XAFS法によって測定



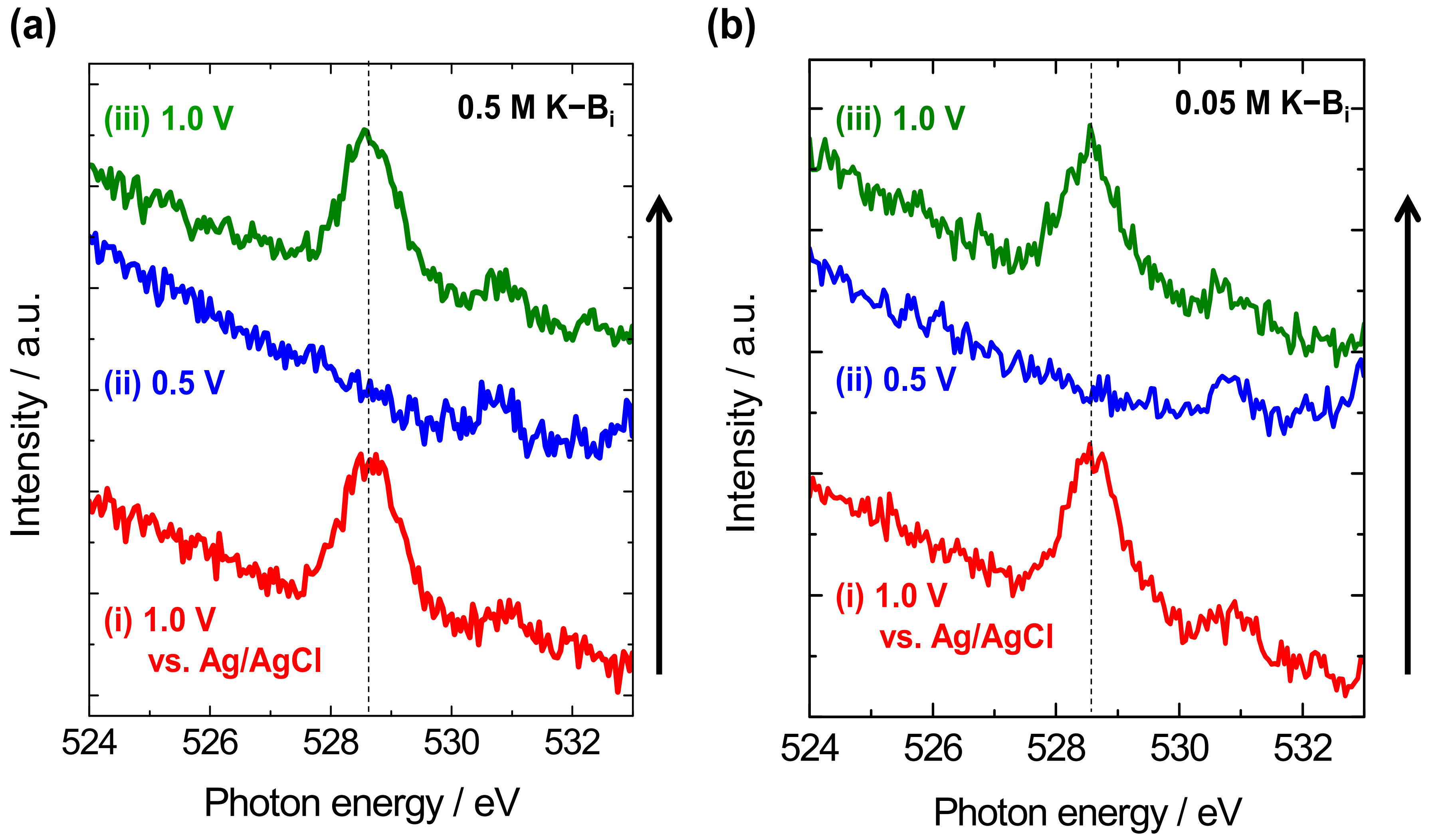
Ni-B_iクラスター



1.0 V印加でNiが高酸化状態

酸素はどうなっているのか？

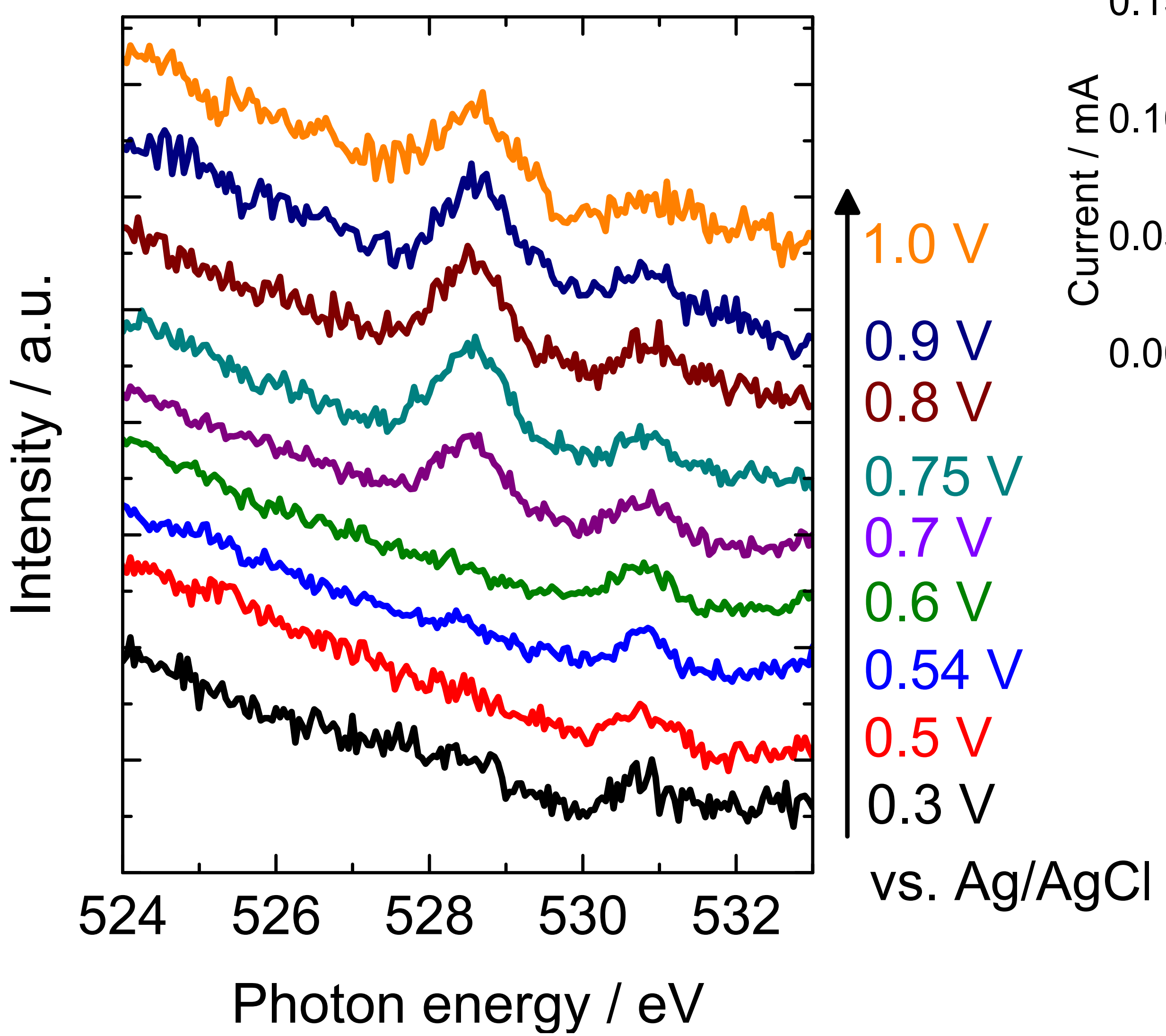
ホウ酸ニッケル(Ni-B$_i$)電極触媒の*in-situ* O-K端XAFSスペクトル



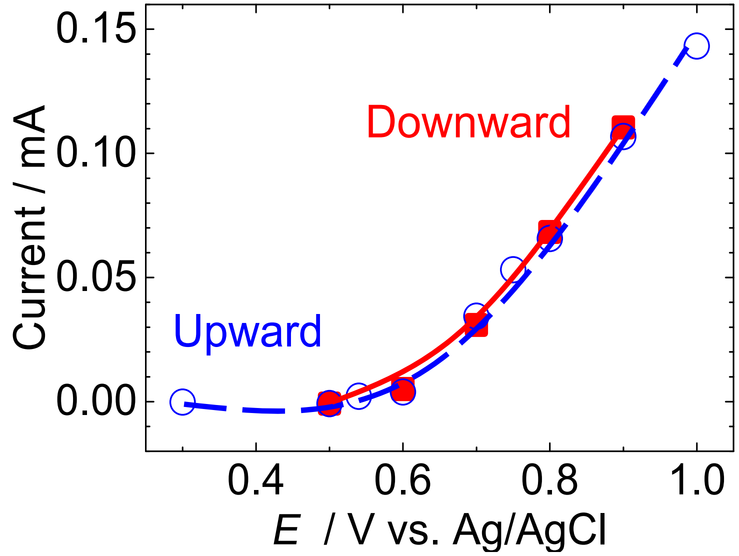
1.0 Vのとき水分解の活性が生じるので、
そのとき生じる化学種を捉えることができた

ホウ酸ニッケル(Ni-B$_i$)電極触媒の*in-situ* O-K端XAFSスペクトル

in-situ O-K端XAFS



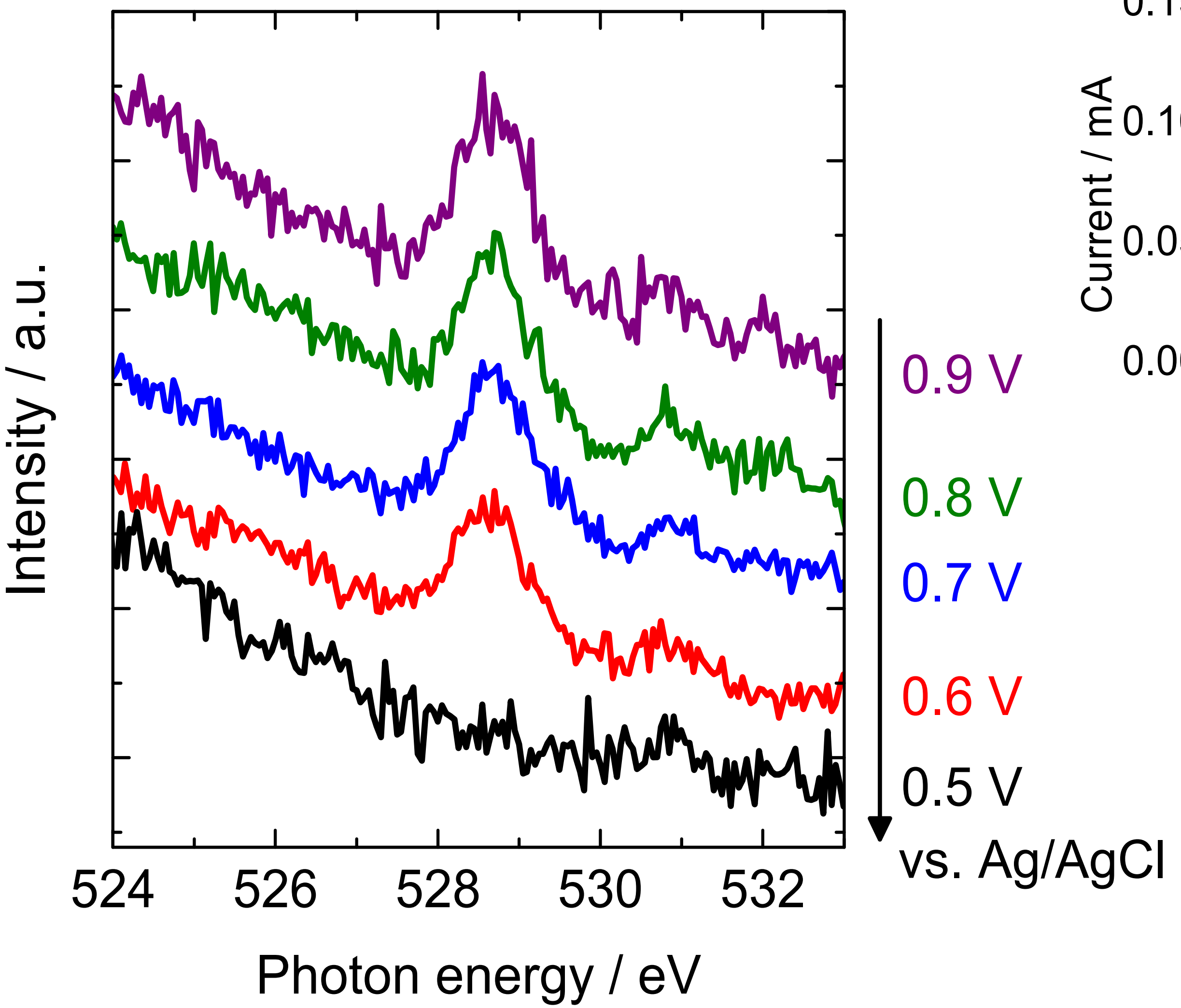
酸素発生電流



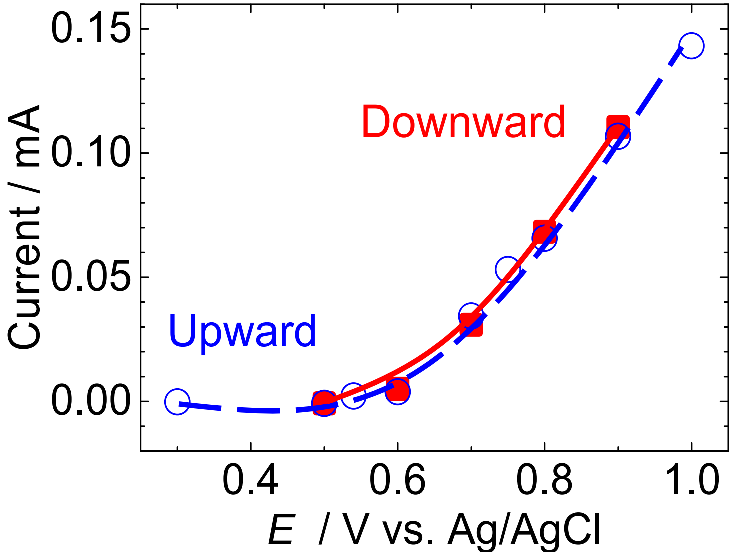
酸素発生電流と共に現れるピーク

ホウ酸ニッケル(Ni-B$_i$)電極触媒の*in-situ* O-K端XAFSスペクトル

in-situ O-K端XAFS

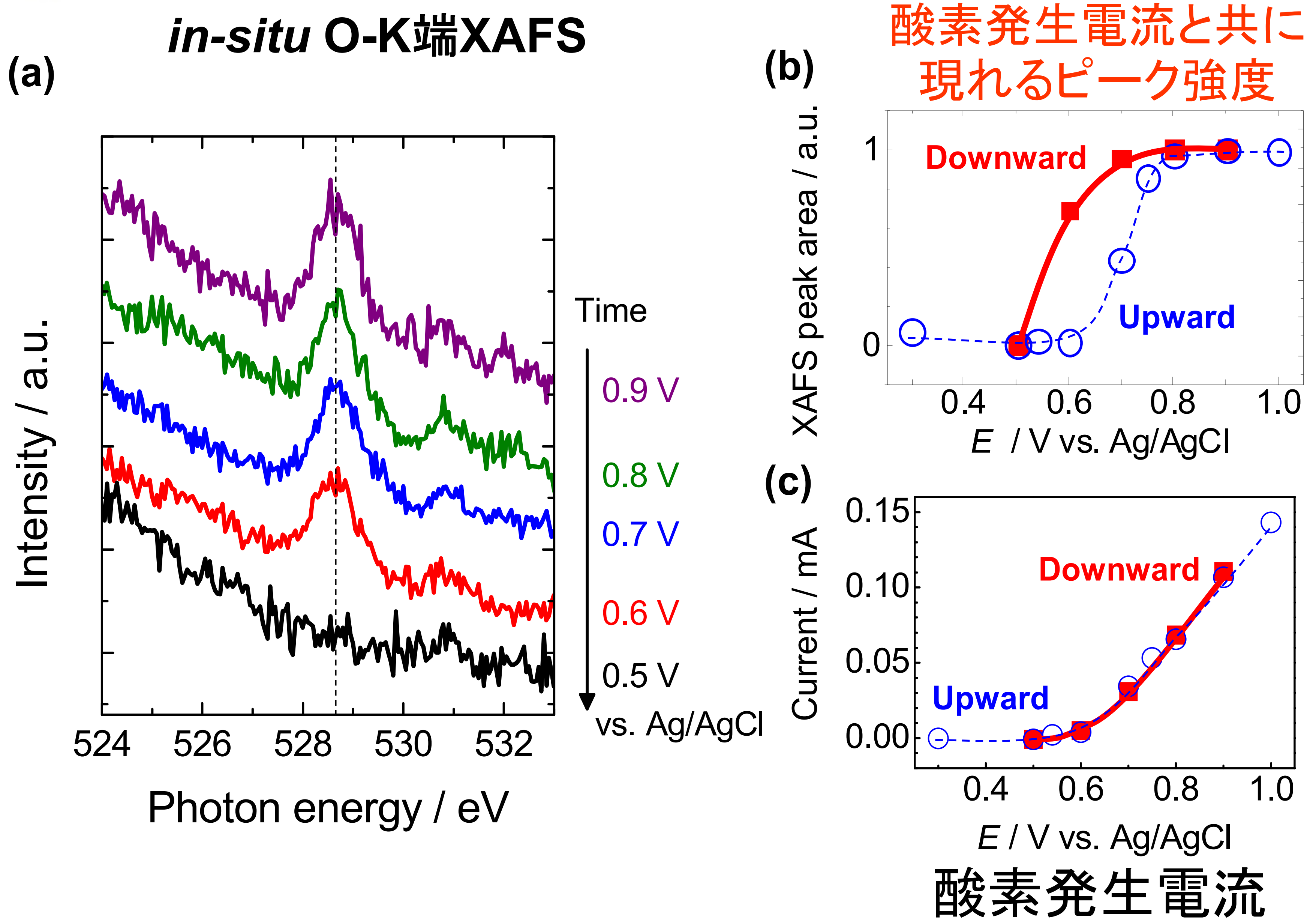


酸素発生電流

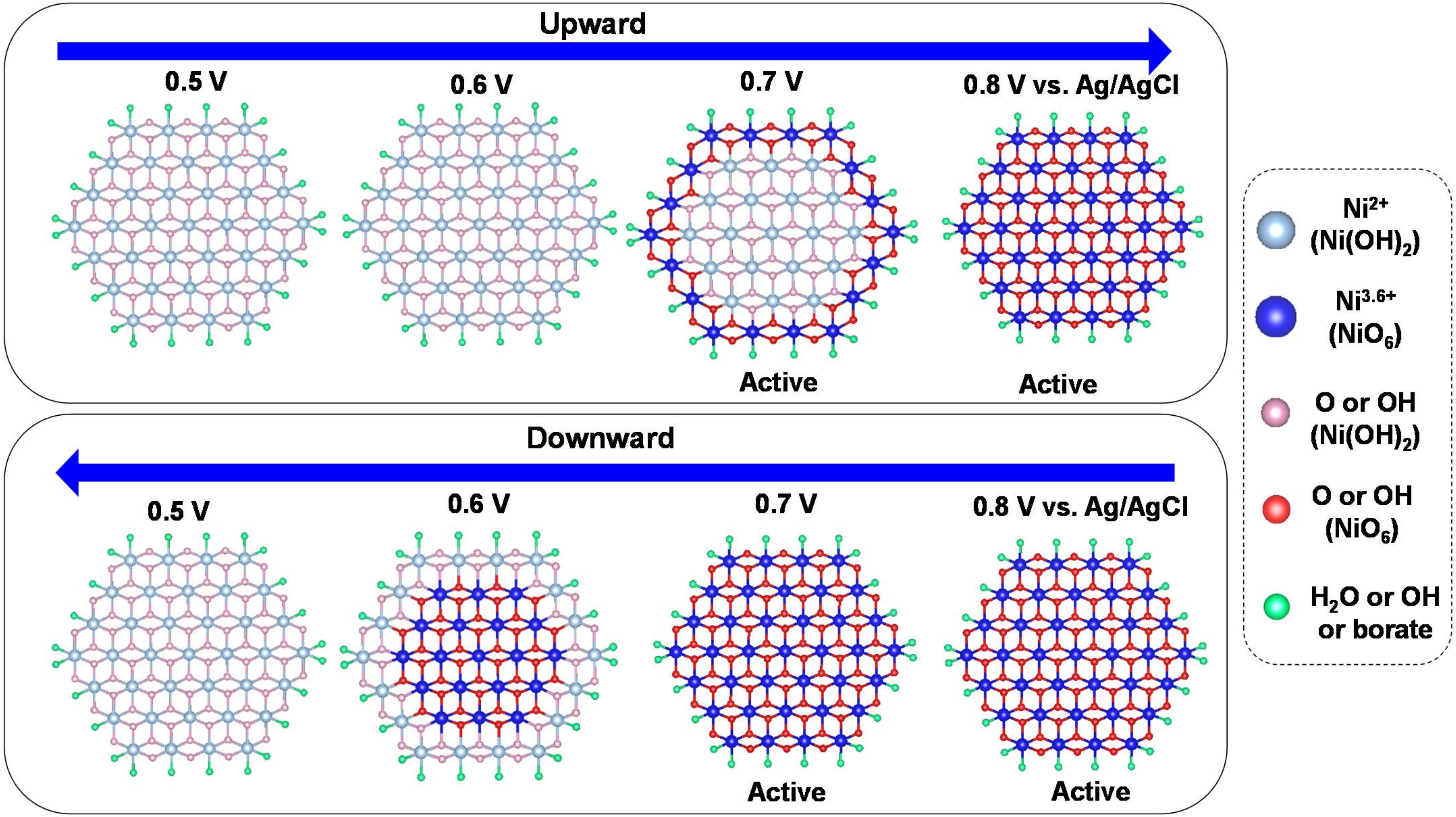


酸素発生電流と共に現れるピーク

ホウ酸ニッケル(Ni-B$_i$)電極触媒の*in-situ* O-K端XAFSスペクトル



ホウ酸ニッケル(Ni-B$_i$)電極触媒の活性化モデル



クラスターの外側が活性サイト

M. Yoshida et al., *J. Phys. Chem. C*, **119**, 19279 (2015).

おわりに

■ 実作動条件に近い環境下で反応が進行している触媒をin-situで観測する軟X線分光手法を紹介した.

■ 応用例として、CO酸化反応に活性な白金族金属表面の活性相および水分解に活性な酸素生成電極触媒の化学状態について紹介した.

■ 触媒が機能しているとき始めてできるものがあるので、実在環境で動いているものの情報を得ることが反応機構の理解に重要である.

学理から実用触媒の開拓へ

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