第37回無機材料に関する最近の研究成果発表会
@住友会館(泉ガーデンタワー 42 階)

原子精度精密合成技術を駆使した高活性水分解光触媒の創製

東京理科大学理学部応用化学科
東京理科大学総合研究機構光触媒国際研究センター

根岸雄一

東京理科大学　根岸研究室

教授 1名，助教 1名，博士研究員 1名，学生 21名

根岸研究室実験室

根岸研究室学生居室

実験室＋居室 ＝ 90 m^2

金属ナノクラスター

- 新規な機能の発現
- 顕著な原子数依存性

例）一連の金クラスター水溶液の写真　J. Am. Chem. Soc., 2005.

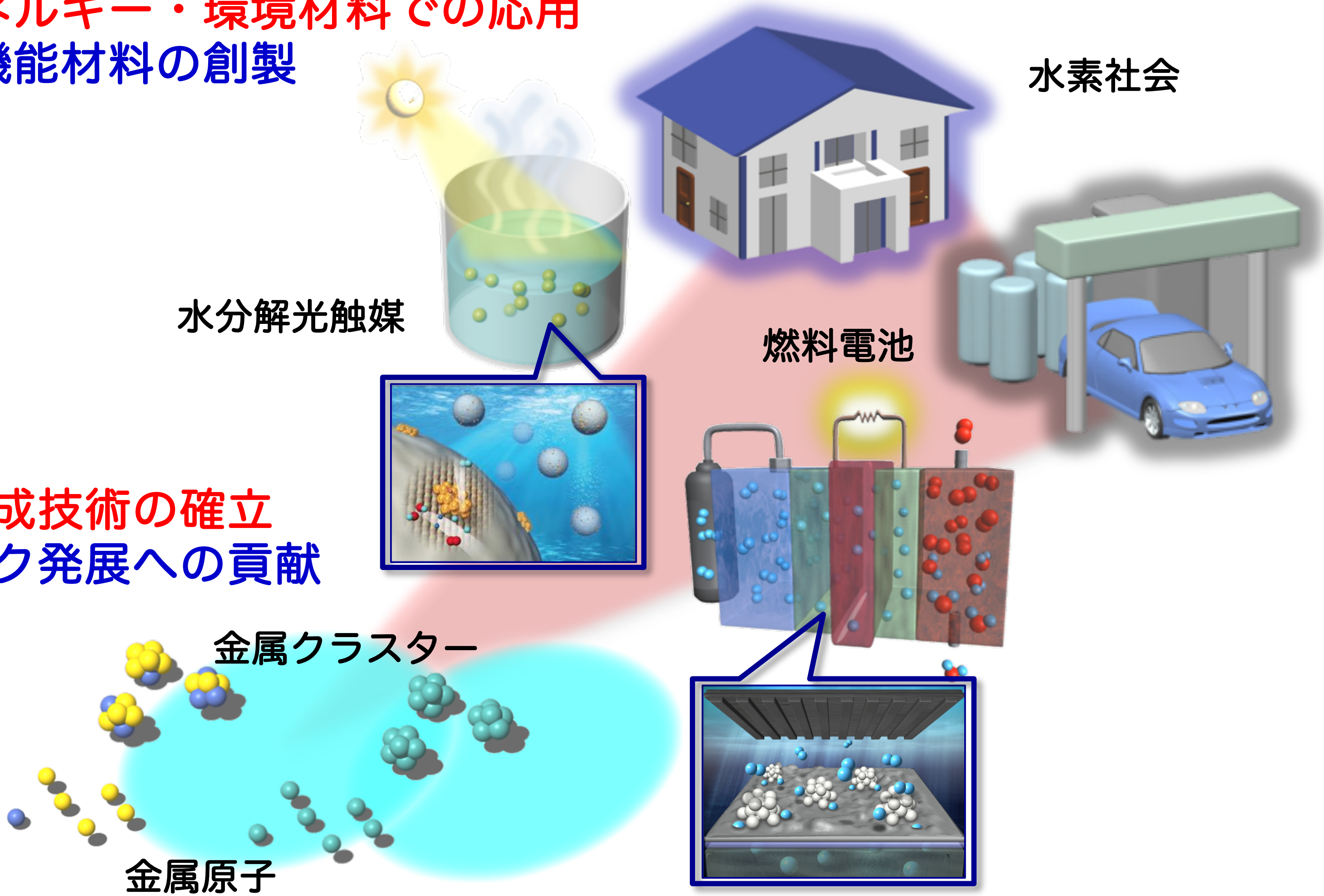
機能性ナノ物質の構成単位

研究目標

ナノテクノロジーサイドより
次世代エネルギー社会移行へ貢献

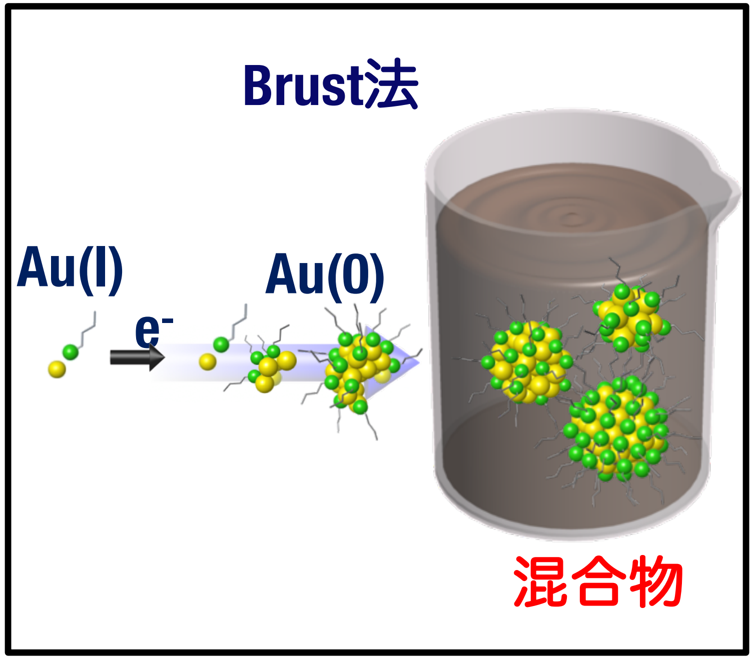
②エネルギー・環境材料での応用
→高機能材料の創製

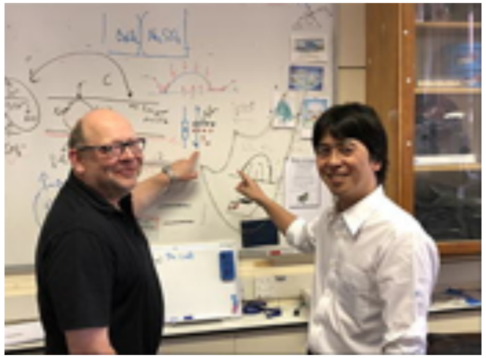
①精密合成技術の確立
→ナノテク発展への貢献



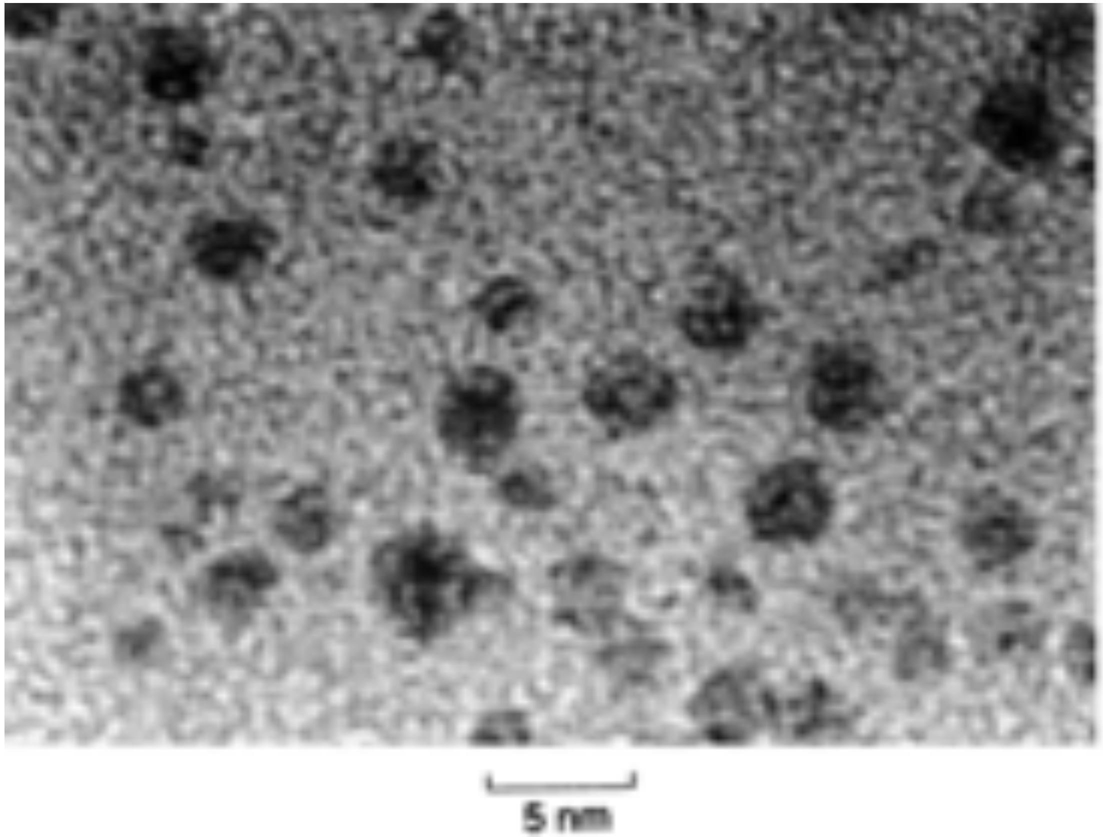
化学合成の可能な金属クラスター

チオラート保護金ナノクラスター





Brust教授
（リバプール大学）

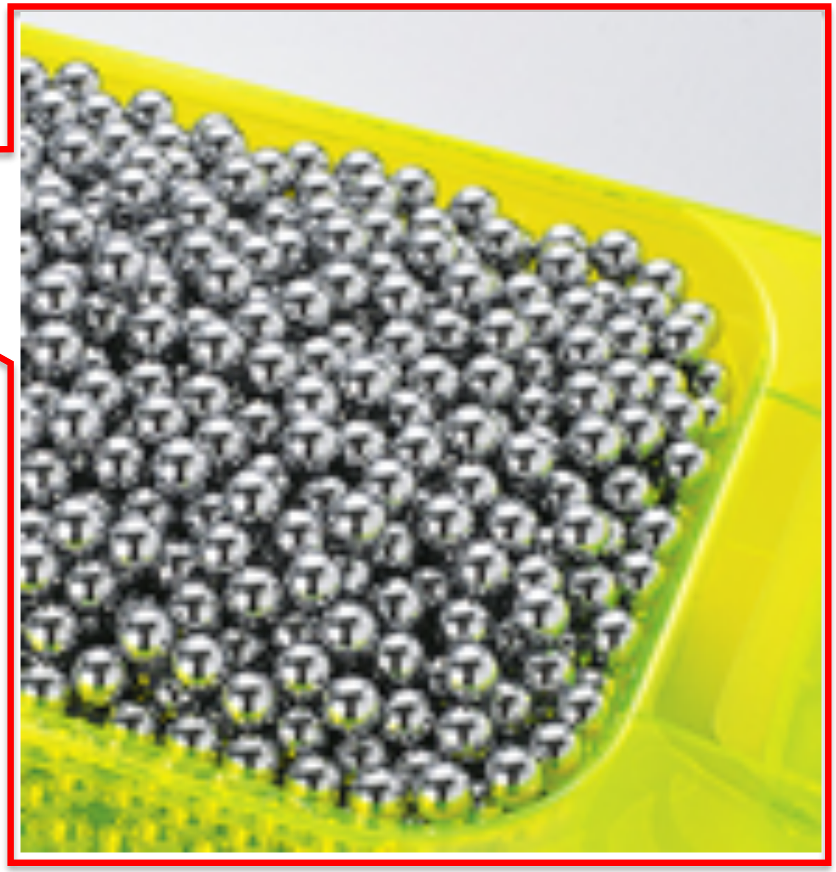


M. Brust,
J. Chem. Soc., Chem. Commun, 1994.

原子の凝集を原子精度で制御するということ

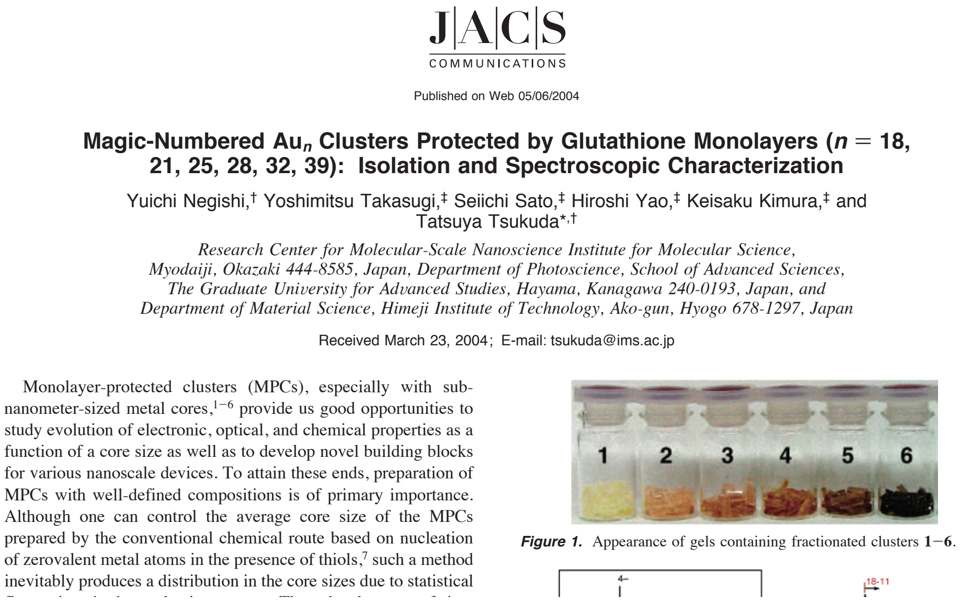
地球を1mとすると…

原子はパチンコ玉ぐらい



日本中にパチンコ玉をばらまいた後、
それらを全て同じ数でビー玉サイズに凝集させるようなものである！

分子研時代の代表的仕事



J|A|C|S COMMUNICATIONS

Published on Web 05/06/2004

Magic-Numbered Au_n Clusters Protected by Glutathione Monolayers (n = 18, 21, 25, 28, 32, 39): Isolation and Spectroscopic Characterization

Yuichi Negishi,[†] Yoshimitsu Takasugi,[‡] Seiichi Sato,[‡] Hiroshi Yao,[‡] Keisaku Kimura,[‡] and Tatsuya Tsukuda*[,†]

Research Center for Molecular-Scale Nanoscience Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, Department of Photoscience, School of Advanced Sciences, The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, Japan, and Department of Material Science, Himeji Institute of Technology, Ako-gun, Hyogo 678-1297, Japan

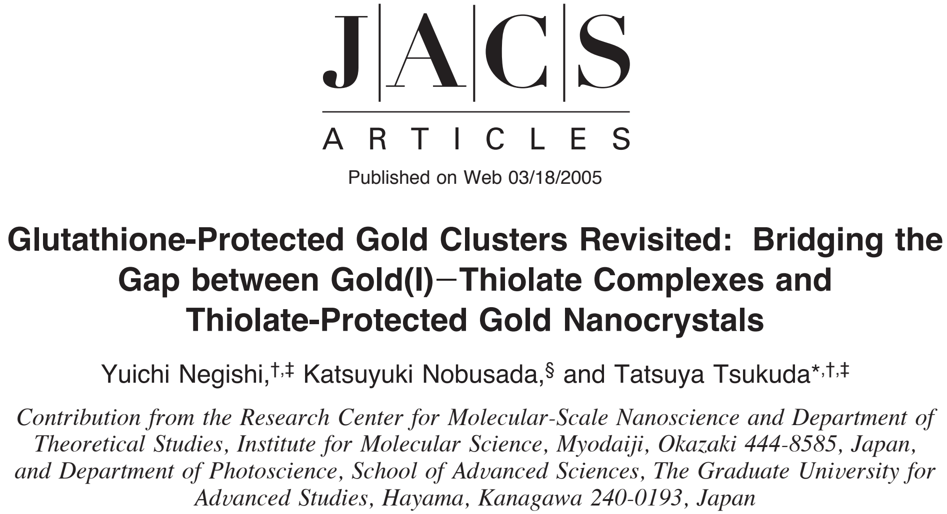
Received March 23, 2004; E-mail: tsukuda@ims.ac.jp

Monolayer-protected clusters (MPCs), especially with sub-nanometer-sized metal cores,[1−6] provide us good opportunities to study evolution of electronic, optical, and chemical properties as a function of a core size as well as to develop novel building blocks for various nanoscale devices. To attain these ends, preparation of MPCs with well-defined compositions is of primary importance. Although one can control the average core size of the MPCs prepared by the conventional chemical route based on nucleation of zerovalent metal atoms in the presence of thiols,[7] such a method inevitably produces a distribution in the core sizes due to statistical

Figure 1. Appearance of gels containing fractionated clusters **1**−**6**.

J. Am. Chem. Soc, 2004.

Cited 504 times (Google scholar)



J|A|C|S ARTICLES

Published on Web 03/18/2005

Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)−Thiolate Complexes and Thiolate-Protected Gold Nanocrystals

Yuichi Negishi,[†,‡] Katsuyuki Nobusada,[§] and Tatsuya Tsukuda*[,†,‡]

Contribution from the Research Center for Molecular-Scale Nanoscience and Department of Theoretical Studies, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, and Department of Photoscience, School of Advanced Sciences, The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, Japan

J. Am. Chem. Soc, 2005.

Cited 1219 times (Google scholar)

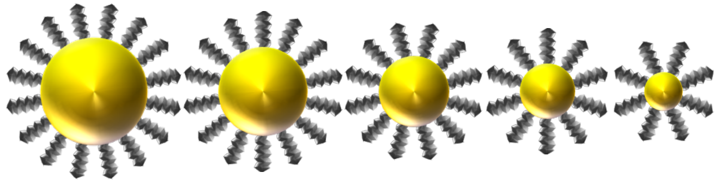
東京理科大学理学部応用化学科への異動

研究室立ち上げ時のラボホームページ

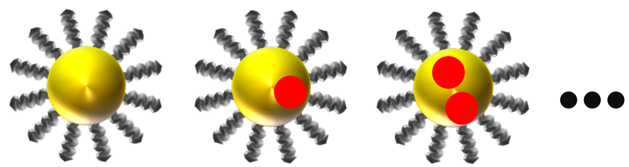
東京理科大学での取り組み

極限的精密合成技術（ナノテクノロジー）の確立

金属コアのサイズ制御



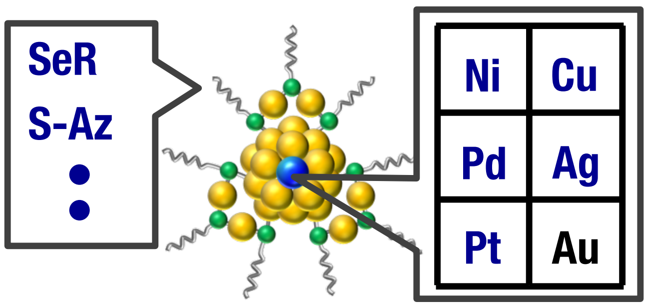
金属コアの組成制御



高機能化

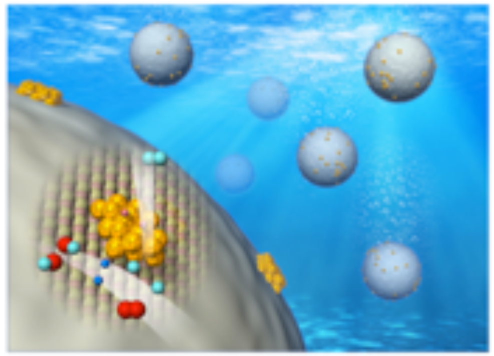
エネルギー・
環境材料への活用

高機能ナノ物質の創製



エネルギー・
環境材料への活用

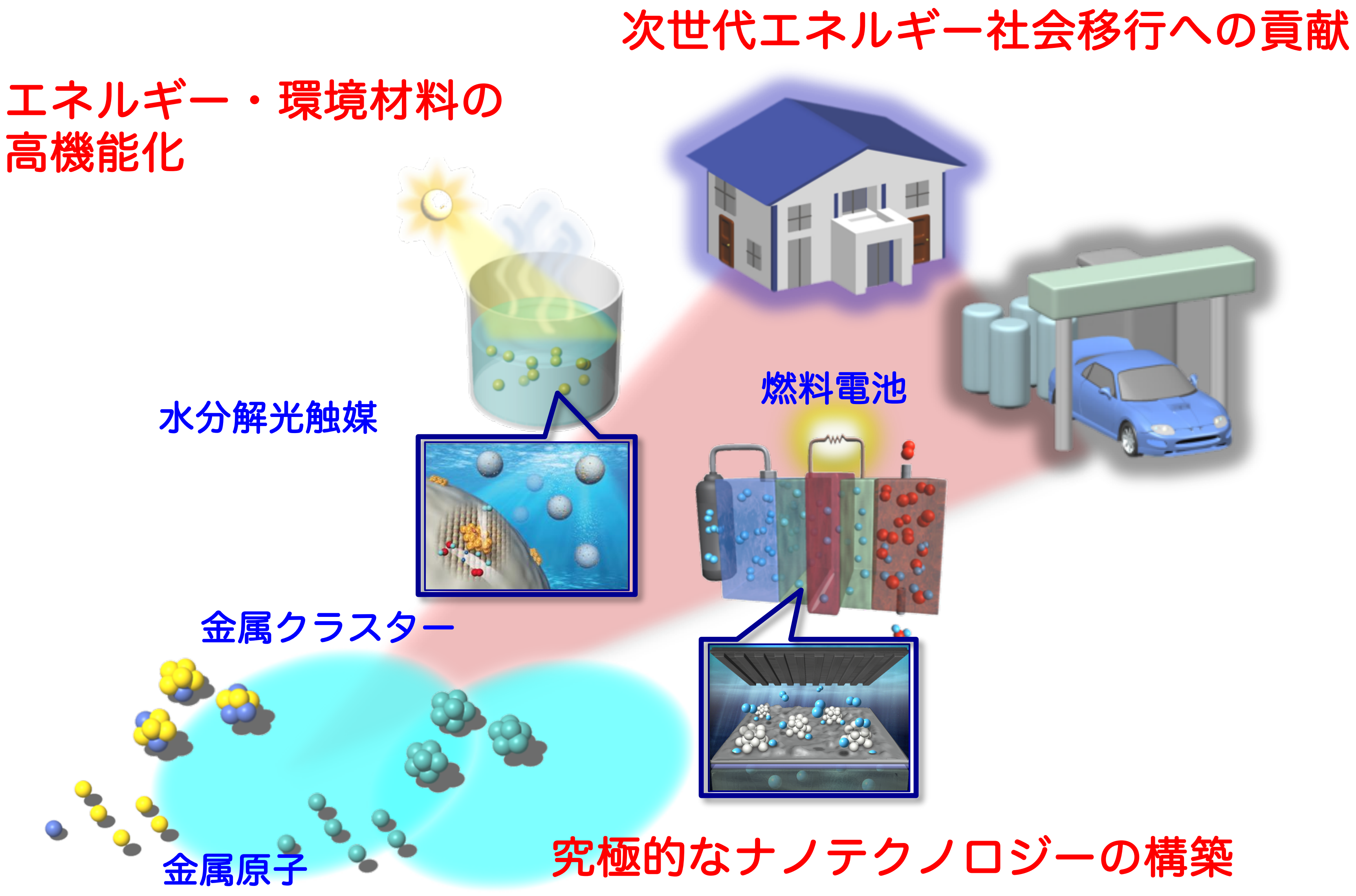
高機能材料の創製



最近の総説例

Coord. Chem. Rev.(Accounts) 2016. J. Phys. Chem. Lett. (Perspective) 2014. Phys. Chem. Chem. Phys.(Perspective) 2013.
Phys. Chem. Chem. Phys.(Perspective) 2016. Bull. Chem. Soc. Jpn.(Award Accounts) 2014.
Chem. Rec.(Personal Accounts) 2017. APL Mater. (Perspective) 2017.

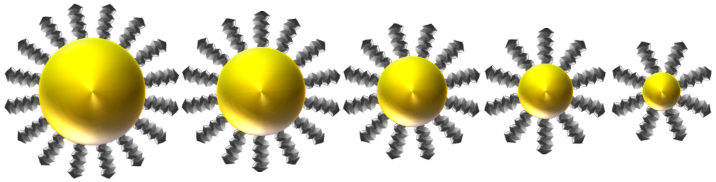
我々の目指しているゴール



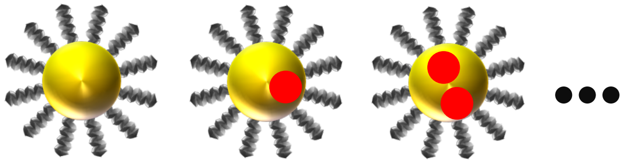
我々の研究

極限的精密合成技術（ナノテクノロジー）の確立

金属コアのサイズ制御



金属コアの組成制御

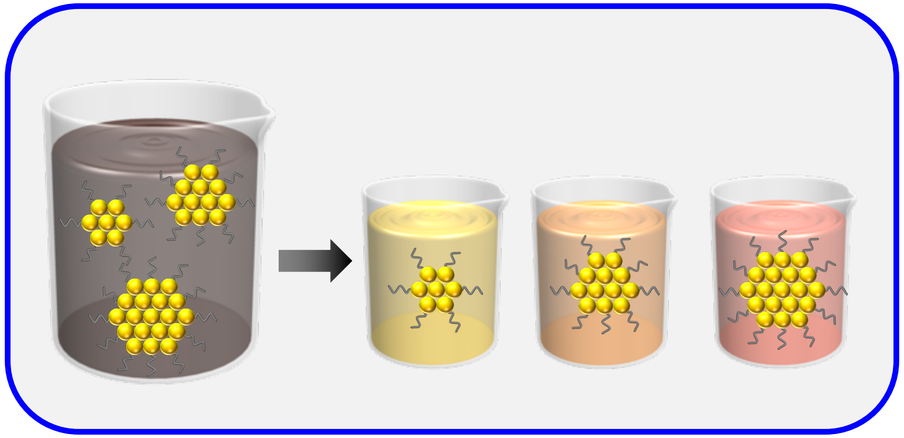


最近の総説例

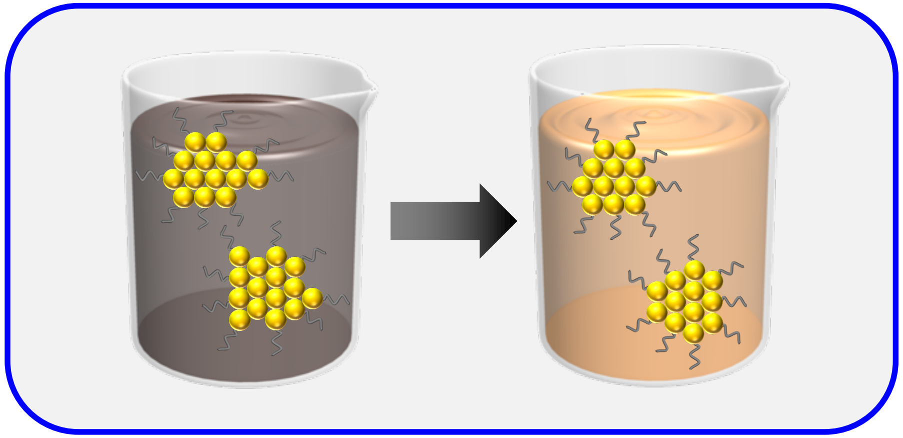
Coord. Chem. Rev.(Accounts) 2016. J. Phys. Chem. Lett. (Perspective) 2014.   Phys. Chem. Chem. Phys.(Perspective) 2013.
Phys. Chem. Chem. Phys.(Perspective) 2016. Bull. Chem. Soc. Jpn.(Award Accounts) 2014.
Chem. Rec.(Personal Accounts) 2017. APL Mater. (Perspective) 2017.

精密合成法

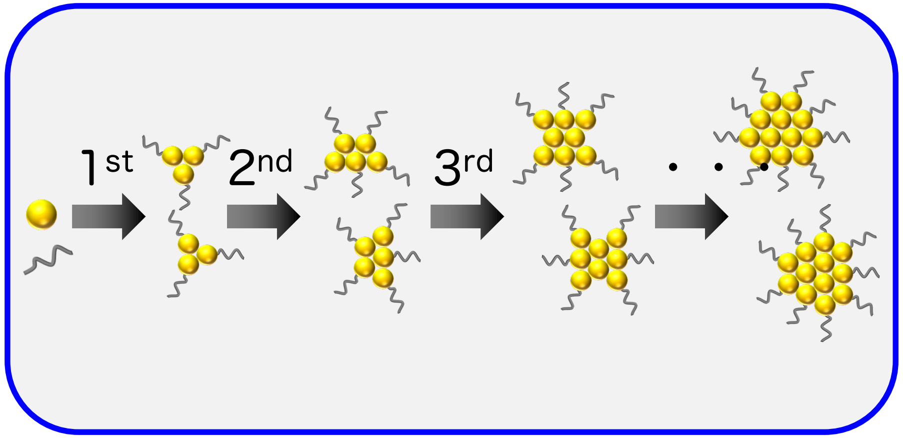
①高分解能分離



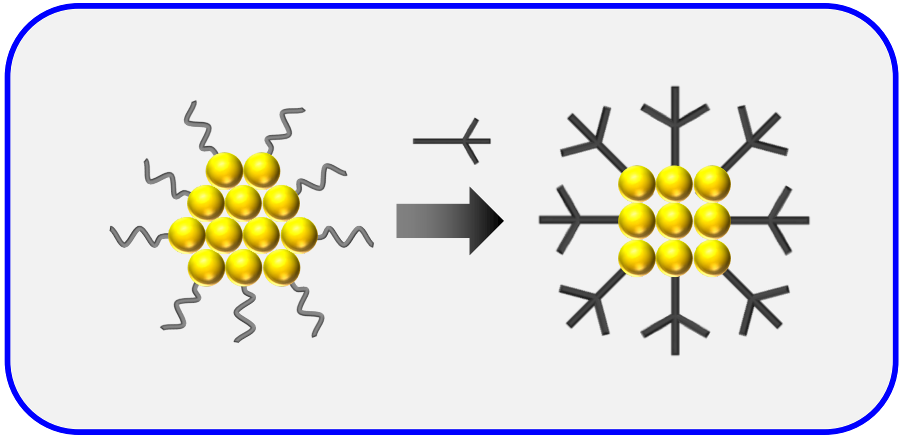
②サイズ収束



③成長速度制御



④配位子交換

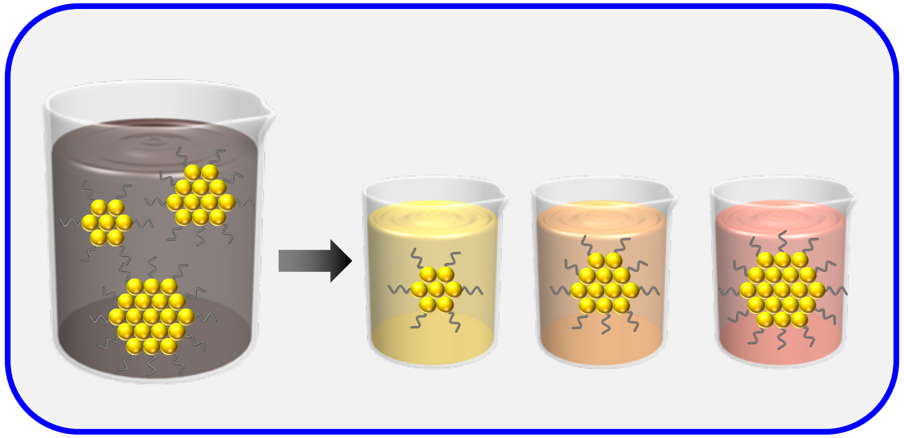


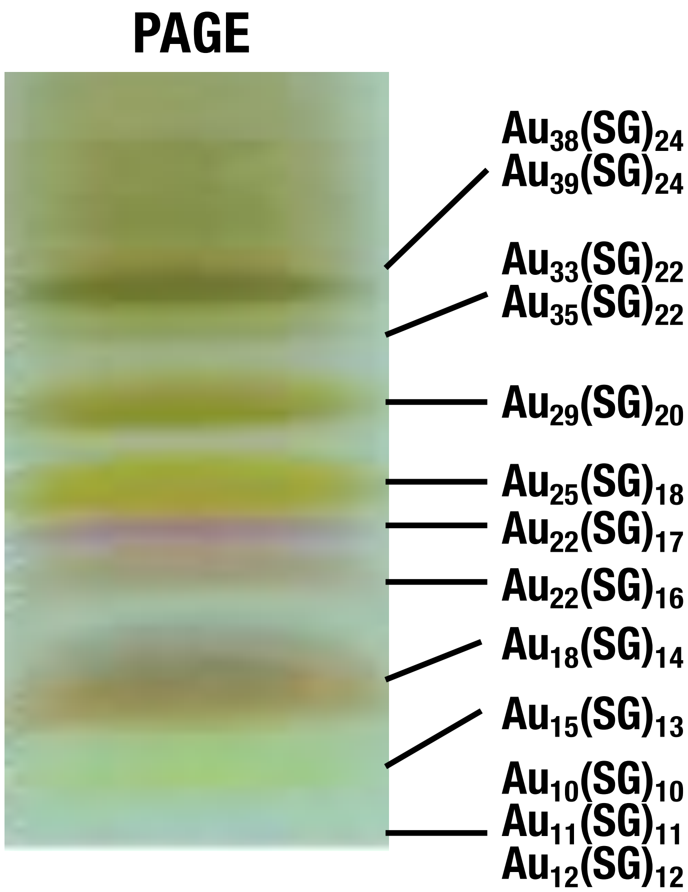
精密合成法①

Y. Negishi & T. Tsukuda, JACS, (2004)(2005)

被引用数計1727 回

①高分解能分離





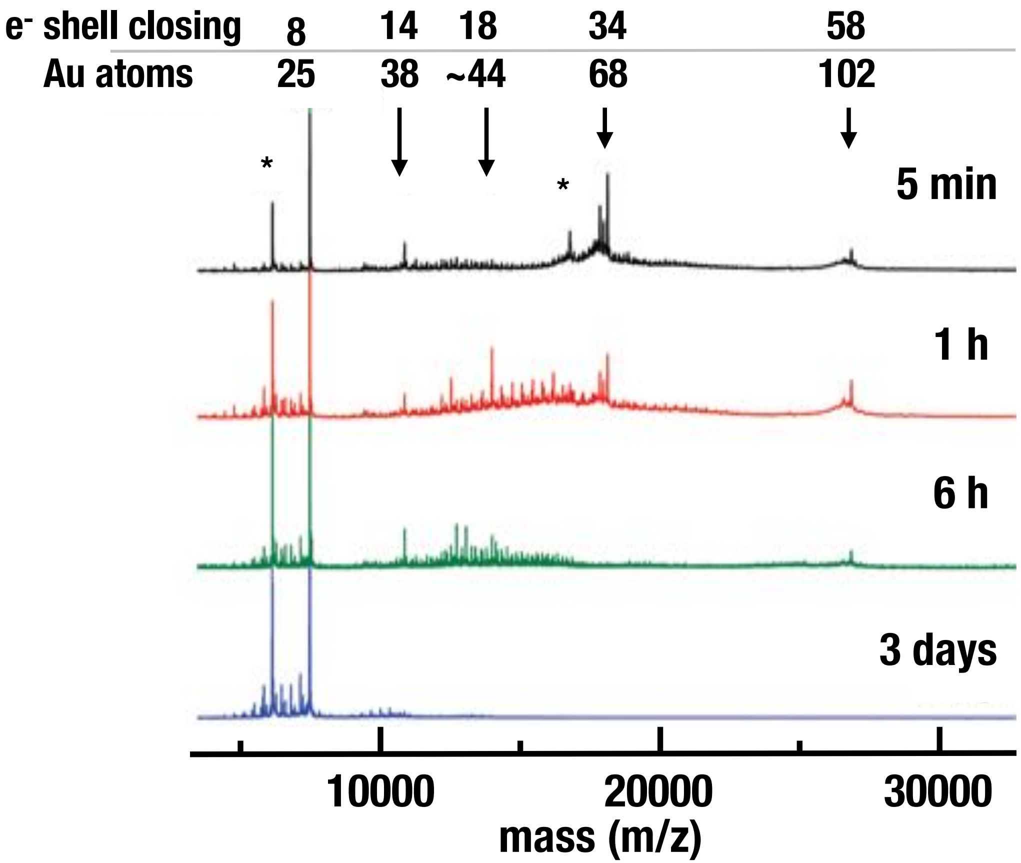
Y. Negishi & T. Tsukuda, J. Am. Chem. Soc. (2005)

精密合成法②

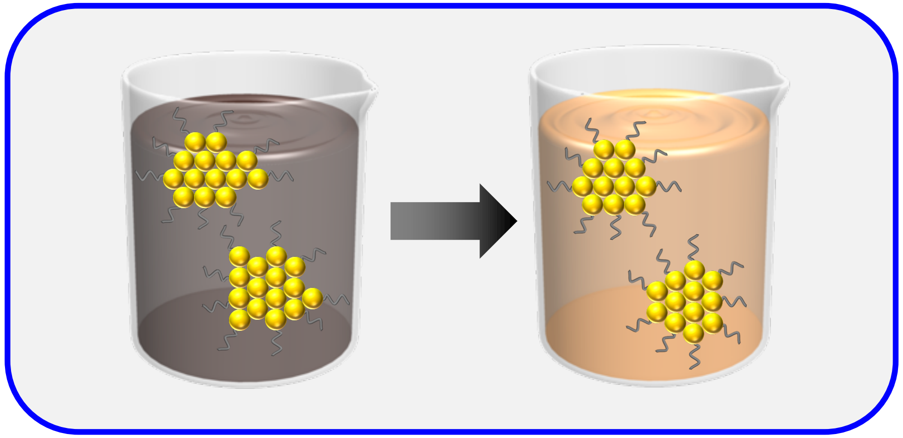
Y. Negishi & T. Tsukuda, JACS, (2005), Small (2007)

②サイズ収束

被引用数計700 回

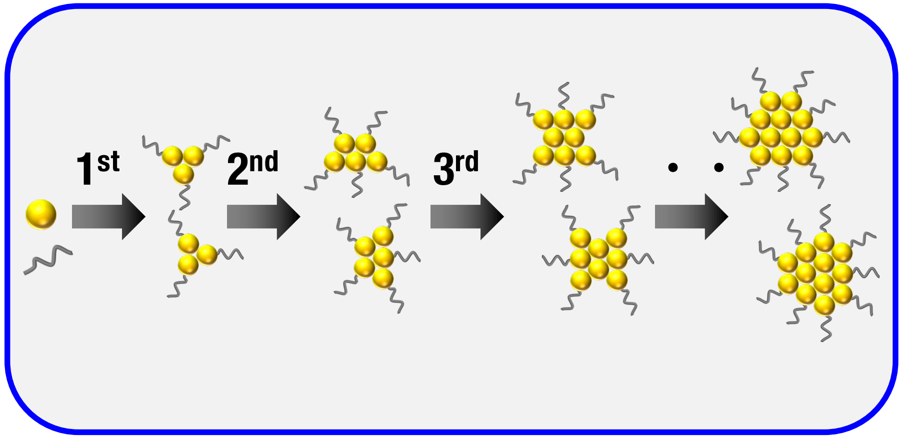


A. Dass et al., J. Am. Chem. Soc. (2009)

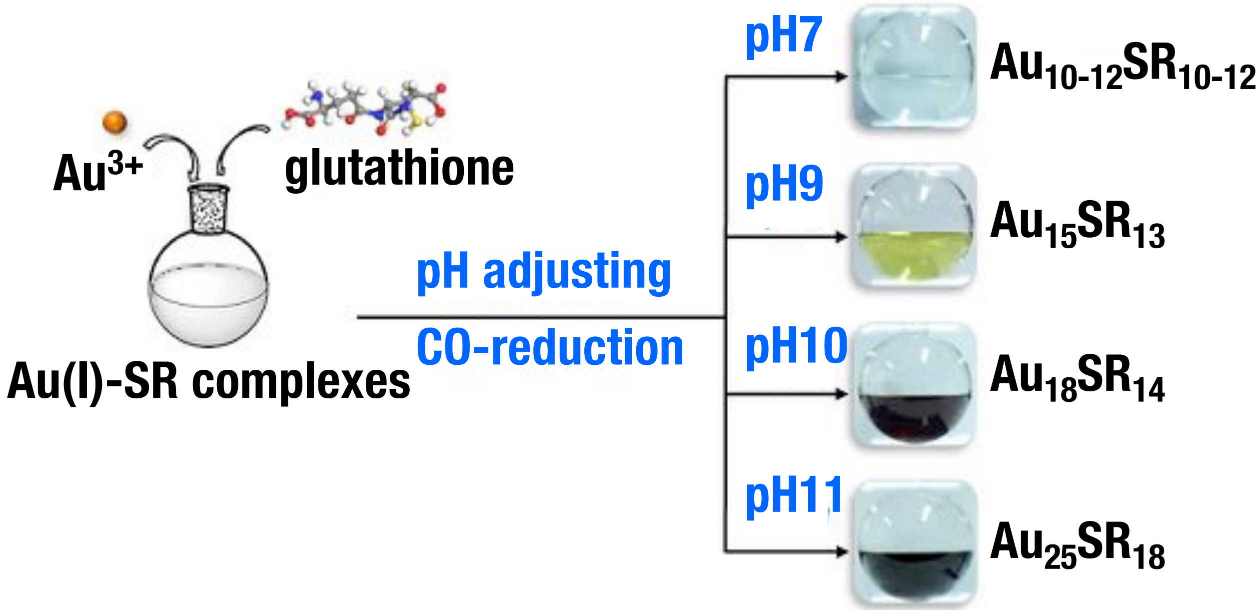


精密合成法③

③成長速度制御

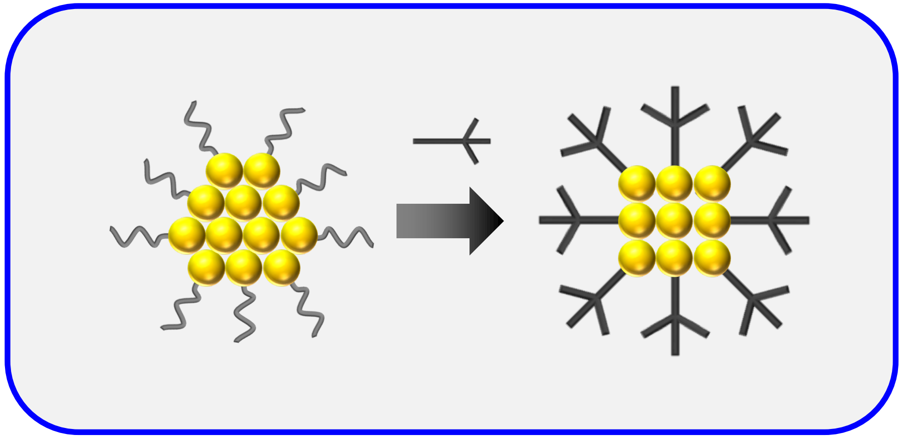


J. Xie et al., Chem. Matter. (2013)

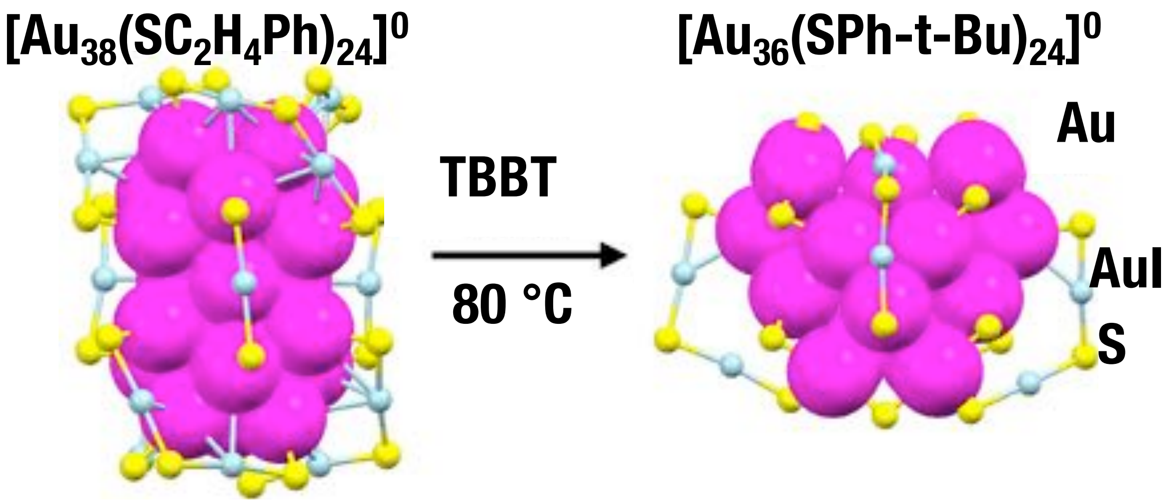


精密合成法④

④配位子交換

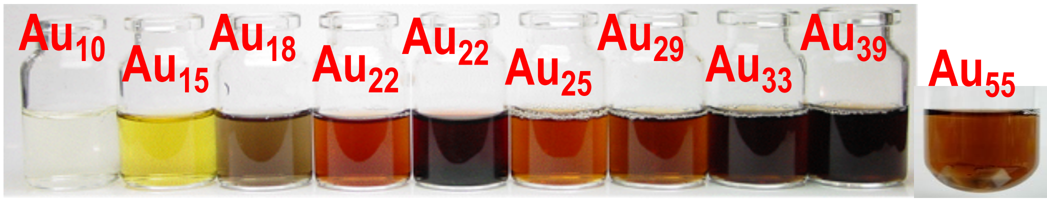


R. Jin et al., ACS Nano (2013)



精密合成に成功した金属クラスター

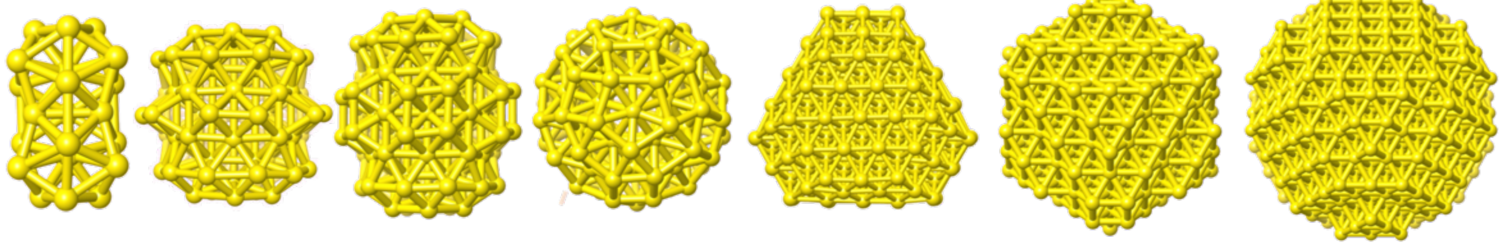
◆ 金クラスター



J. Am. Chem. Soc. (2004)
J. Am. Chem. Soc. (2005)
J. Am. Chem. Soc. (2005)
J. Am. Chem. Soc. (2006)

J. Am. Chem. Soc. (2007)
J. Am. Chem. Soc. (2008)
J. Phys. Chem. Lett. (2012)
J. Phys. Chem. Lett. (2012)
J. Am. Chem. Soc. (2015)

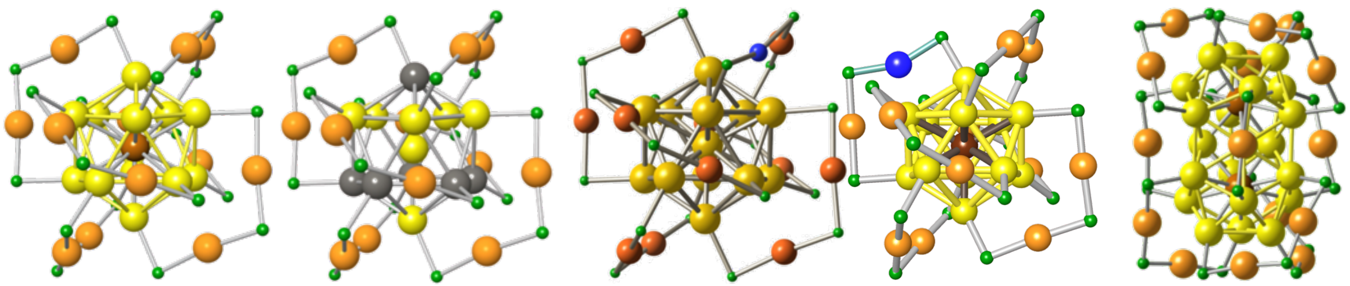
Au_{38} Au_{104} Au_{130} Au_{144} Au_{226} Au_{329} Au_{520}



◆ 合金クラスター

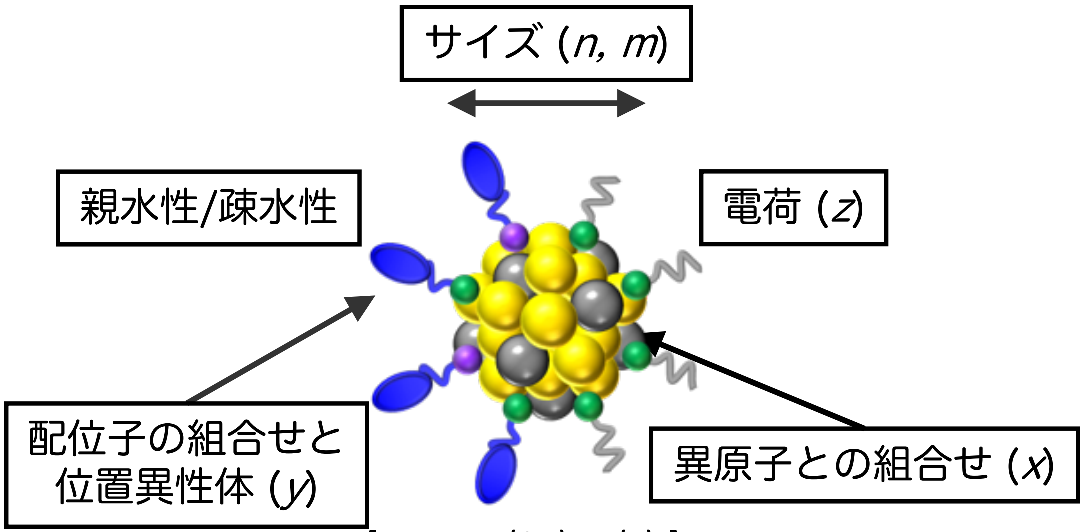
Chem. Commun. (2010)
Chem. Commun. (2012)
J. Phys. Chem. Lett. (2012)
Chem. Commun. (2013)
J. Am. Chem. Soc. (2013)
Nanoscale (2014)
Nanoscale (2015)
Dalton Trans. (2016)

$Au_{24}Pd$ $Au_{25-n}Ag_n$ $Au_{25-n}Cu_n$ $Au_{24-n}Cu_nPd$ $Au_{36}Pd_2$



我々の精密合成法技術

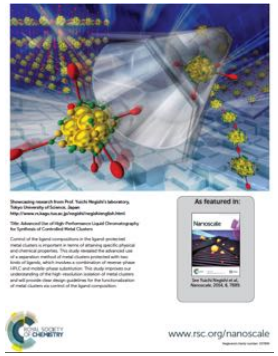
金属クラスターの自在制御可能



$[Au_{n-x}M_x(SR)_{m-y}(L)_y]^z$　　M = Ag, Cu, ...
L = SR', SeR', TeR'...

PCCP 2016

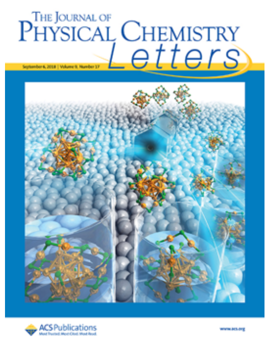
Nanoscale 2015



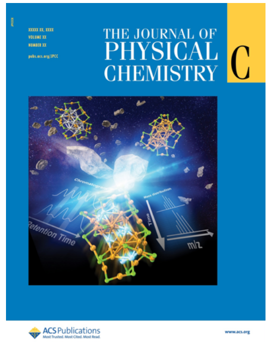
IECR 2017

BCSJ 2019

JPCL 2018



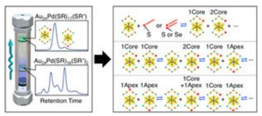
JPCC 2019



ACS Nano 2015
Research Highlight

ge Reactions

To investigate, Niihori *et al.* (DOI: 10.1021/acsnano.5b03435) probed the products from ligand-exchange reactions of phenylethanethiolate-protected $Au_{24}Pd$ clusters ($Au_{24}Pd(SC_2H_4Ph)_{18}$) with thiol, disulfide, or diselenide using reverse-phase high-performance liquid chromatography. This method separated out each coordination isomer from the reaction with high resolution, enabling them to be evaluated quantitatively, and provided more information about the nature of the reaction. The researchers found that the reactions appear to begin preferentially at thiolates that are bound directly to the metal core. Because the reaction occurred between clusters in the cluster solution, this led to variations in coordination isomer distribution of the clusters in solution. Controlling the coordination isomer distribution of the reactant clusters enabled control of the distribution of the products. The authors suggest that these results could help optimize the creation of desired metal clusters in other ligand-exchange reactions.



IN NANO

J. Am. Chem. Soc 2015
Highlight in Nat. Nanotech.

research highlights

GOLD NANOPARTICLES
Metallic up to a point
J. Am. Chem. Soc. http://doi.org/zj7 (2014)

The chemical properties of gold nanoparticles change with size. In particular, as the size of the nanoparticles gets smaller, their electronic structure changes from that typical of a metal, with surface electrons that behave in a collective manner, to that typical of a molecule, with discrete energy levels. But at what size exactly does this transition occur? To find this out, Hannu Häkkinen, Tatsuya Tsukuda, Yuichi Negishi and colleagues have now analysed the optical absorption and X-ray diffraction spectra of a series of thiolate-protected gold clusters composed of precise numbers of atoms, from $Au_{\sim 520}$ to Au_{38}.

The researchers — who are based at the University of Jyväskylä, the University of Tokyo and the Tokyo University of Science — find that there is a clear transition in the optical absorption spectra from a featureless plasmonic band, typical of metals, to a band with vibronic structures, typical of molecules, when the size of the cluster reduces from 187 to 144 gold atoms. As confirmation of the loss of metallic behaviour at around this size, the team show clusters with 144 atoms or fewer no longer have the face-centred cubic crystal structure typical of metallic gold.

Furthermore, owing to the good agreement between the X-ray spectra and density functional theory calculations, Häkkinen and colleagues are able to propose new structures for several Au clusters with more than 100 atoms. These clusters can be thought of as having core–shell structures in which the core Au atoms have a different geometry to the shell Au atoms. *AM*

Nanoscale 2018

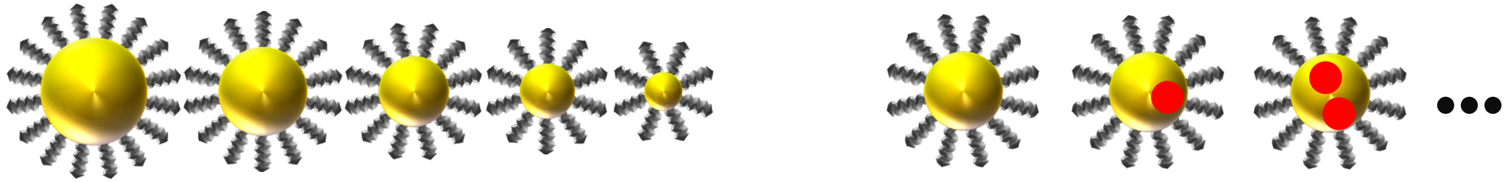
Chem. Rec. 2017

会報 2016

我々の研究

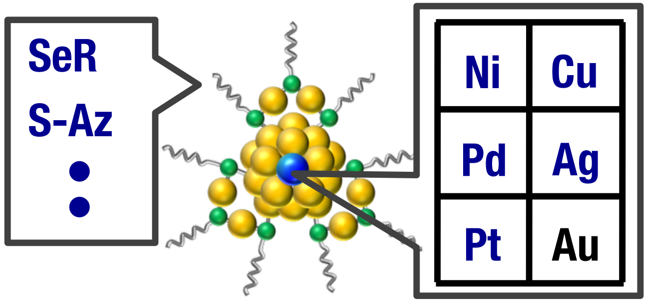
極限的精密合成技術（ナノテクノロジー）の確立

金属コアのサイズ制御　　　金属コアの組成制御



高機能化

高機能ナノ物質の創製



最近の総説例

Coord. Chem. Rev.(Accounts) 2016. J. Phys. Chem. Lett. (Perspective) 2014. Phys. Chem. Chem. Phys.(Perspective) 2013.
Phys. Chem. Chem. Phys.(Perspective) 2016. Bull. Chem. Soc. Jpn.(Award Accounts) 2014.
Chem. Rec.(Personal Accounts) 2017. APL Mater. (Perspective) 2017.

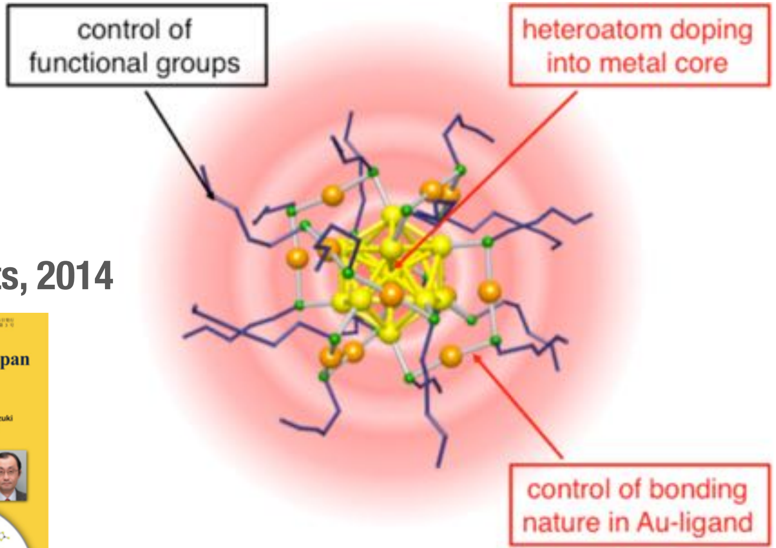
我々の高機能化手段

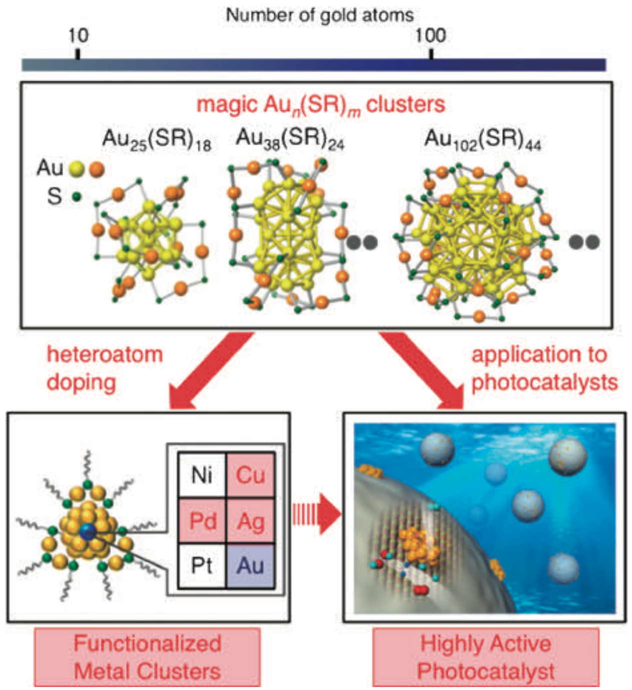
新しいコンセプトの導入

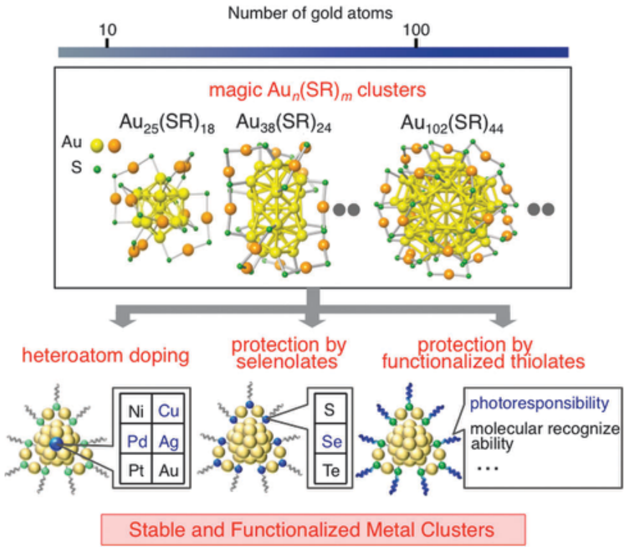
Perspective, 2014

Accounts, 2014

Perspective, 2013







少し古い研究成果のまとめ

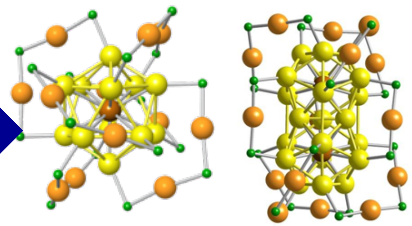
分野内にて機能化手段の一つとして認識

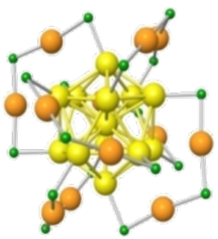
X	XI
Ni	Cu
Pd	Ag
Pt	Au

$Pd_xAu_{n-x}(SR)_m$

PCCP (2010) Chem. Comm. (2012)
Nanoscale (2013) JPCL (2013)

被引用数計 491



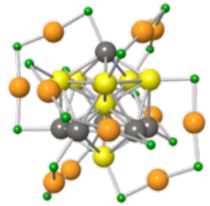


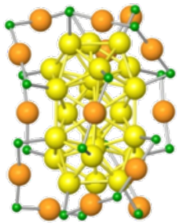
X	XI
Ni	Cu
Pd	Ag
Pt	Au

$Ag_xAu_{25-x}(SR)_{18}$

Chem. Comm. (2010)

被引用数 251



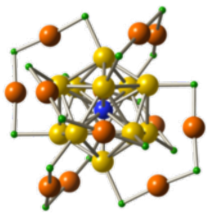


X	XI
Ni	Cu
Pd	Ag
Pt	Au

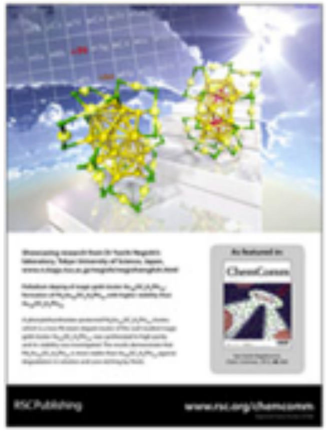
$Cu_xAu_{25-x}(SR)_{18}$

J. Phys. Chem. Lett. (2012)
Chem. Commun. (2013)

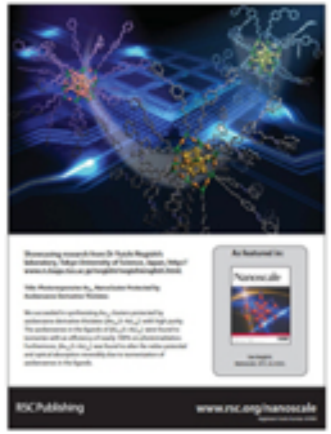
被引用数計 238



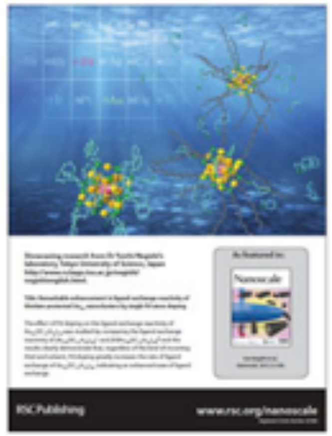
Chem. Comm. 2012



Nanoscale 2012



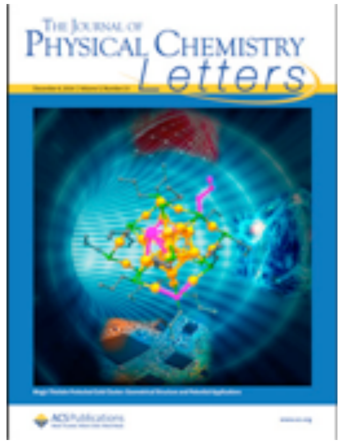
Nanoscale 2013



Chem. Comm. 2013

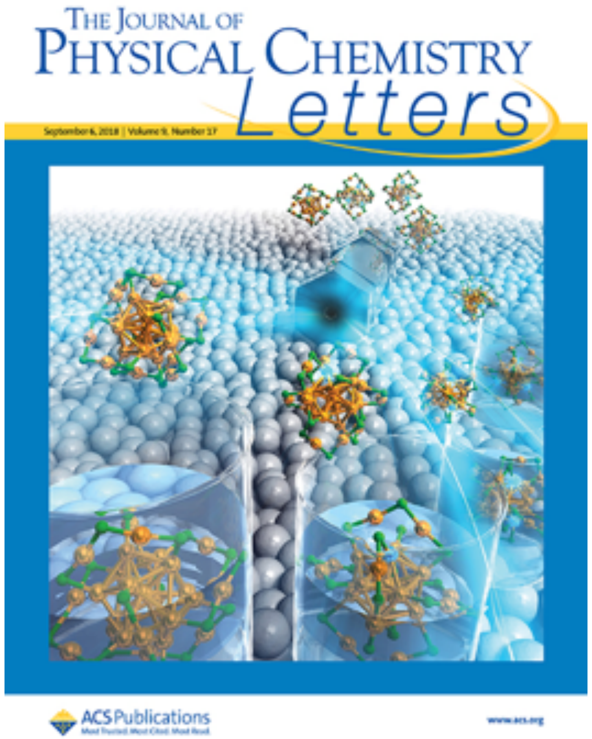
PCCP 2013

JPCL. 2014



最近の技術①

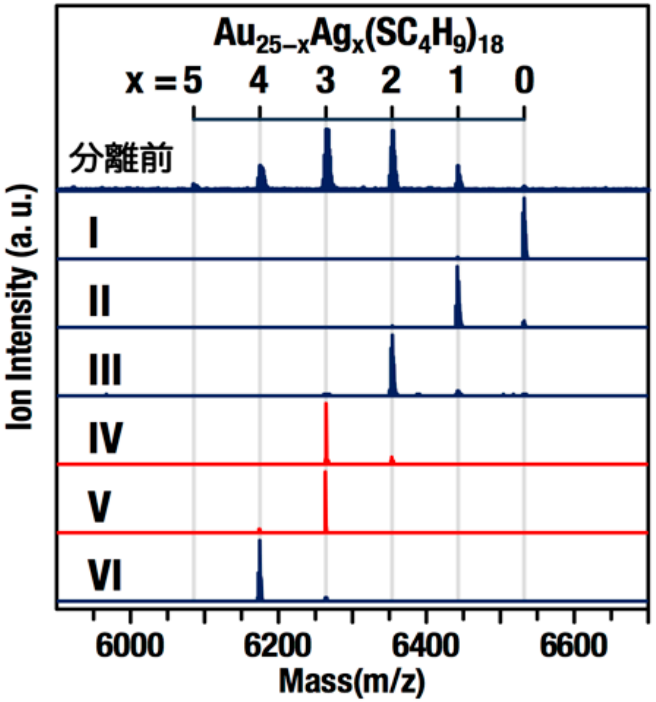
J. Phys. Chem. Lett. 2018



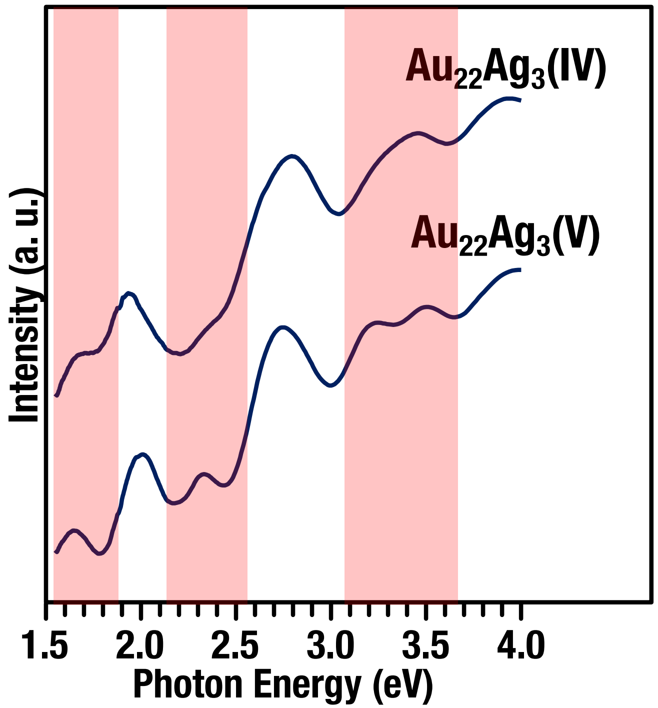
逆相HPLC

精密分離

分離種の化学組成



UV-Vis吸収スペクトル

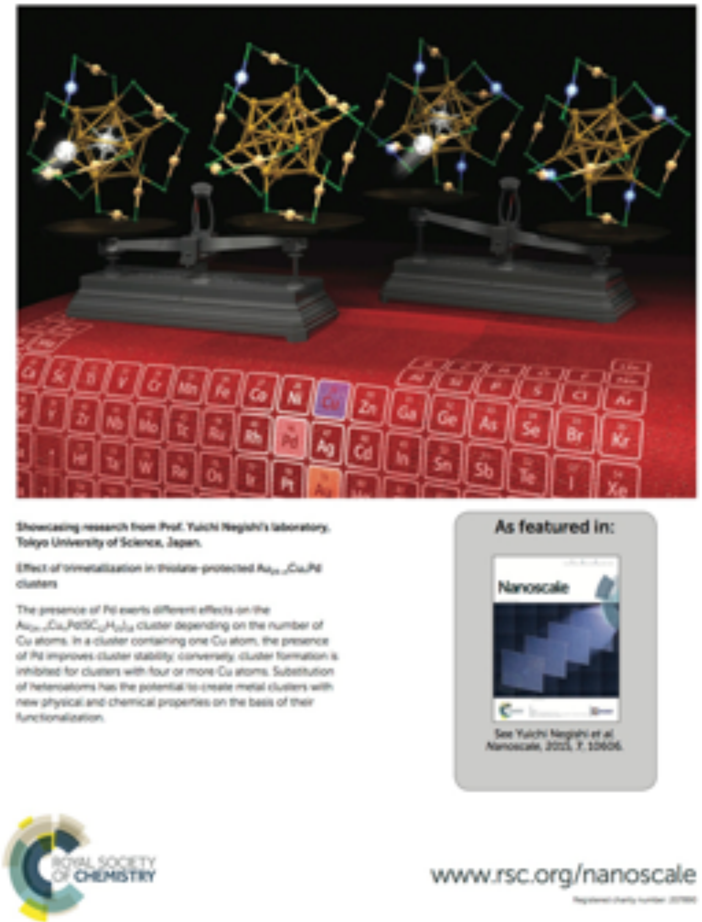


金銀合金クラスターの原子精度での分離の実現

最近の技術②

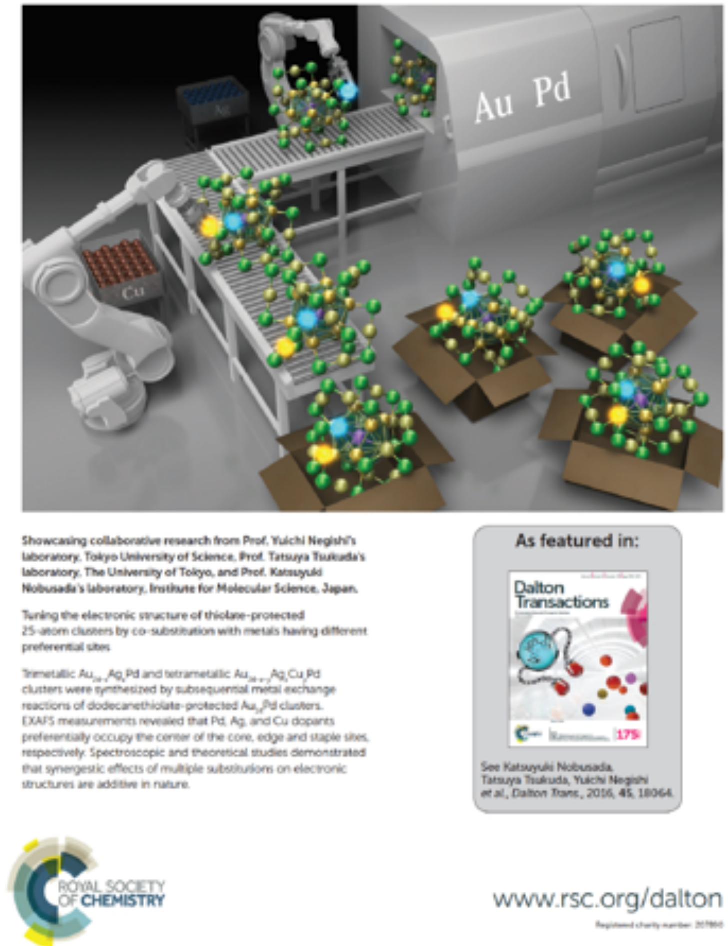
3金属元素クラスター
:$Au_{24-x}Cu_xPd(SR)_{18}$

Nanoscale 2015



4金属元素クラスター
:$Au_{24-x-y}Ag_xCu_yPd(SR)_{18}$

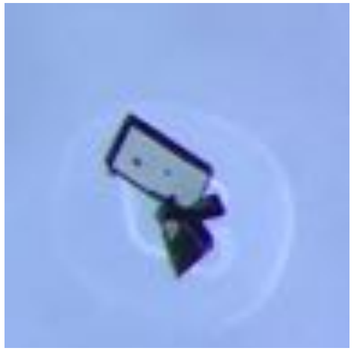
Dalton Trans. 2016



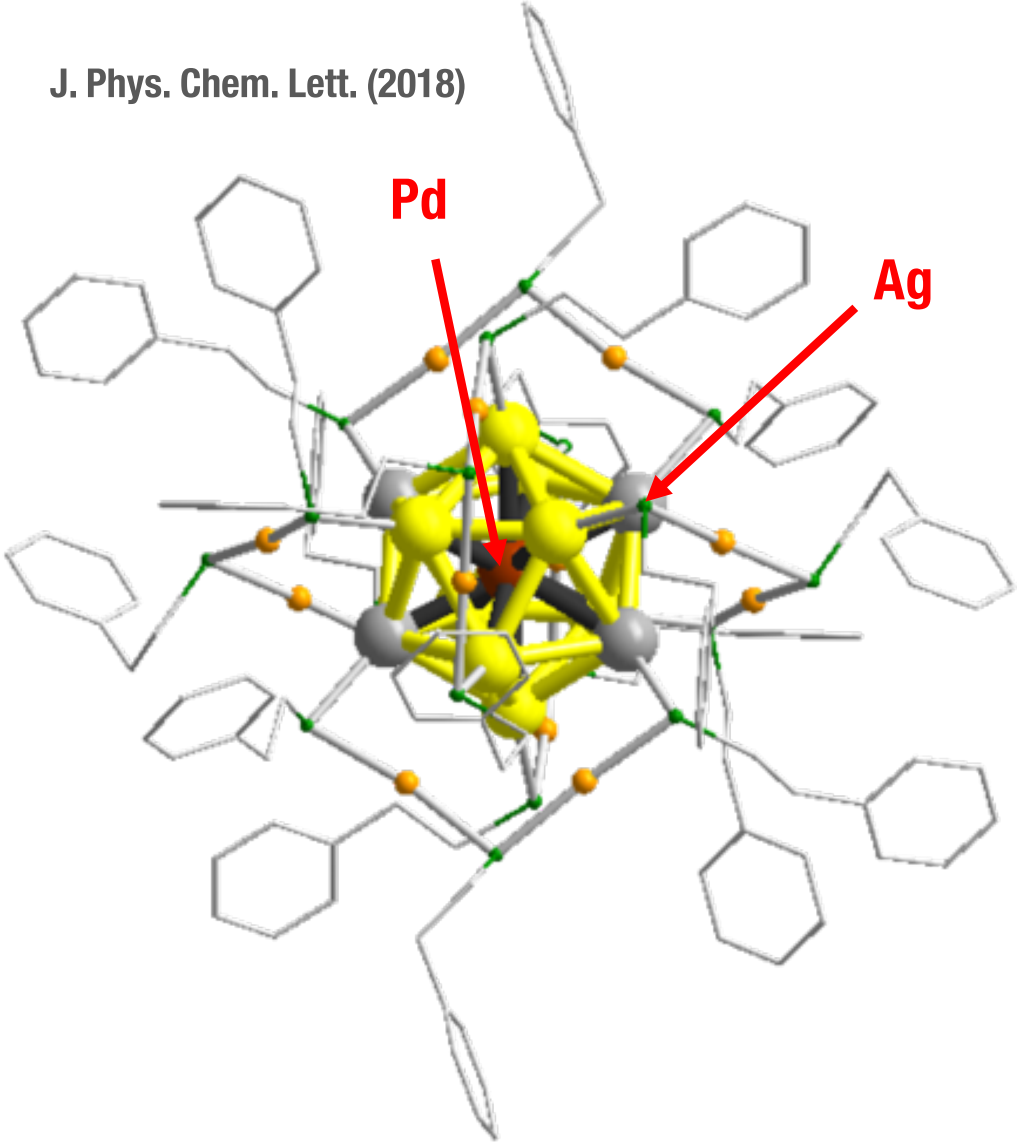
多元素置換による機能の重ね合わせに成功

最近の技術③

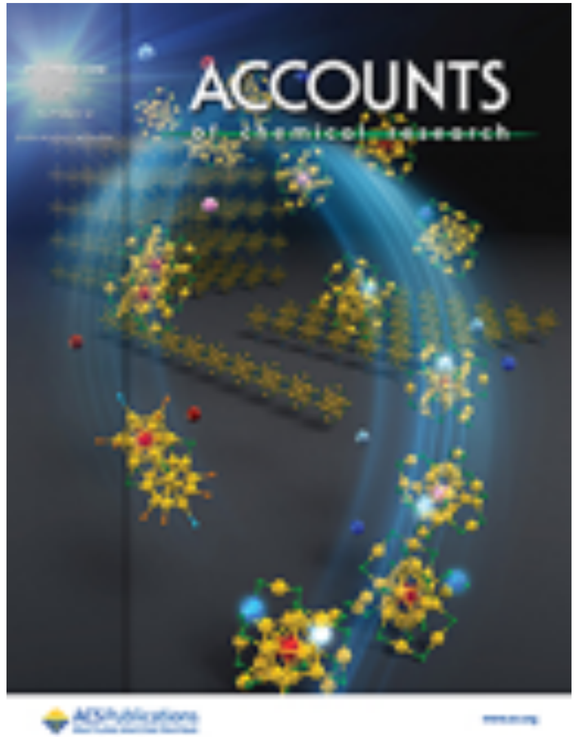
単結晶写真



J. Phys. Chem. Lett. (2018)

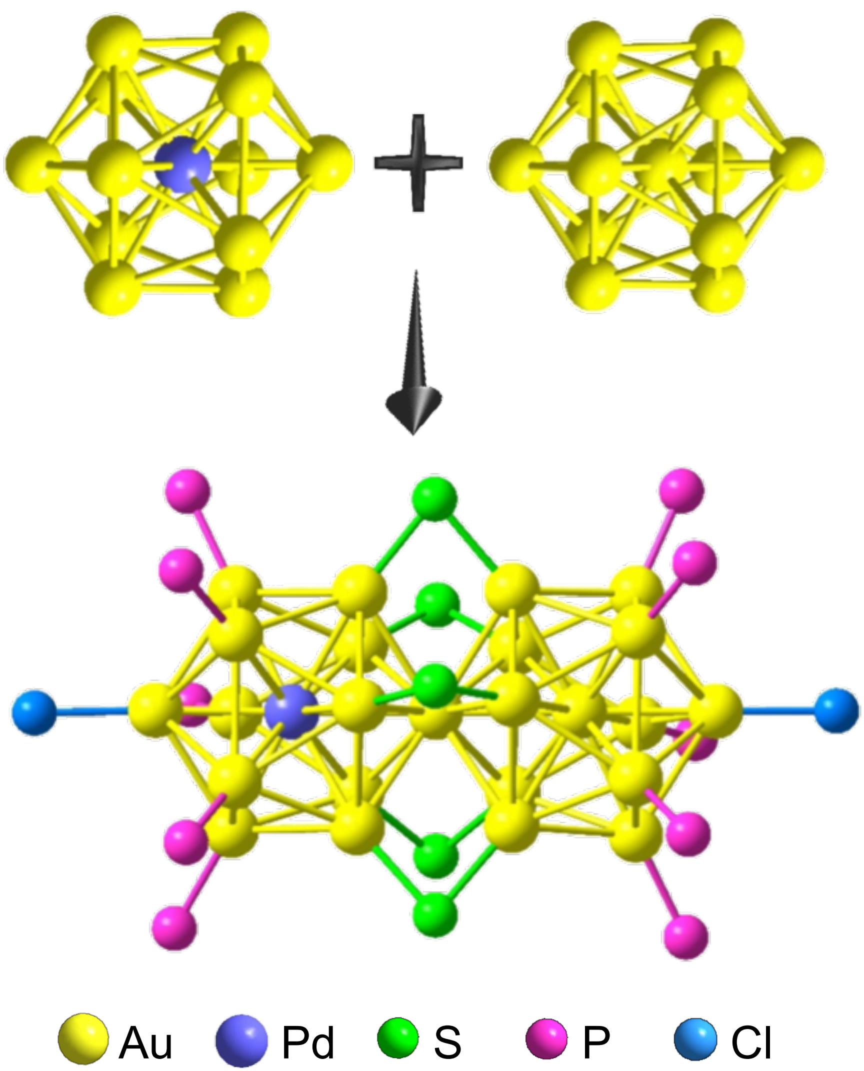


Acc. Chem. Res. 2018

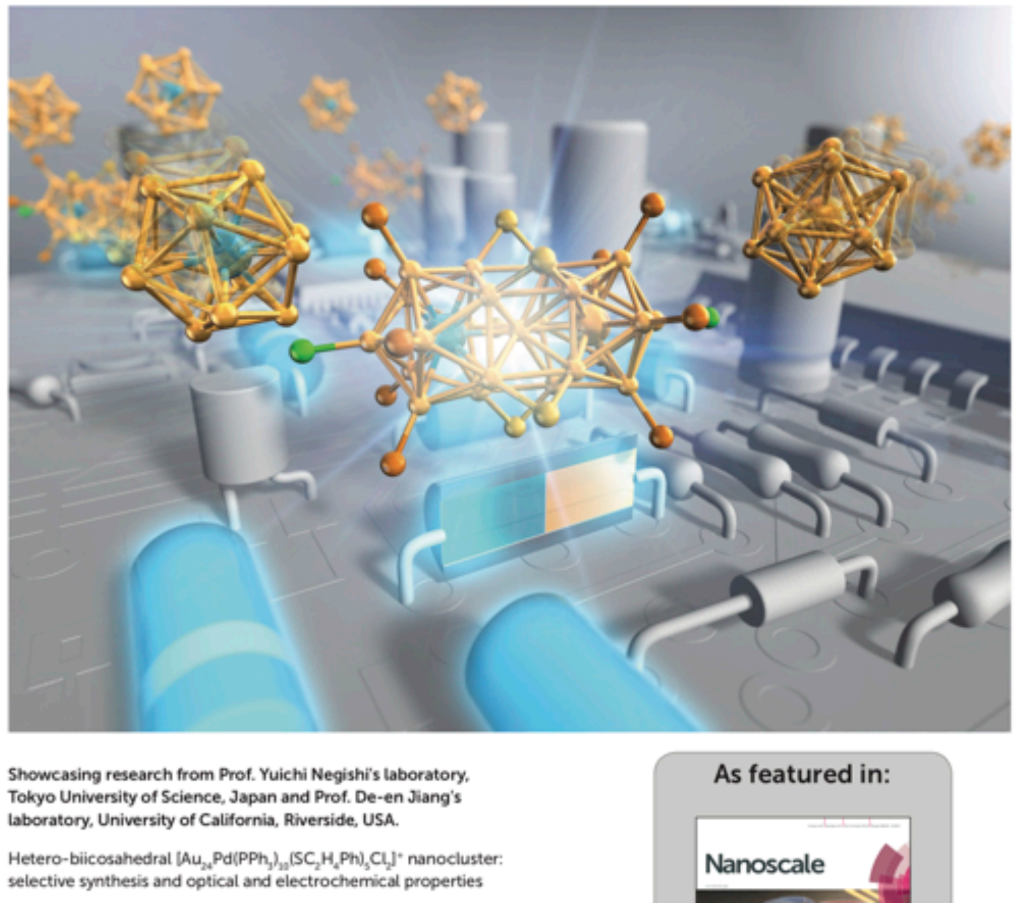


構造観測の利用により異元素のドープ位置の制御に成功

最近の技術④



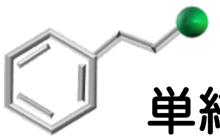
Nanoscale 2018



ヘテロな金属コアをもつロッド型クラスターの選択的合成

最近の技術⑤

配位子構造



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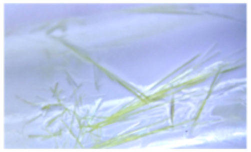
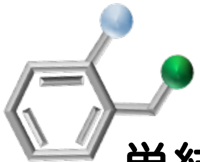
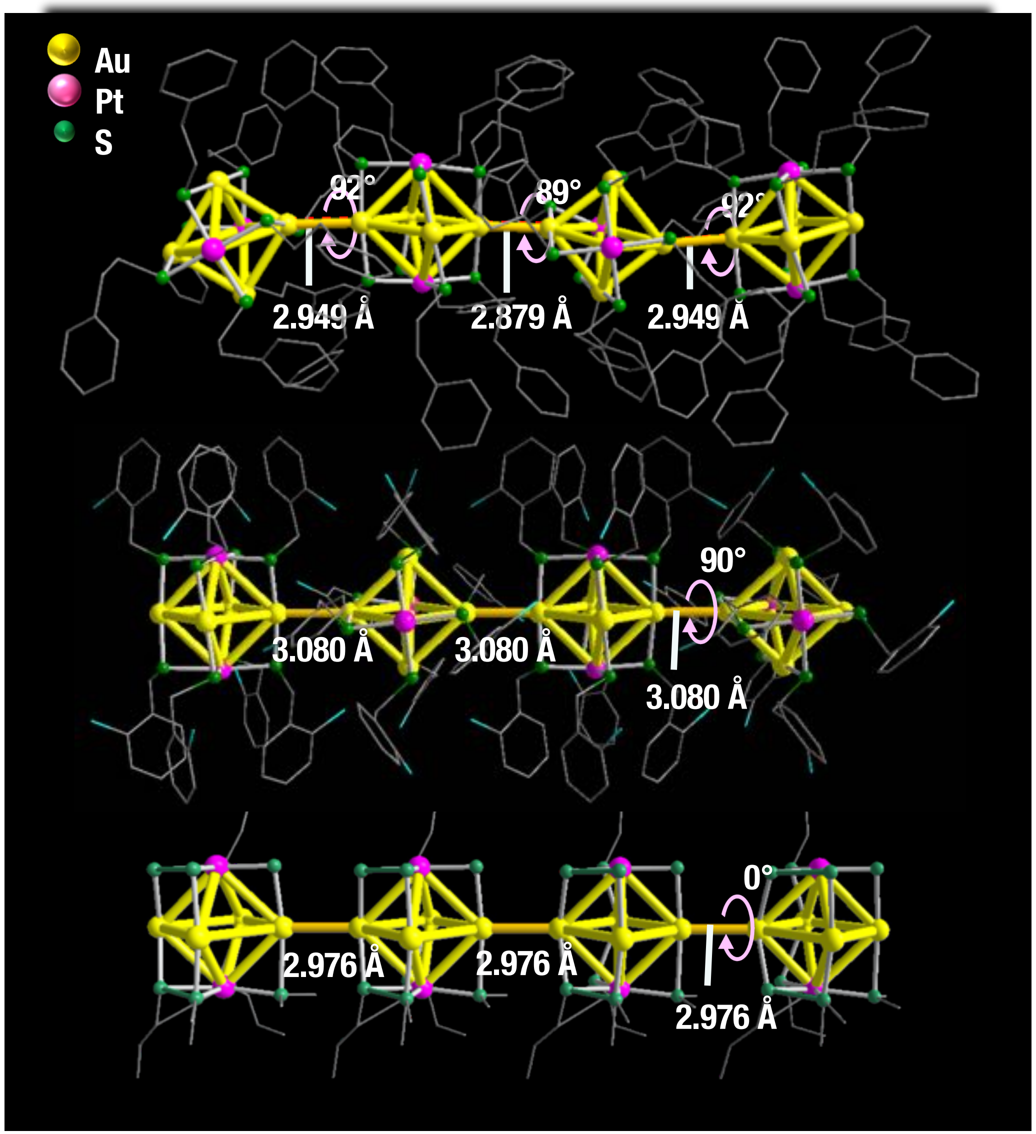


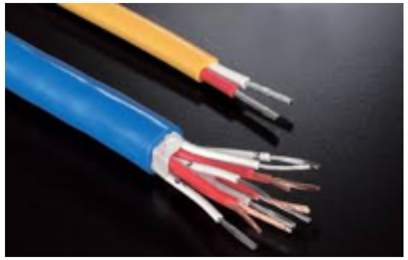


単結晶写真

単結晶写真



Mater. Horizon, in press.
Selected as Front Cover



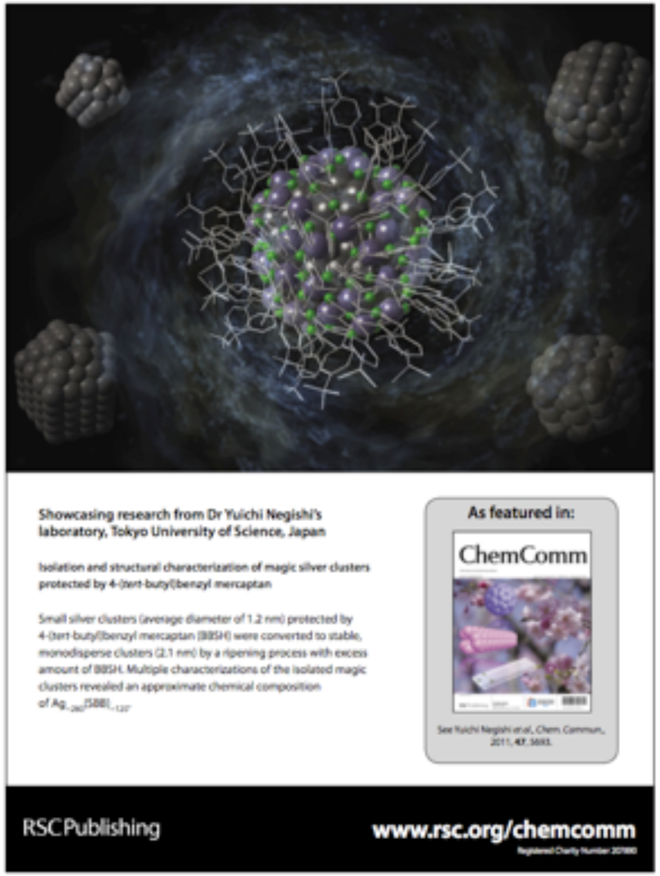
合金クラスターの一次元連結構造の

銀クラスター

銀クラスター

:$Ag_{\sim280}(SBB)_{\sim120}$

Chem. Comm. 2011



簡便かつ選択的な合成法の確立に成功

銀クラスター

銀クラスター

:$Ag_{\sim280}(SBB)_{\sim120}$

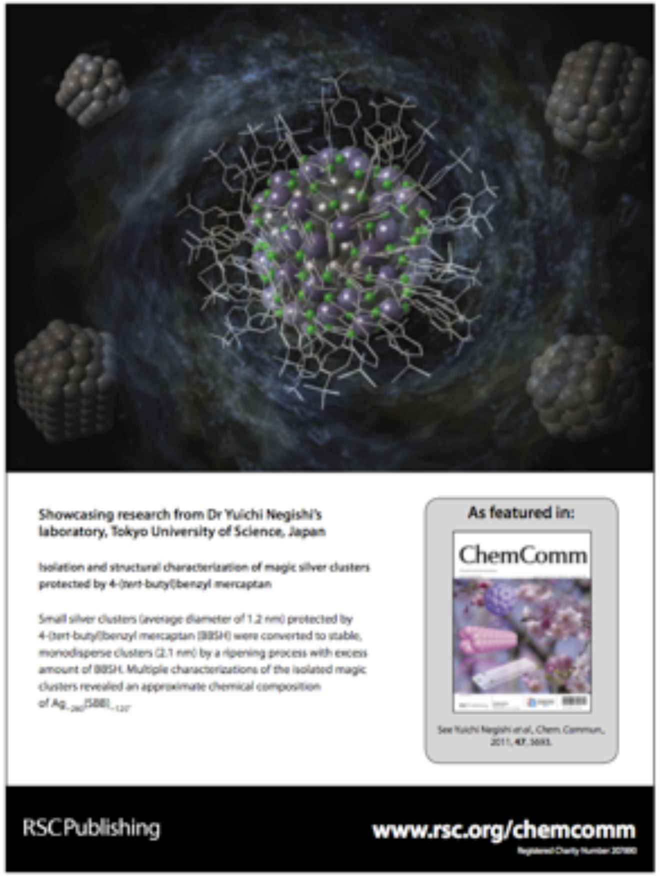
Chem. Comm. 2011

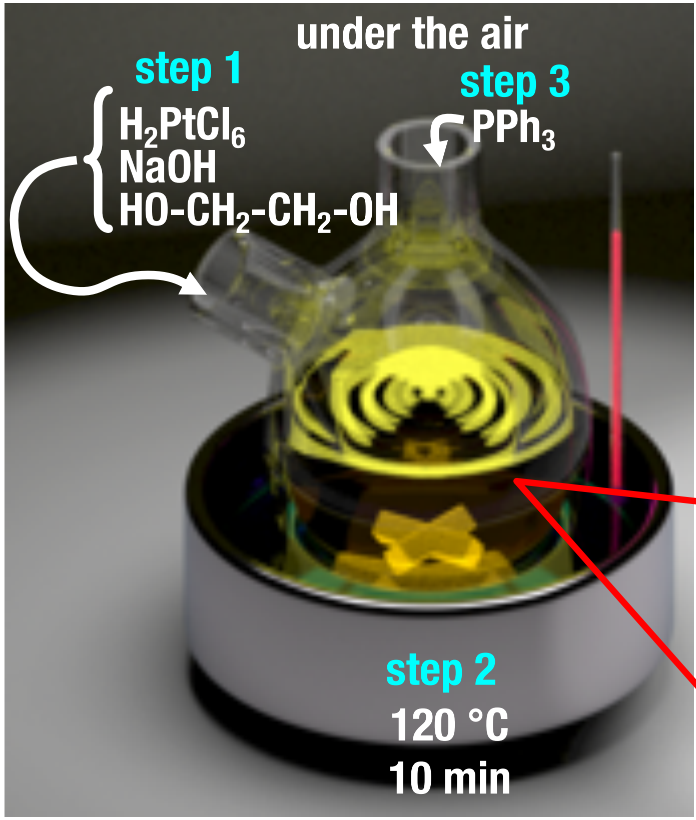
白金クラスター

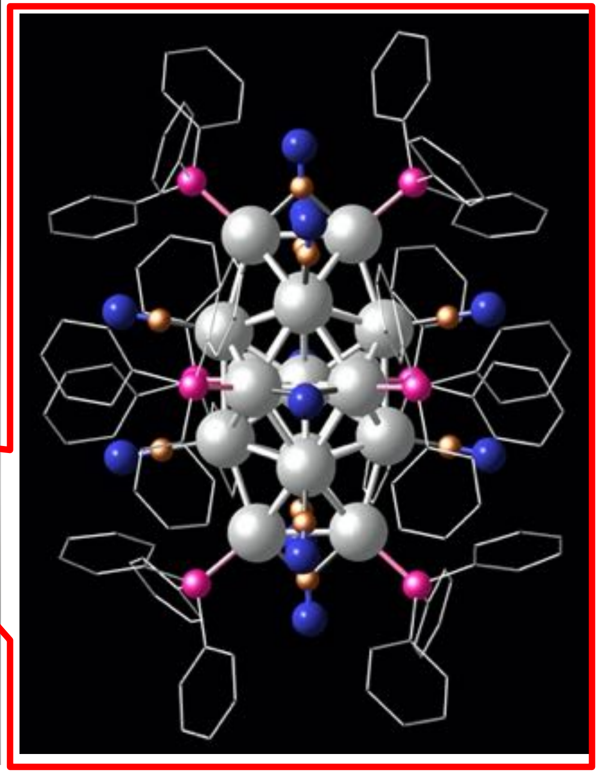
:$[Pt_{17}(CO)_{12}(PPh_3)_8]^+$

J. Phys. Chem. C 2017

Invited to special issue







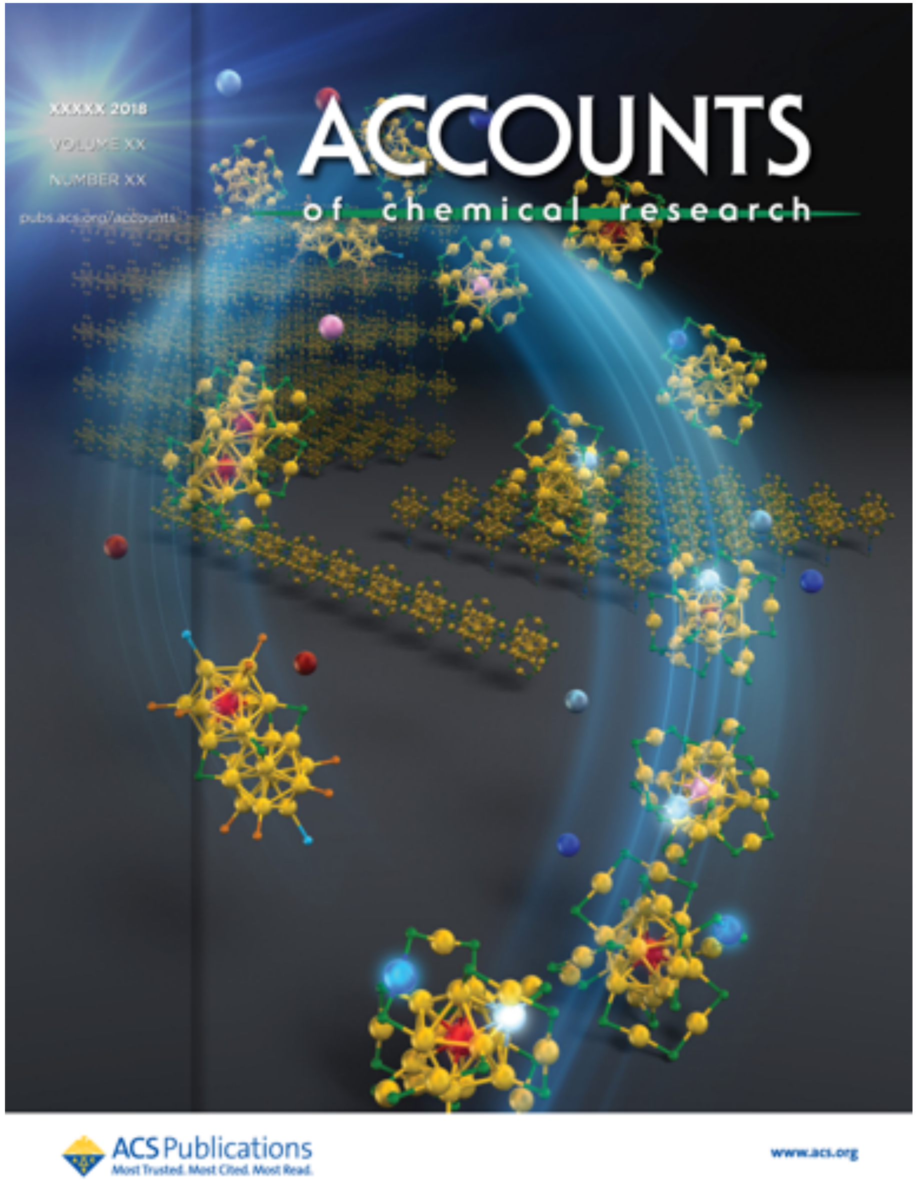
簡便かつ選択的な合成法の確立に成功

機能性金属クラスターの創製に関する総説

PCCP (Perspective) (2013).

J. Phys. Chem. Lett. (Perspective). (2014)

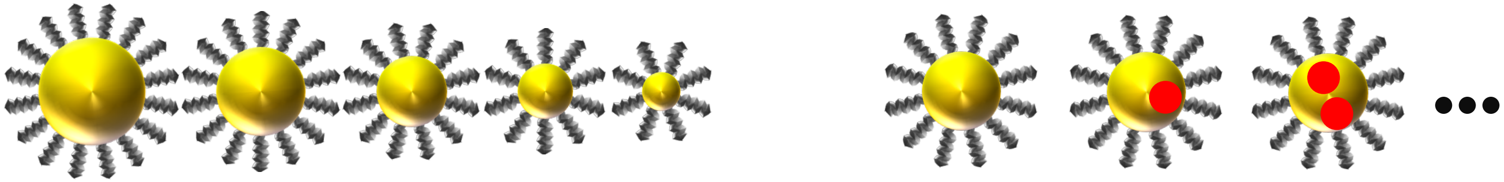
Acc. Chem. Res. (2018).



我々の研究

極限的精密合成技術（ナノテクノロジー）の確立

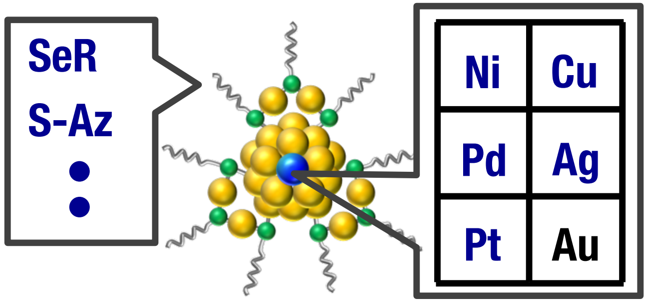
金属コアのサイズ制御　　金属コアの組成制御



高機能化

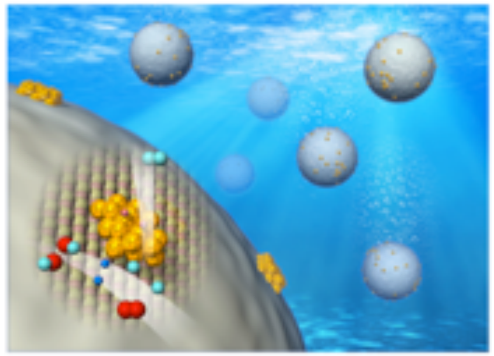
エネルギー・
環境材料への活用

高機能ナノ物質の創製



エネルギー・
環境材料への活用

高機能材料の創製



最近の総説例

Coord. Chem. Rev.(Accounts) 2016. J. Phys. Chem. Lett. (Perspective) 2014.   Phys. Chem. Chem. Phys.(Perspective) 2013.
Phys. Chem. Chem. Phys.(Perspective) 2016. Bull. Chem. Soc. Jpn.(Award Accounts) 2014.
Chem. Rec.(Personal Accounts) 2017. APL Mater. (Perspective) 2017.

金属クラスターの応用

Nanoscale Adv. (2020).

Nanoscale Advances

ROYAL SOCIETY OF CHEMISTRY

REVIEW

View Article Online
View Journal

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Cite this: DOI: 10.1039/c9na00583h

Photo/electrocatalysis and photosensitization using metal nanoclusters for green energy and medical applications

Tokuhisa Kawawaki,[a] Yuichi Negishi *[a] and Hideya Kawasaki *[b]

Received 15th September 2019
Accepted 17th October 2019

DOI: 10.1039/c9na00583h

rsc.li/nanoscale-advances

Owing to the rapidly increasing demand for sustainable technologies in fields such as energy, environmental science, and medicine, nanomaterial-based photo/electrocatalysis has received increasing attention. Recently, synthetic innovations have allowed the fabrication of atomically precise metal nanoclusters (NCs). These NCs show potential for green energy and medical applications. The present article primarily focuses on evaluation of the recent developments in the photo/electrocatalytic and photosensitizing characteristics of metal and alloy NCs. The review comprises two sections: (i) photo/electrocatalysis for green energy and (ii) photosensitization for biomedical therapy applications. Finally, the challenges associated with the use of metal NCs are presented on the basis of current developments.

1. Introduction

During the past few decades, photocatalysis and electrocatalysis have received significant attention as a result of the increasing demand for sustainable technologies in the fields of energy, environmental science, and medicine.[1–7] Photo/electrocatalytic approaches rely on electronic excitation, and their performance depends on the ability to create electron (e^-)–hole (h^+) pairs that successively undergo chemical reactions with other compounds *via* oxidative (*e.g.*, $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$) and reductive reactions (*e.g.*, $2H^+(aq) + 2e^- \rightarrow H_2(g)$). Many advanced nanomaterial-based photo/electrocatalysts have been synthesized and reported, and their advantages include large surface-to-volume effects, numerous catalytic active sites, quantum size effects and high stability.[1–7] These catalysts are considered to be promising for energy and environmental applications, such as photo/electro water splitting to generate hydrogen (H_2) and conversion of carbon dioxide (CO_2). Furthermore, they are used in the fuel industry and in water treatment and disinfection, air purification, and self-cleaning surfaces.[1–6] Usually, the term "photo/electrocatalysis" refers to photo/electrochemical reactions, which involve an electron transfer. Conversely, when energy transfer occurs in

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Assistant Professor of the Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, received PhD degree (2015) in Applied Chemistry from the University of Tokyo. Since 2016, he worked as Japan Society for the Promotion of Science (JSPS) Postdoctoral fellow (PD) at the University of Melbourne. Since 2017, he worked as JSPS super PD (SPD) at Kyoto University. In 2019, he moved to the current position. His current research topics include synthesis of metal nanoparticles and nanoclusters in solutions and their applications for photoelectrochemistry.

Professor of the Department of Applied Chemistry at Tokyo University of Science. He received his PhD degree in Chemistry in 2001 under the supervision of Prof. Atsushi Nakajima from Keio University. Before joining Tokyo University of Science in 2008, he was employed as an assistant professor at Keio University and at the Institute for Molecular Science. His current research interests include the precise synthesis of stable and functionalised metal nanoclusters and their applications in energy and environmental materials.

Volume 2
Number 1
January 2020
Pages 1–522

Nanoscale Advances

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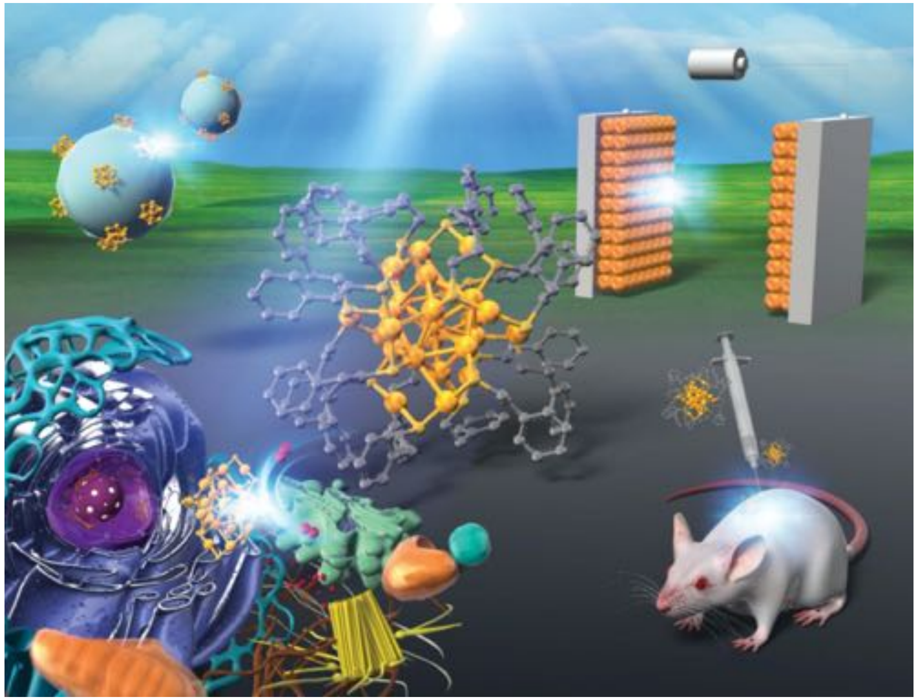


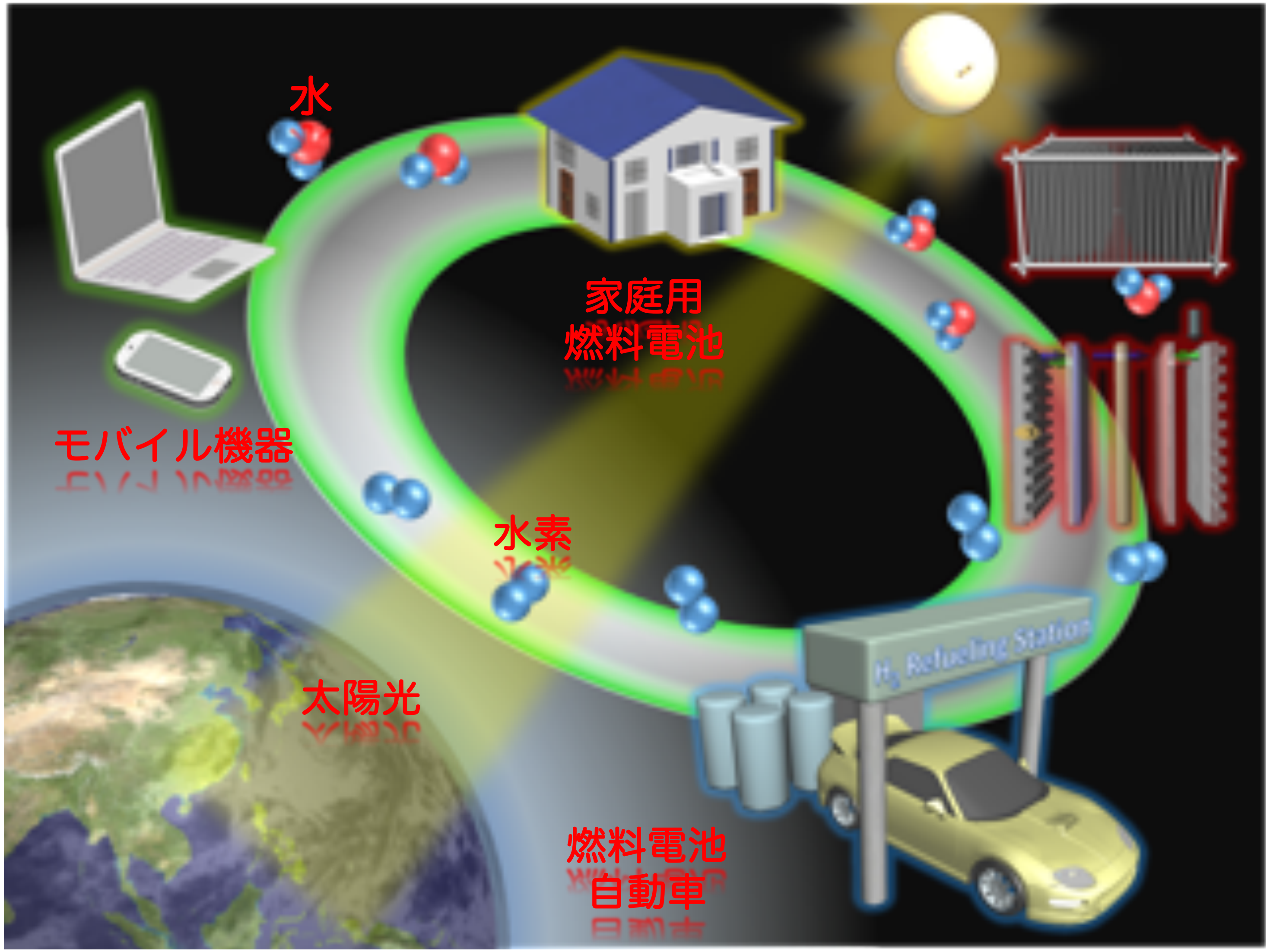
ISSN 2516-0230

ROYAL SOCIETY OF CHEMISTRY

REVIEW ARTICLE
Yuichi Negishi, Hideya Kawasaki *et al.*
Photo/electrocatalysis and photosensitization using metal nanoclusters for green energy and medical applications

NCNST

エネルギー・環境問題のない未来像

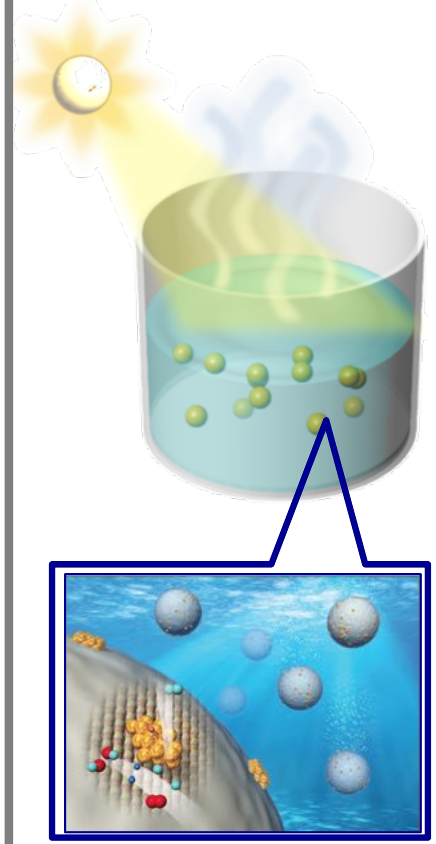


クリーンで再生可能な水素をエネルギー源とした社会への期待

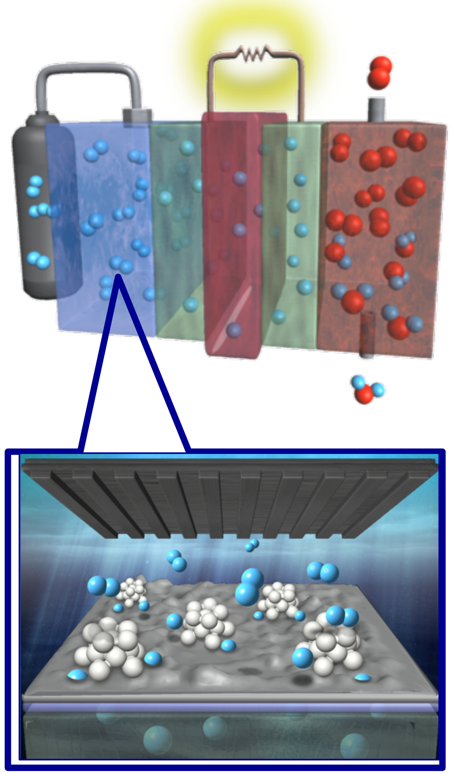
我々のエネルギー環境材料高機能化への取り組み

CO_2排出ゼロの社会へ

・水分解光触媒

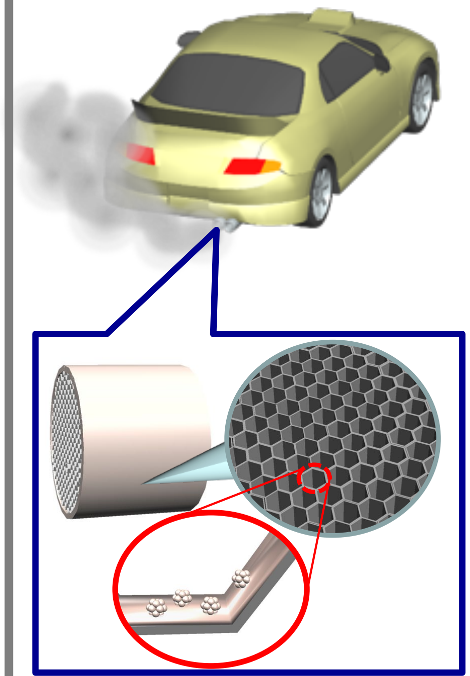


・燃料電池触媒

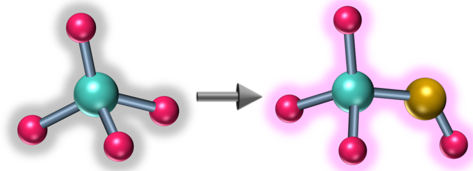


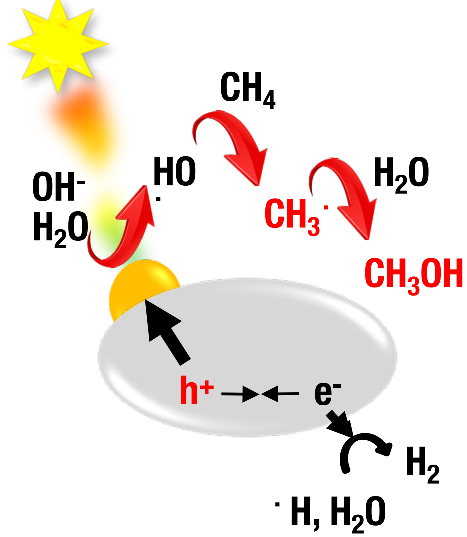
CO_2排出の低減された社会へ

・排ガス処理触媒



・メタン利用触媒





本学の水分解光触媒への取り組み

藤嶋昭
(前学長
/現センター長)

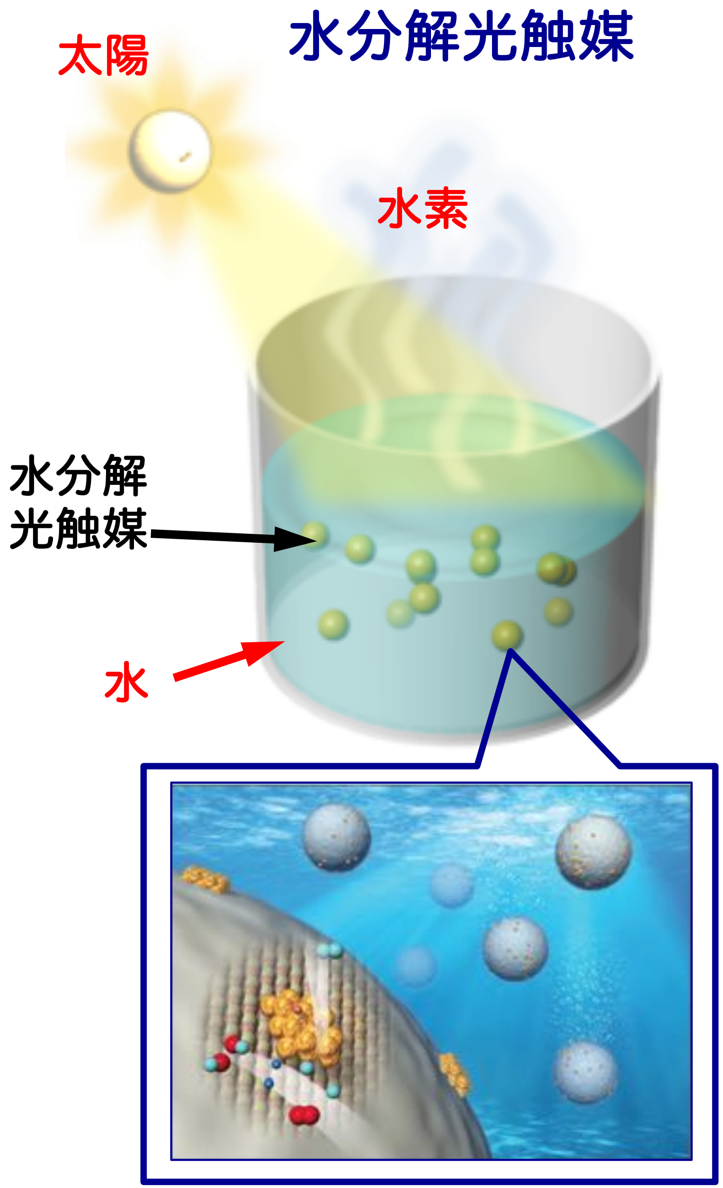
参考) 藤嶋先生らによる
水分解光触媒の発見

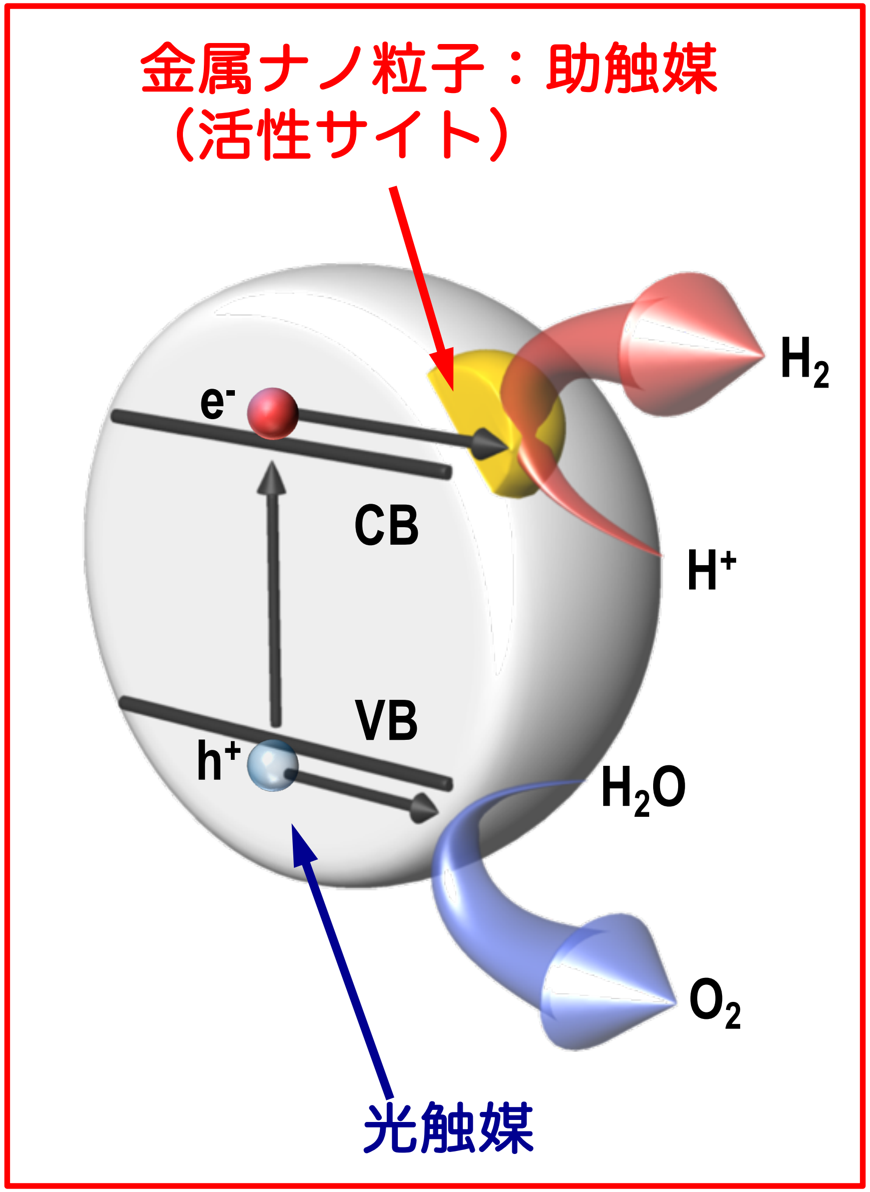
Newtonより引用

理科大の強みの分野

活性部位の厳密制御によるエネルギー・環境材料の高機能化へ

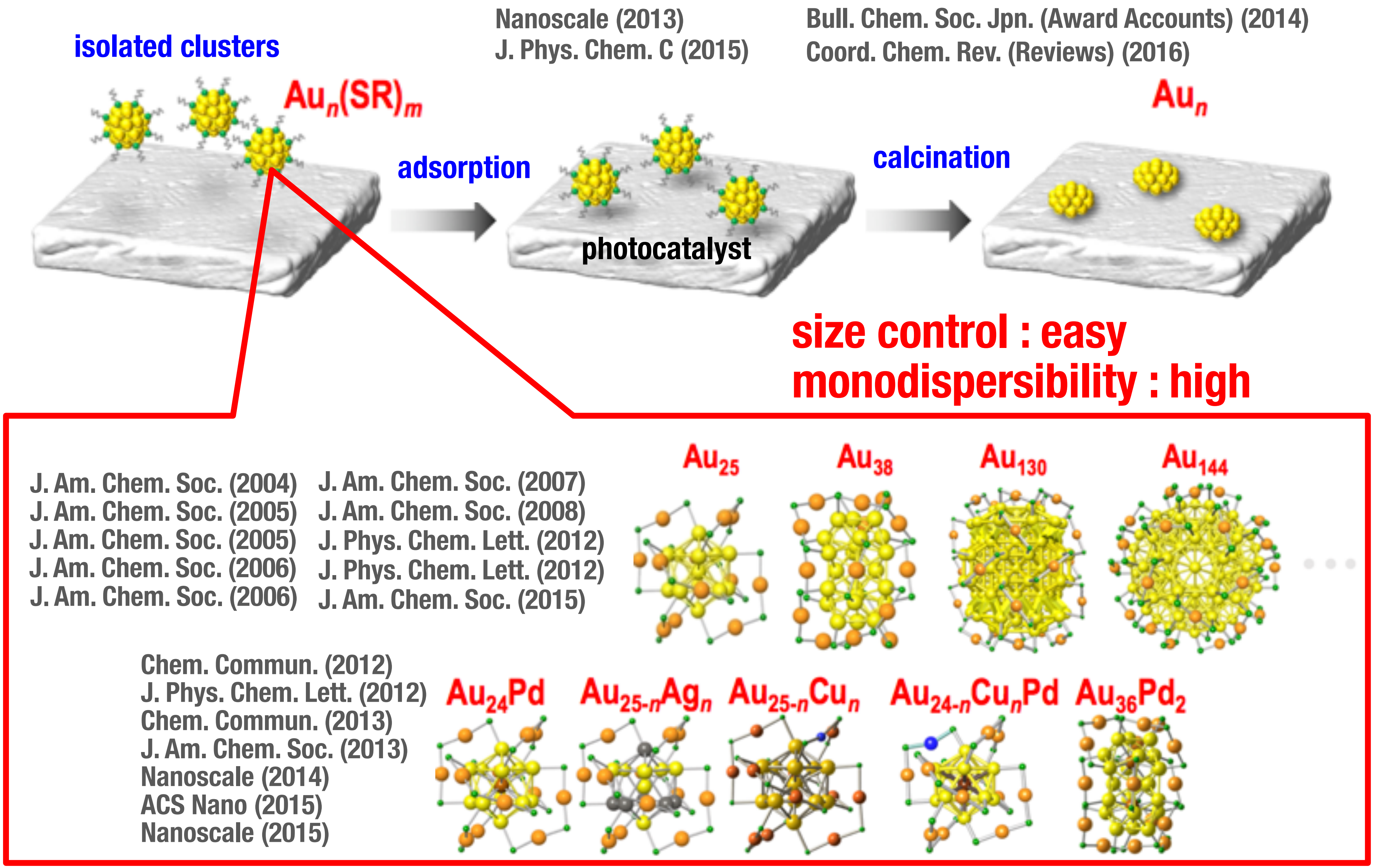
我々の水分解光触媒への取り組み





活性部位の厳密制御によるエネルギー・環境材料の高機能化へ

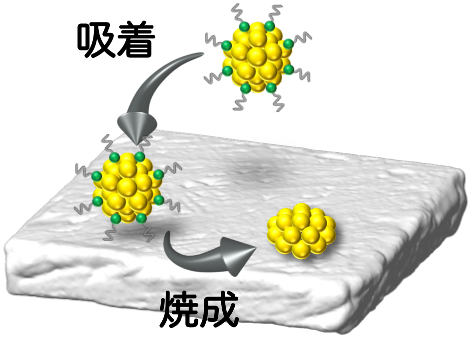
助触媒の担持方法



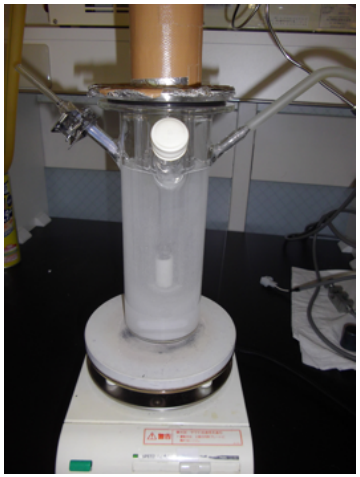
isolated clusters
$Au_n(SR)_m$
adsorption
Nanoscale (2013)
J. Phys. Chem. C (2015)
photocatalyst
calcination
Bull. Chem. Soc. Jpn. (Award Accounts) (2014)
Coord. Chem. Rev. (Reviews) (2016)
Au_n
size control : easy
monodispersibility : high
J. Am. Chem. Soc. (2004)
J. Am. Chem. Soc. (2005)
J. Am. Chem. Soc. (2005)
J. Am. Chem. Soc. (2006)
J. Am. Chem. Soc. (2006)
J. Am. Chem. Soc. (2007)
J. Am. Chem. Soc. (2008)
J. Phys. Chem. Lett. (2012)
J. Phys. Chem. Lett. (2012)
J. Am. Chem. Soc. (2015)
Au_{25}
Au_{38}
Au_{130}
Au_{144}
Chem. Commun. (2012)
J. Phys. Chem. Lett. (2012)
Chem. Commun. (2013)
J. Am. Chem. Soc. (2013)
Nanoscale (2014)
ACS Nano (2015)
Nanoscale (2015)
$Au_{24}Pd$
$Au_{25-n}Ag_n$
$Au_{25-n}Cu_n$
$Au_{24-n}Cu_nPd$
$Au_{36}Pd_2$

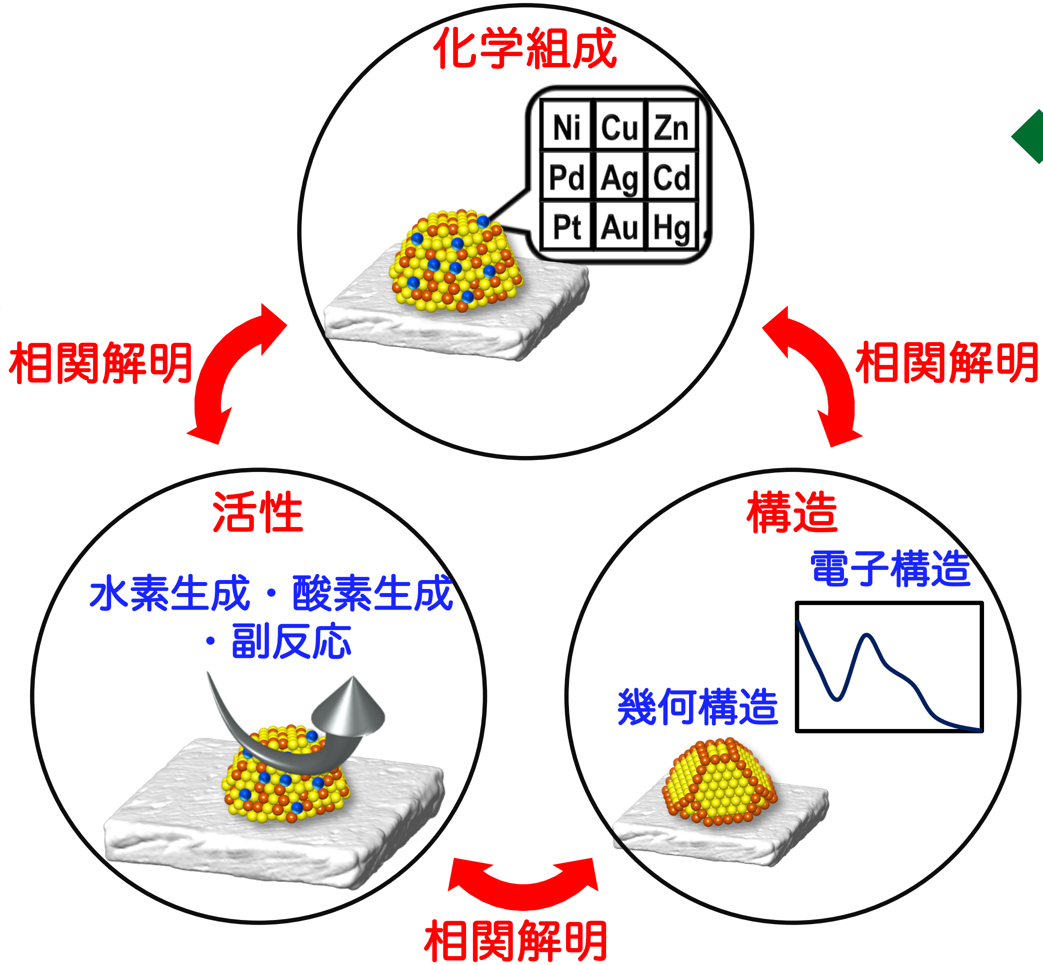
研究方法

◆ 精密担持



◆ 活性測定

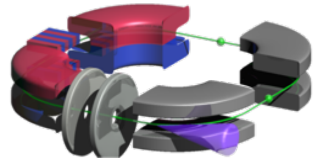




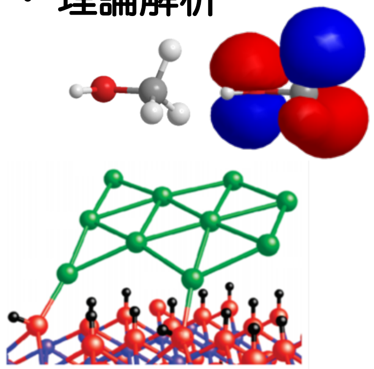
高活性化へのキーファクターの解明
高活性化に適したクラスターの創製
→ 高活性光触媒の創製

◆ 構造解析

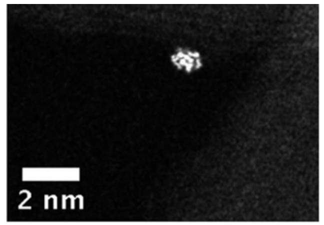
・放射光実験



・理論解析



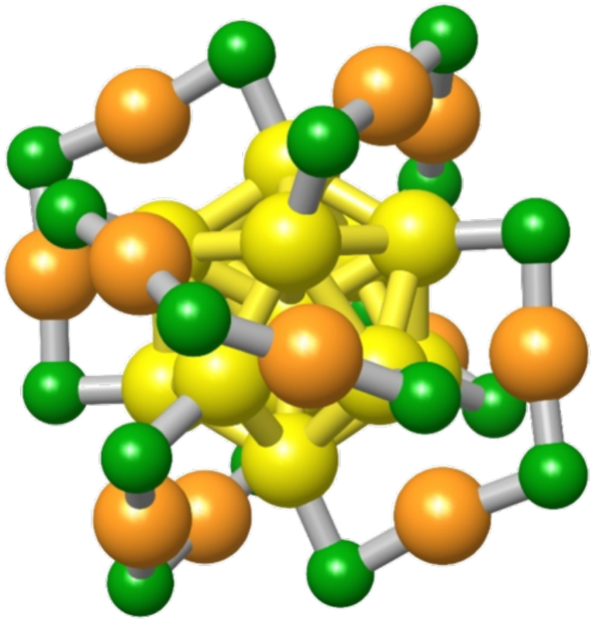
・高分解能測定



研究例

precursor of cocatalyst

$Au_{25}(SG)_{18}$

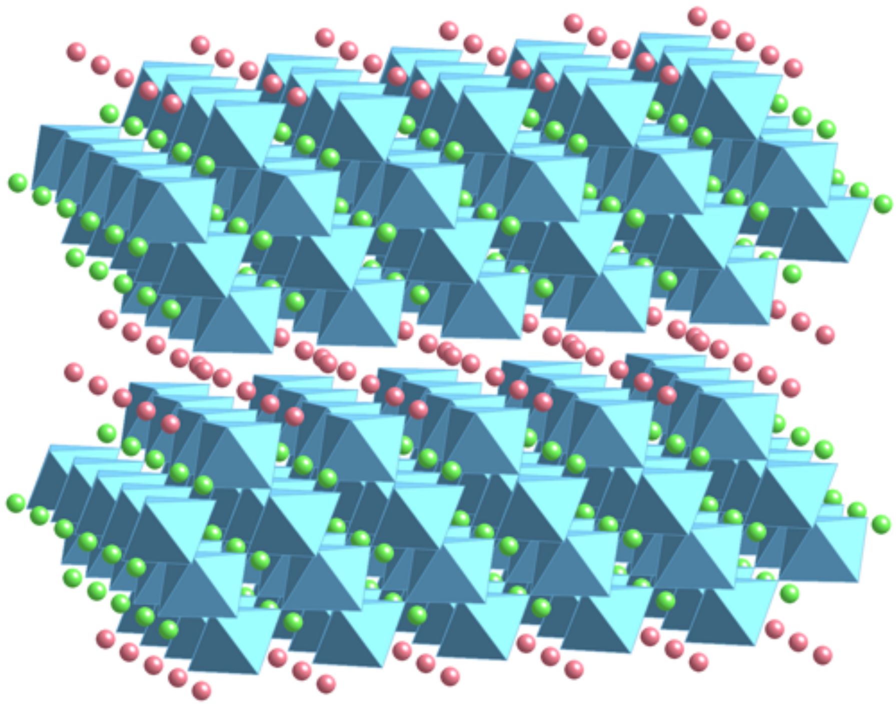


SG: glutathionate

J. Am. Chem. Soc, 2005.

photocatalyst

$BaLa_4Ti_4O_{15}$



Ba or La

Ba

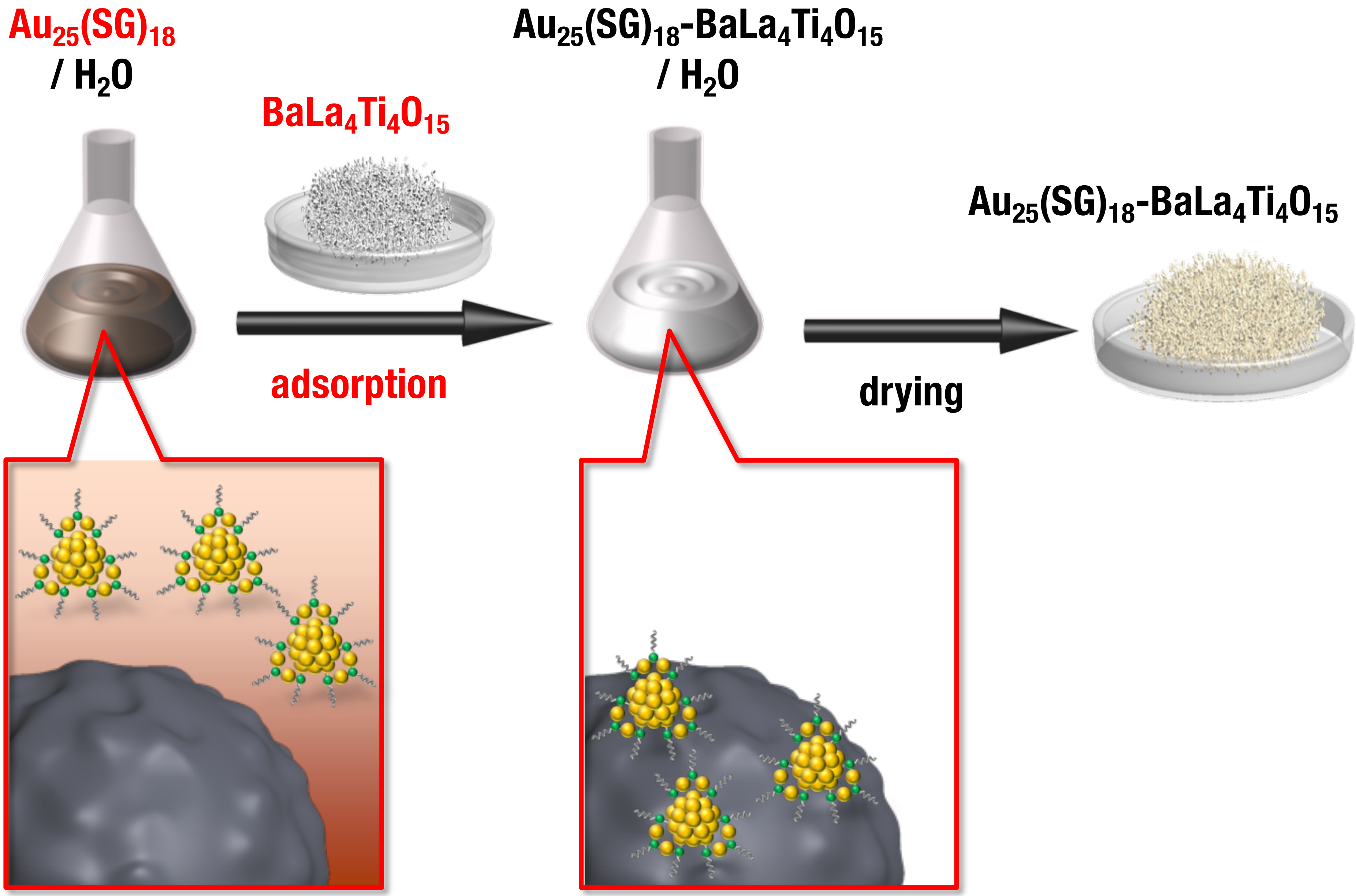
TiO_6

A. Kudo, et al.,
J. Am. Chem. Soc., 2011.

Prof. Kudo (TUS)

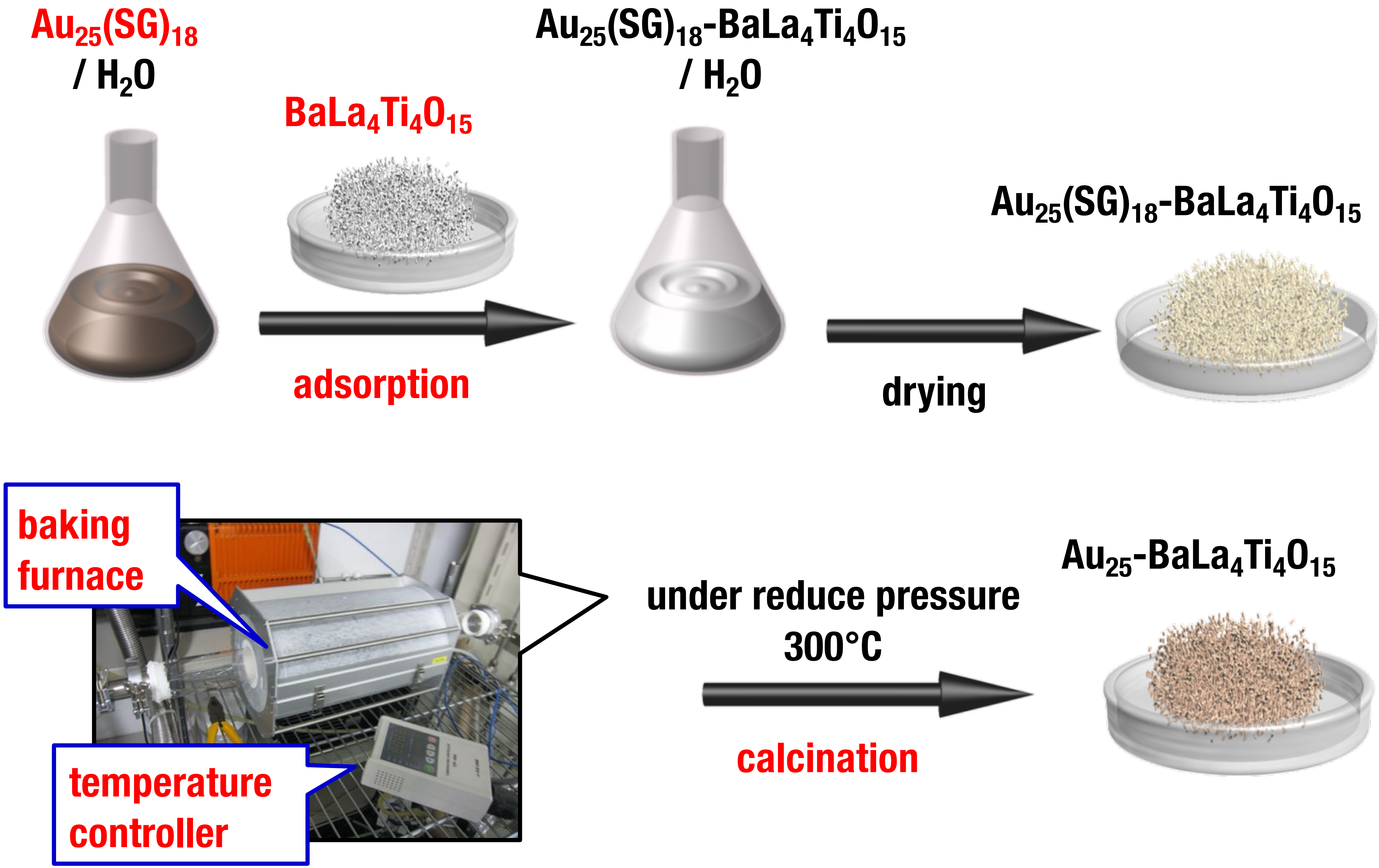
Chem. Soc. Rev. 2009.
7,315 times cited

吸着



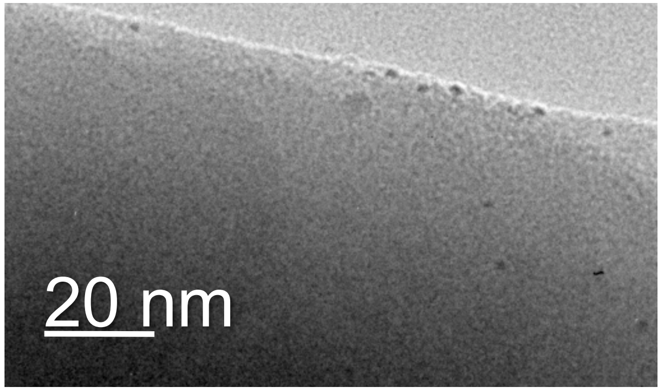
$Au_{25}(SG)_{18}$ / H_2O
$BaLa_4Ti_4O_{15}$
adsorption
$Au_{25}(SG)_{18}$-$BaLa_4Ti_4O_{15}$ / H_2O
drying
$Au_{25}(SG)_{18}$-$BaLa_4Ti_4O_{15}$

焼成

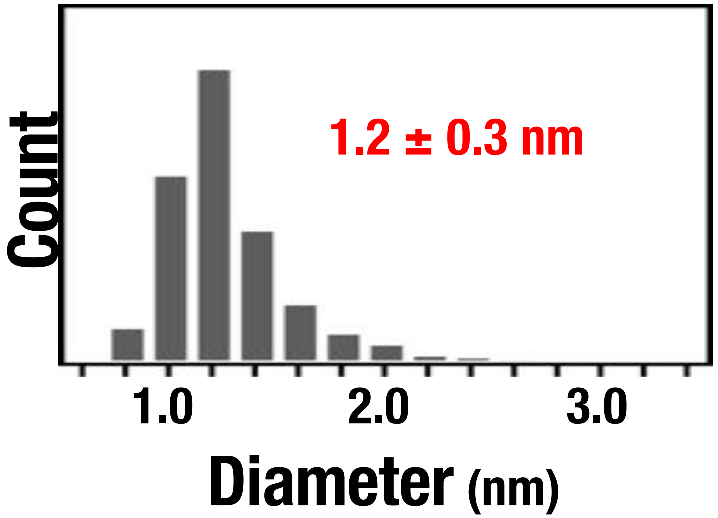

Au25(SG)18
/ H2O
BaLa4Ti4O15
adsorption
Au25(SG)18-BaLa4Ti4O15
/ H2O
drying
Au25(SG)18-BaLa4Ti4O15
baking
furnace
temperature
controller
under reduce pressure
300°C
calcination
Au25-BaLa4Ti4O15

焼成後のサンプル

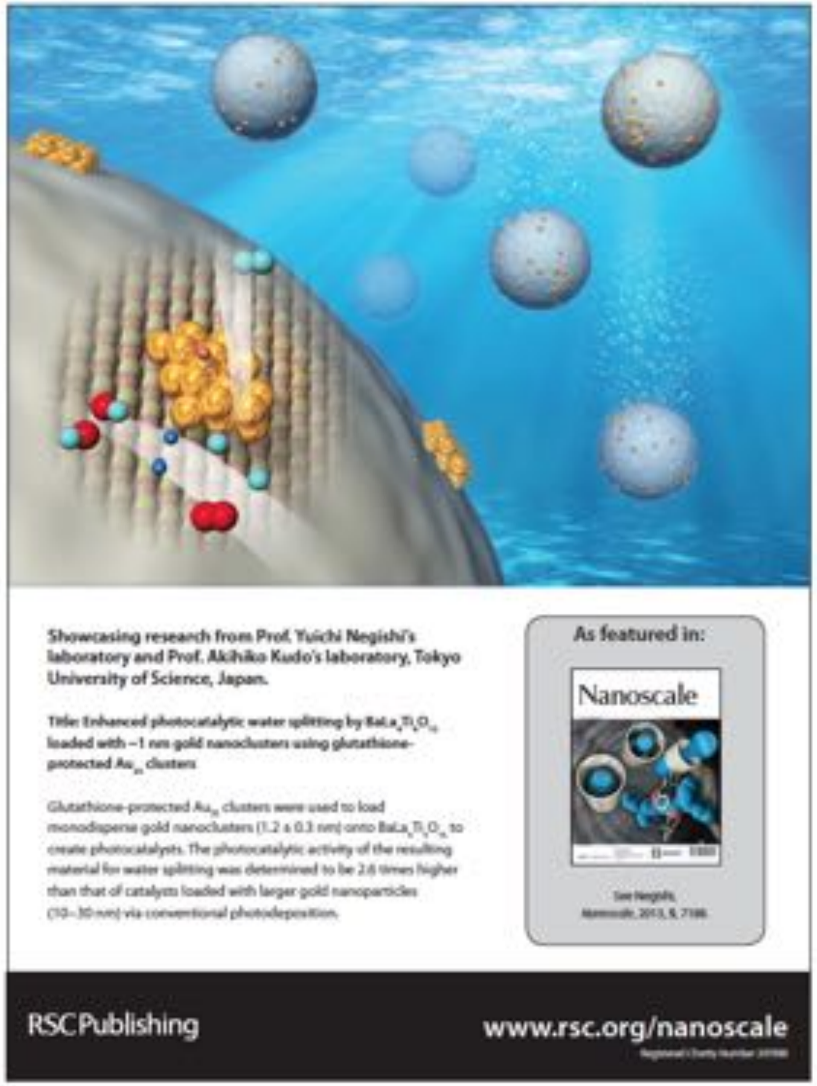
TEM image



Histogram



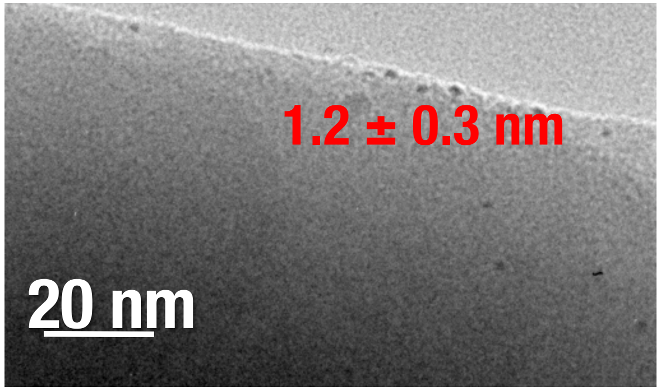
Nanoscale, 2013.



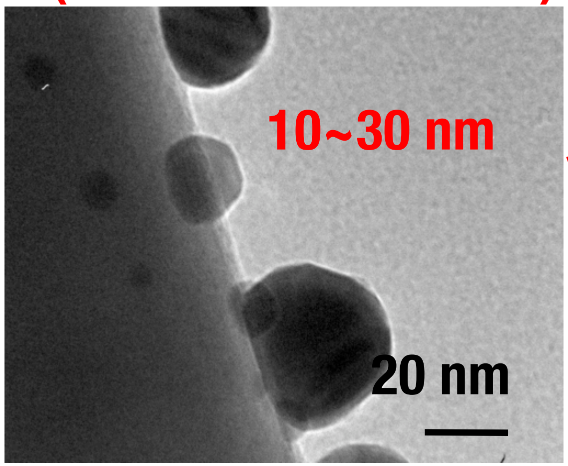
Gold cluster cocatalyst was loaded while maintaining the cluster size.

水分解光触媒活性の測定

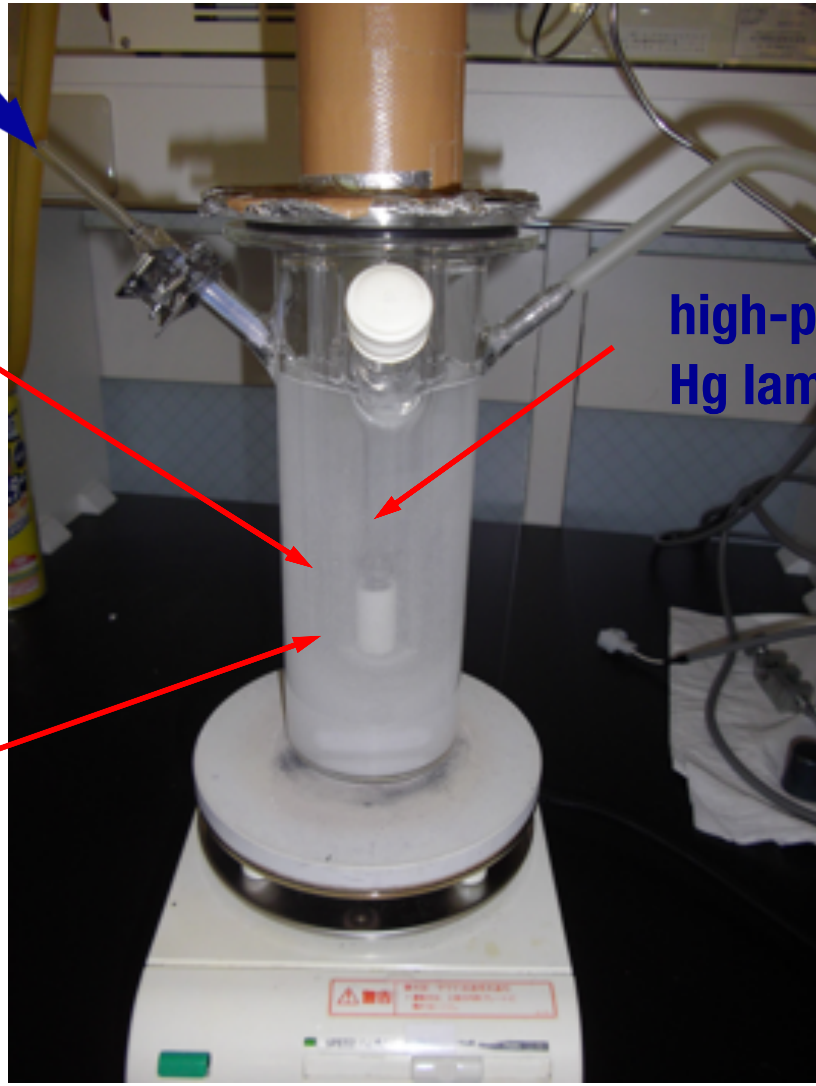
Au_{25}-$BaLa_4Ti_4O_{15}$
(present method)



Au_{NP}-$BaLa_4Ti_4O_{15}$
(conventional method)

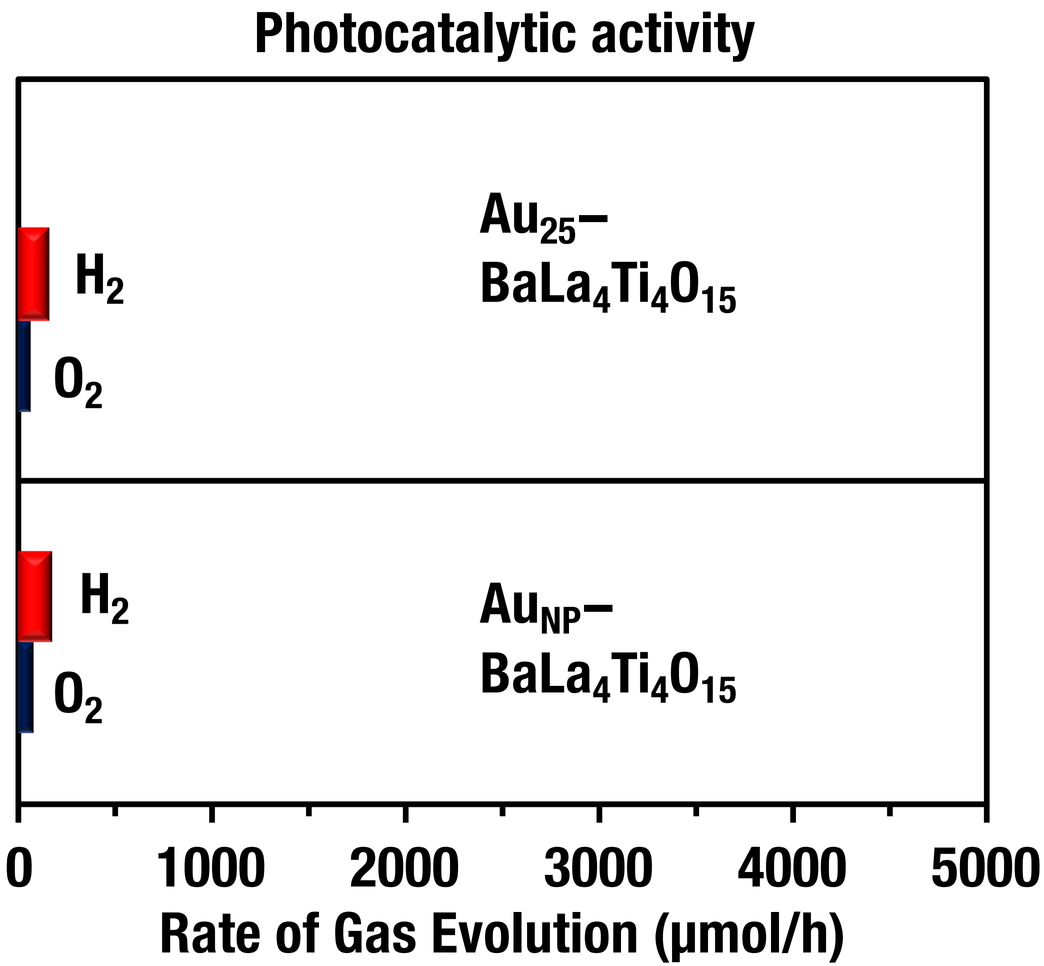


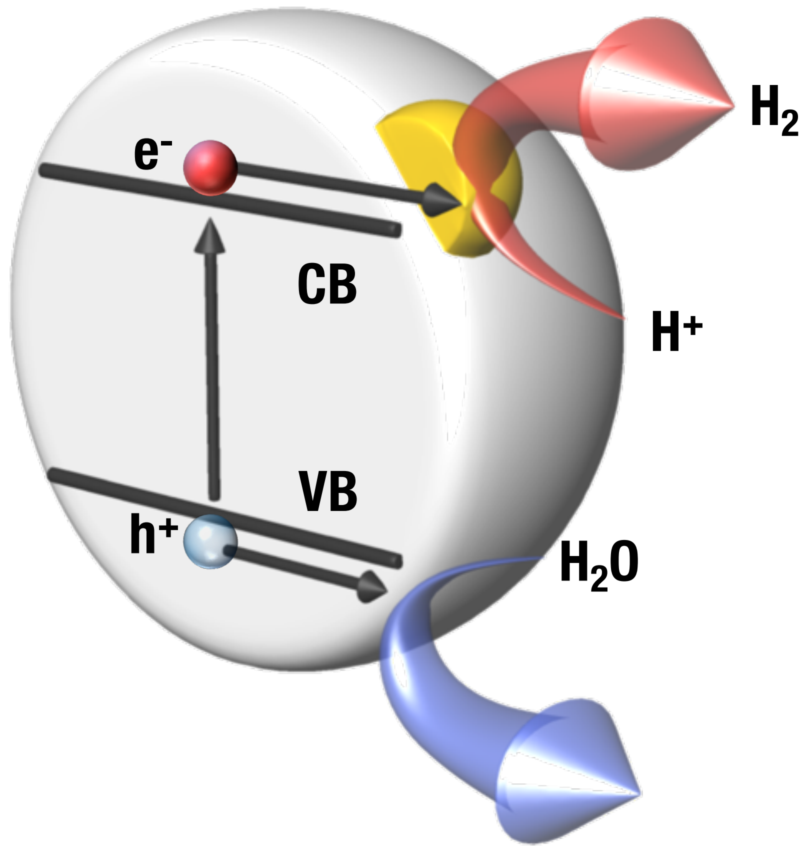
Ar



high-presure
Hg lamp

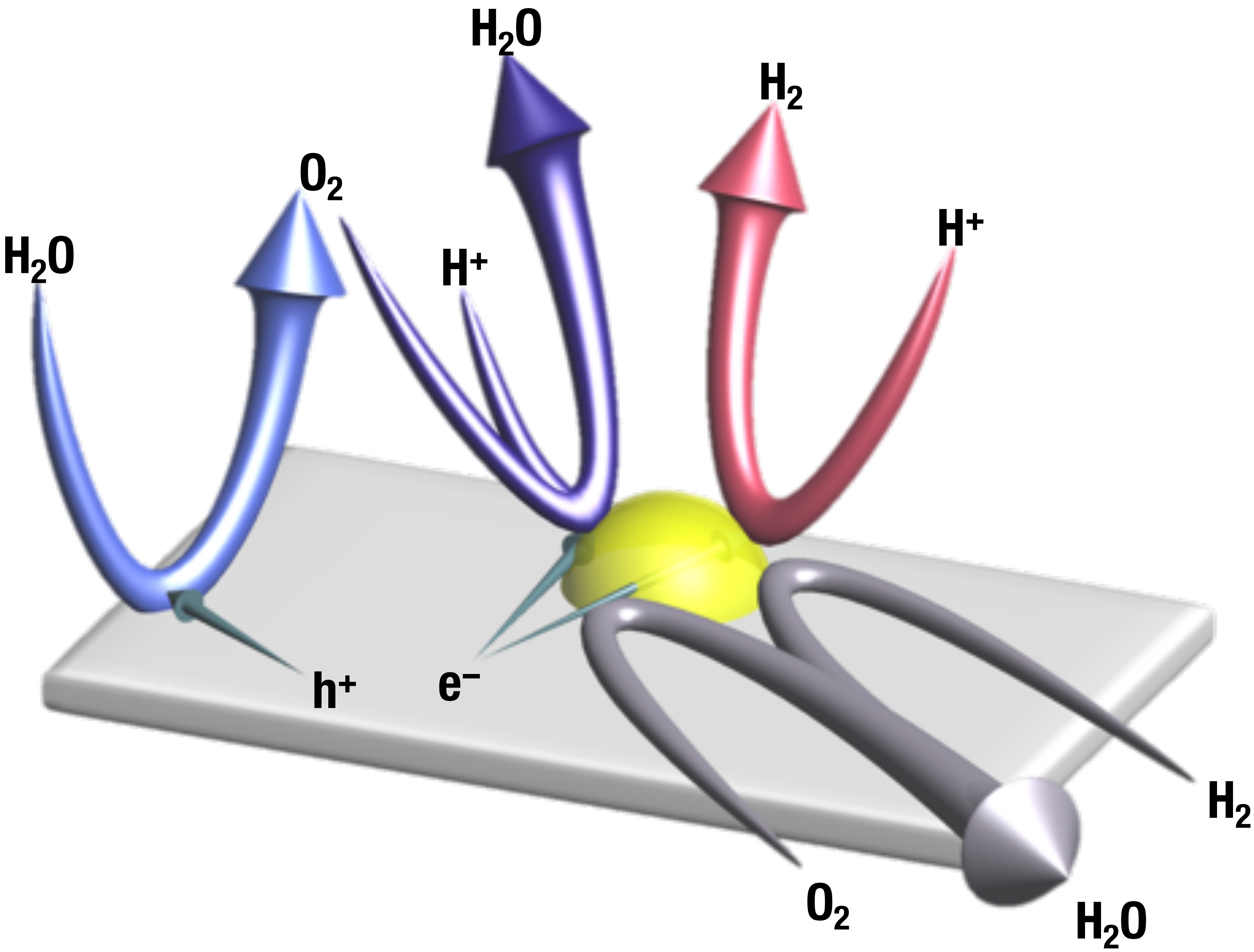
水分解活性



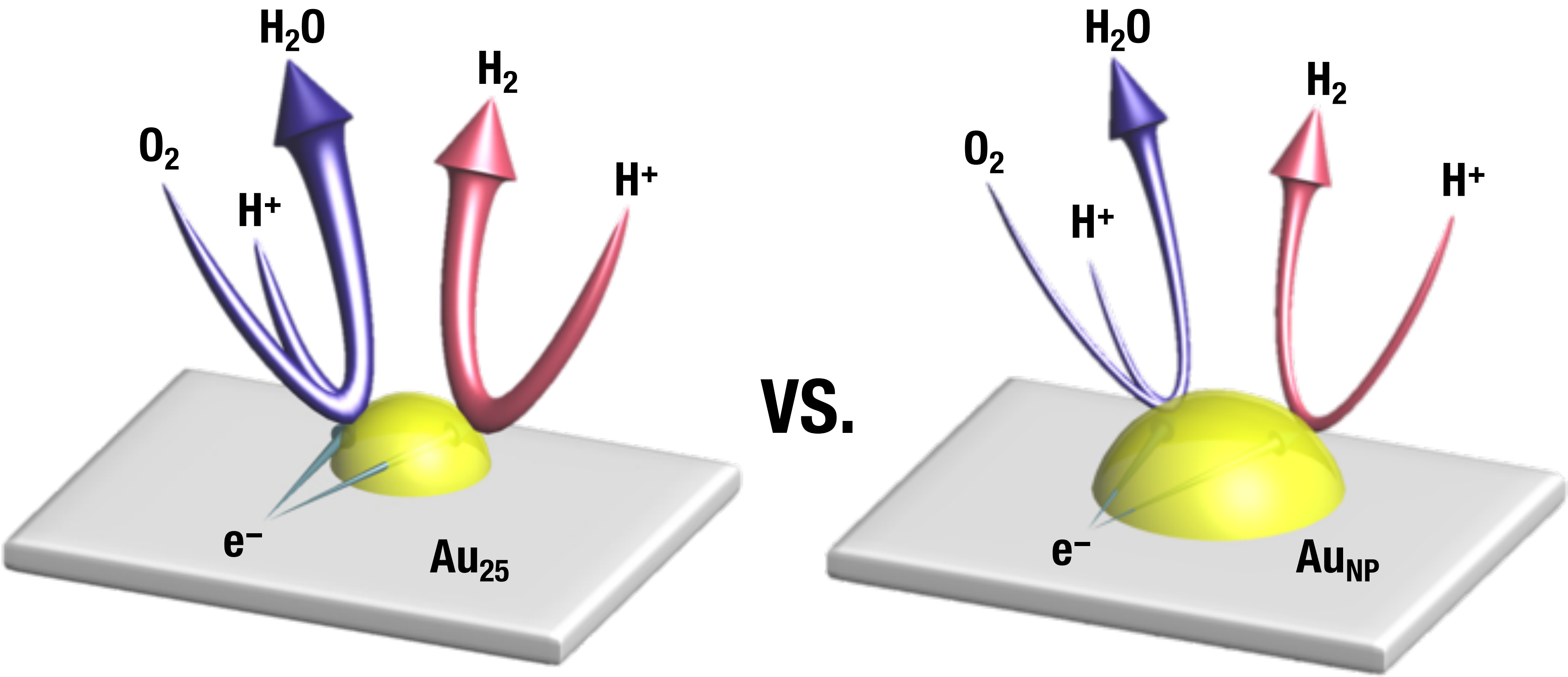


Water-splitting phtocatalytic activity of this material cannot be improved by mere miniaturization of cocatalyst

水分解時に起こる反応

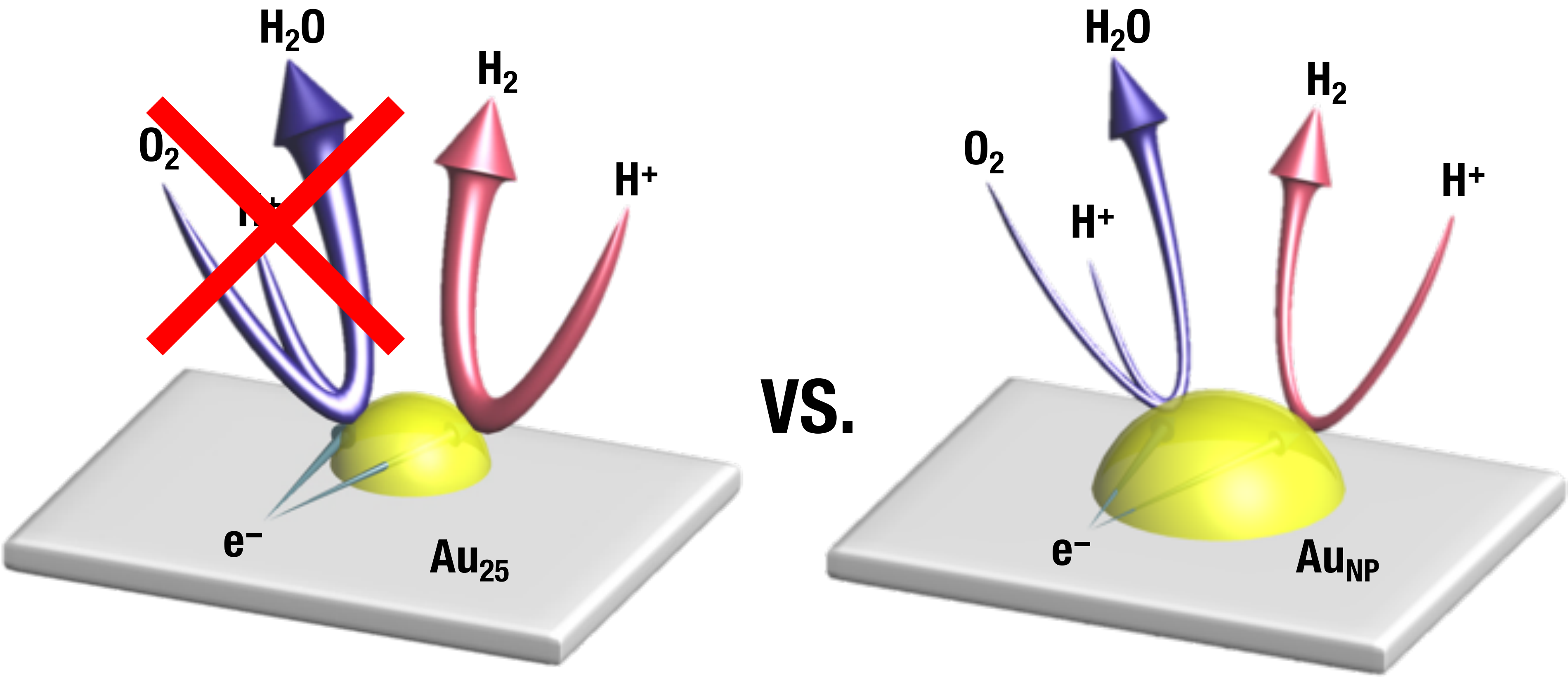


助触媒の微細効果



Miniaturization of cocatalyst improves not only hydrogen evolution ability but also oxygen photoreduction reaction

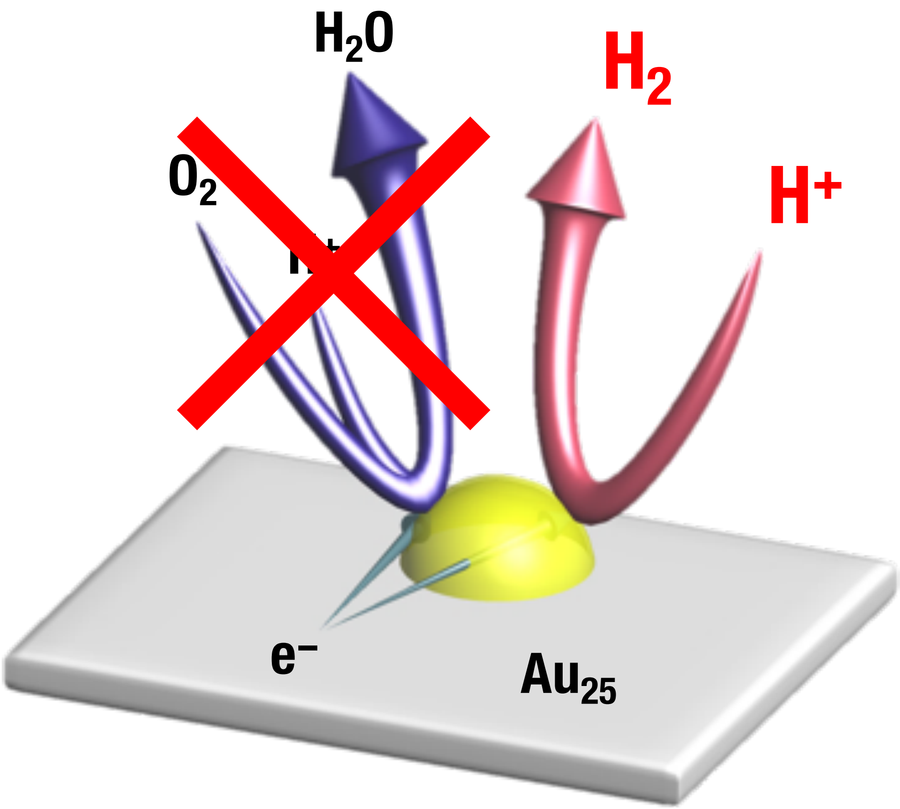
助触媒の微細効果



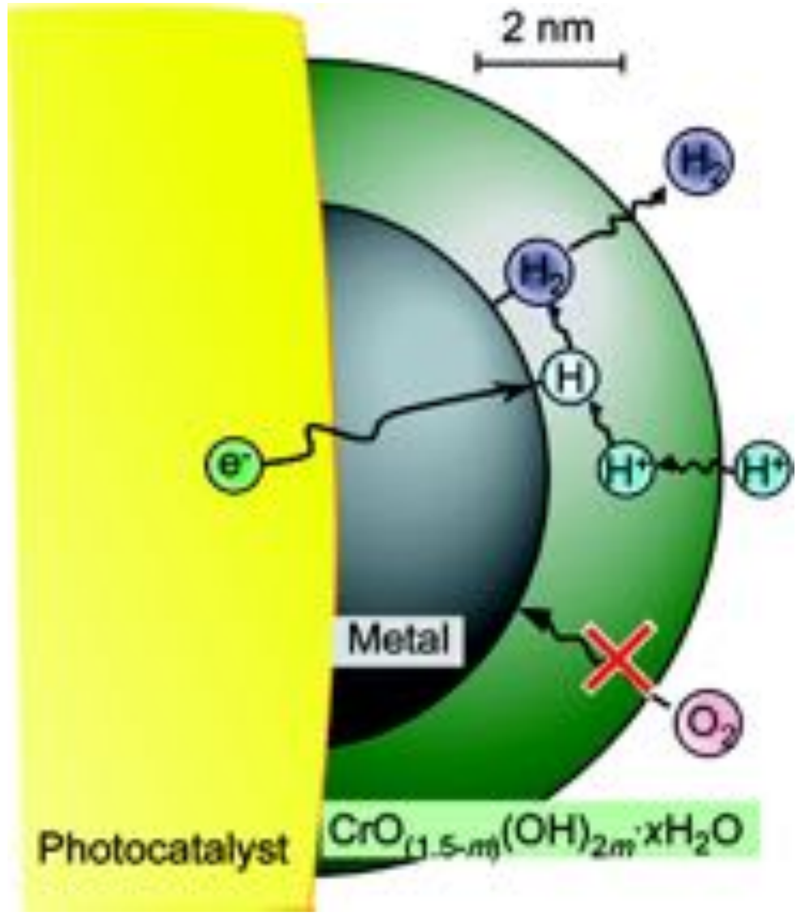
Miniaturization of cocatalyst improves not only hydrogen evolution ability but also oxygen photoreduction reaction

If oxygen photoreduction reaction can be suppressed, highly active water-splitting photocatalyst can be created using high hydrogen evolution ability of small clusters

助触媒の微細効果



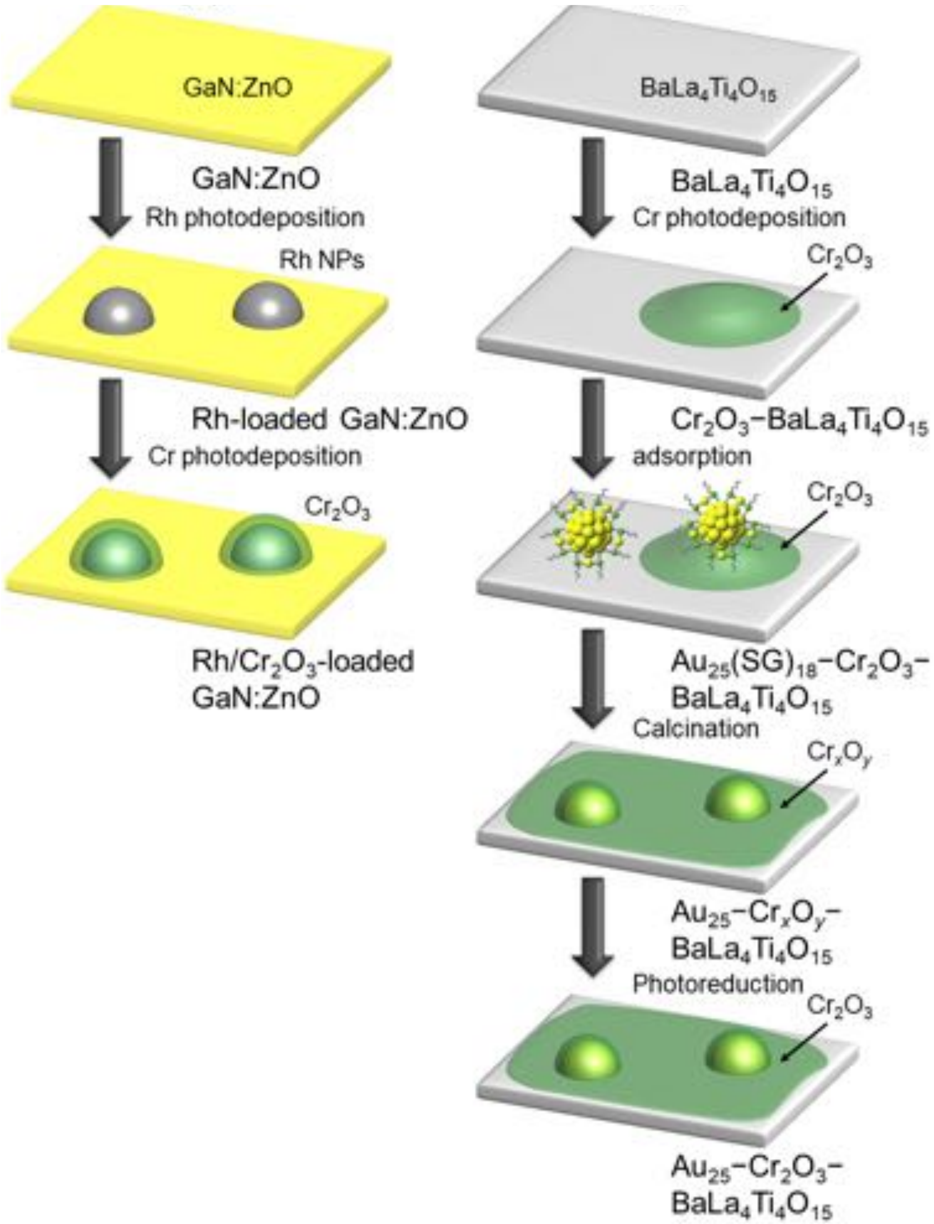
M. Yoshida, K. Domen, et al., J. Phys. Chem. C, (2009), 113, 10151.



Formation of Cr_2O_3 shell is powerful method to suppress only oxygen photoreduction reaction

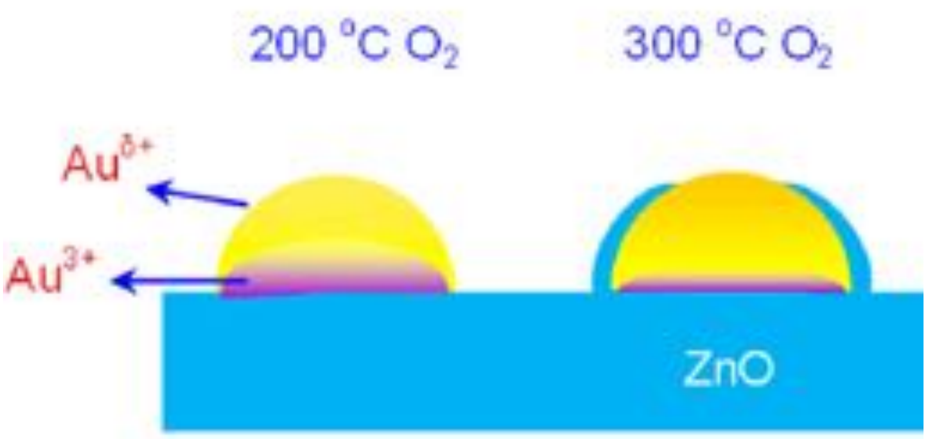
SMSI効果によるCr_2O_3膜の形成

K. Domen, et al., **New Method**

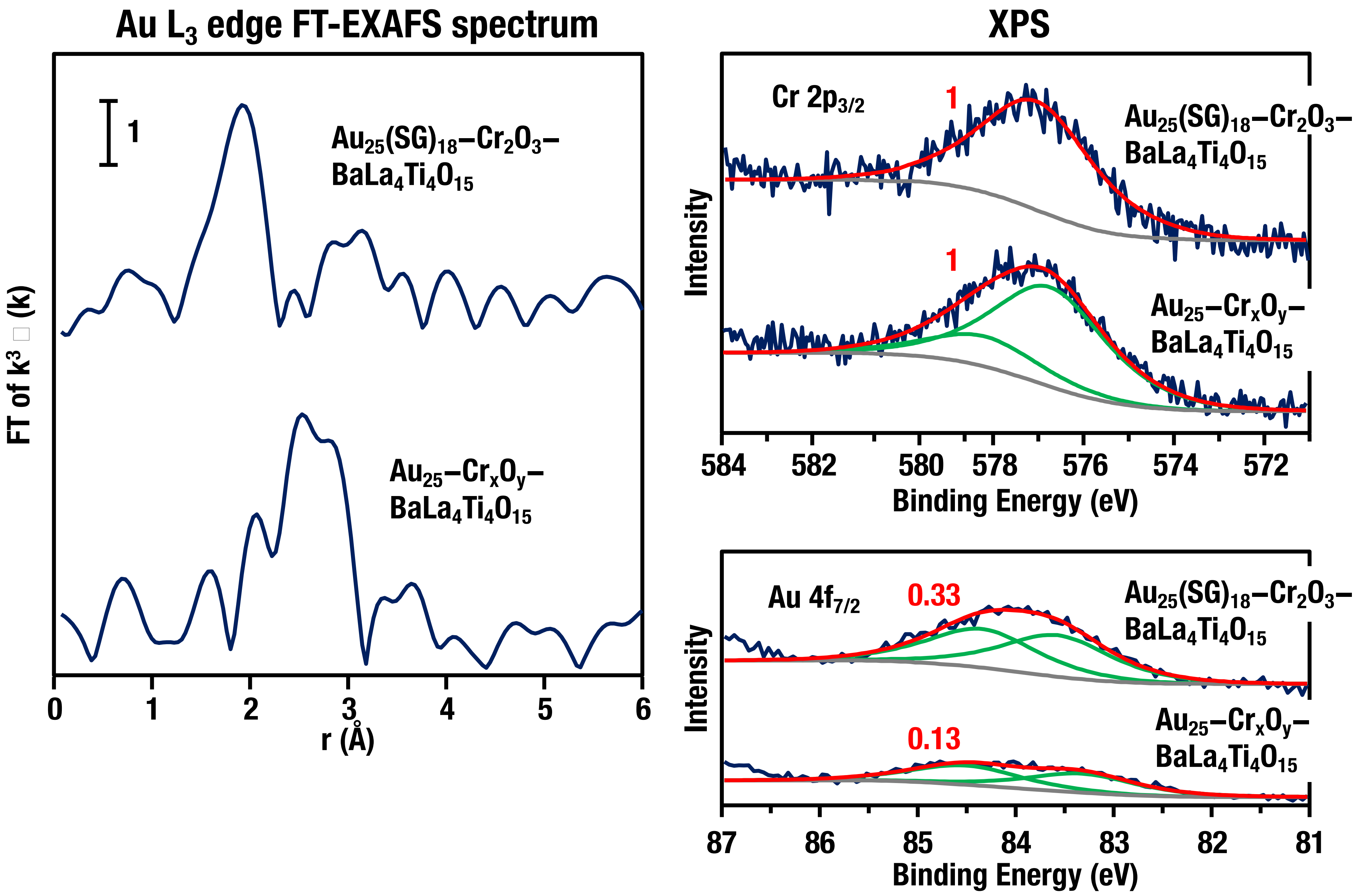


strong metal–support interaction （SMSI）

X. Liuet al. J. Am. Chem. Soc. (2012)



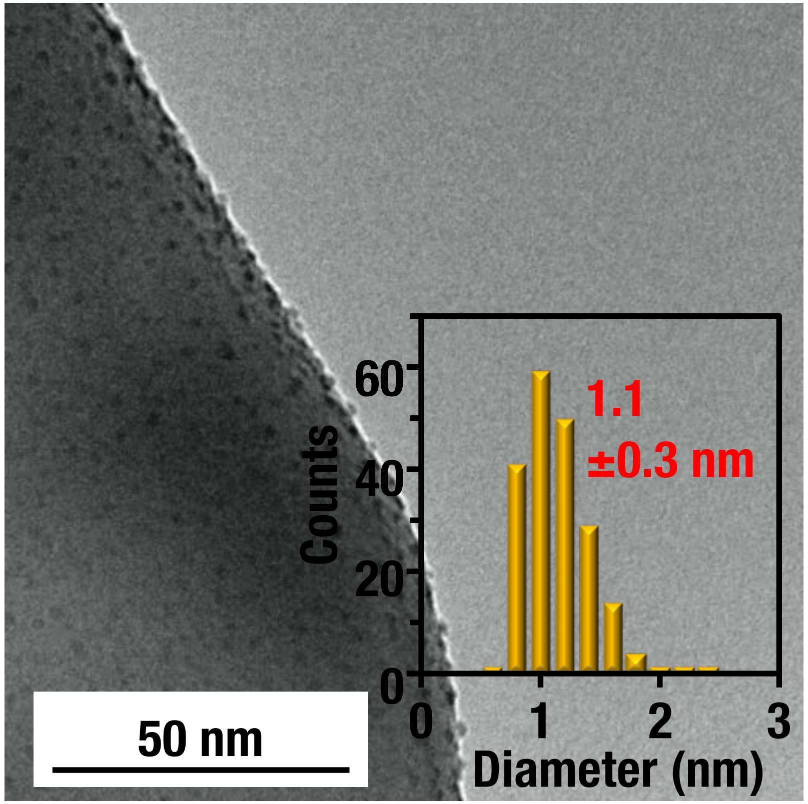
反応メカニズムの確認



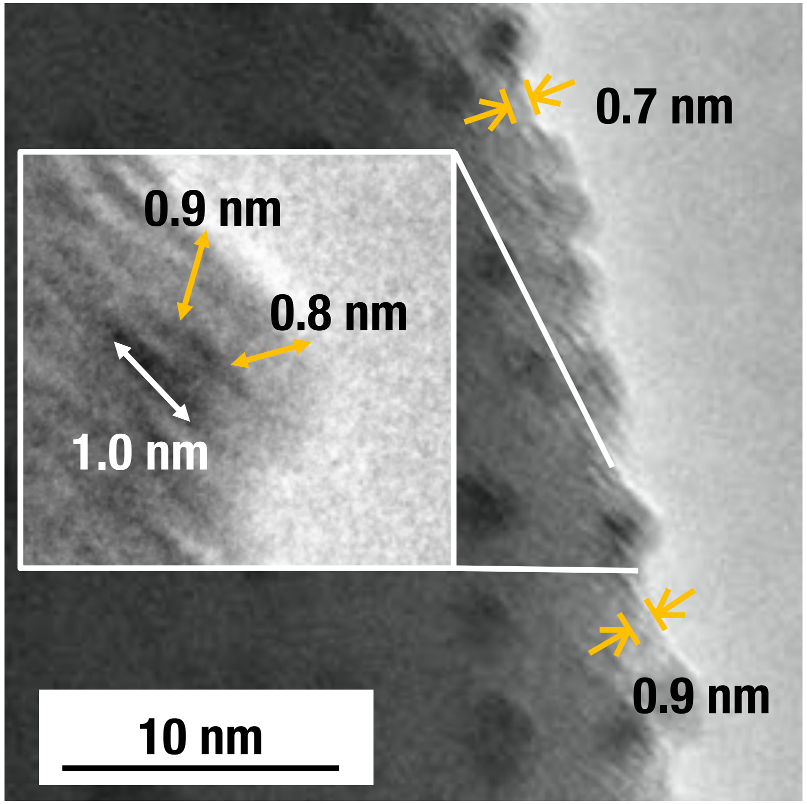
Au L3 edge FT-EXAFS spectrum
1
Au25(SG)18–Cr2O3–BaLa4Ti4O15
Au25–CrxOy–BaLa4Ti4O15
FT of k3 (k)
0 1 2 3 4 5 6
r (Å)
XPS
Cr 2p3/2
1
Au25(SG)18–Cr2O3–BaLa4Ti4O15
1
Au25–CrxOy–BaLa4Ti4O15
Intensity
584 582 580 578 576 574 572
Binding Energy (eV)
Au 4f7/2
0.33
Au25(SG)18–Cr2O3–BaLa4Ti4O15
0.13
Au25–CrxOy–BaLa4Ti4O15
Intensity
87 86 85 84 83 82 81
Binding Energy (eV)

焼成後のサンプルのTEMイメージ

TEM image

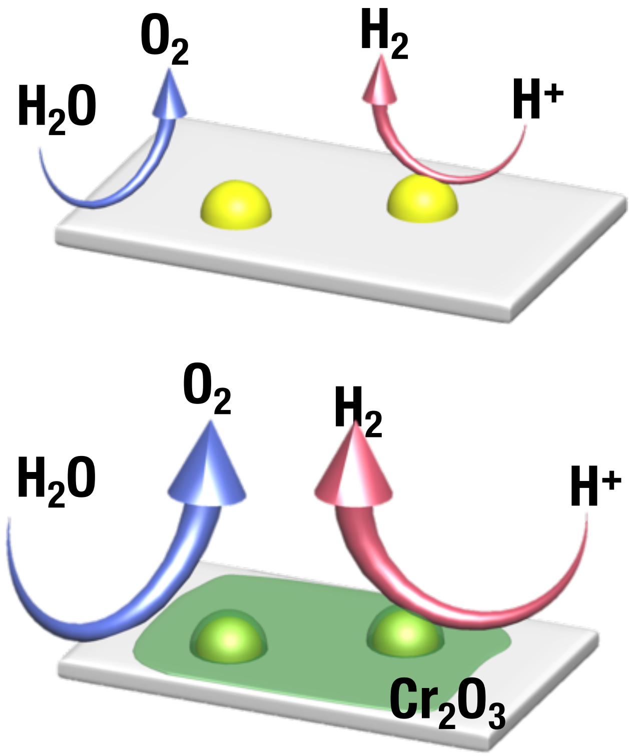


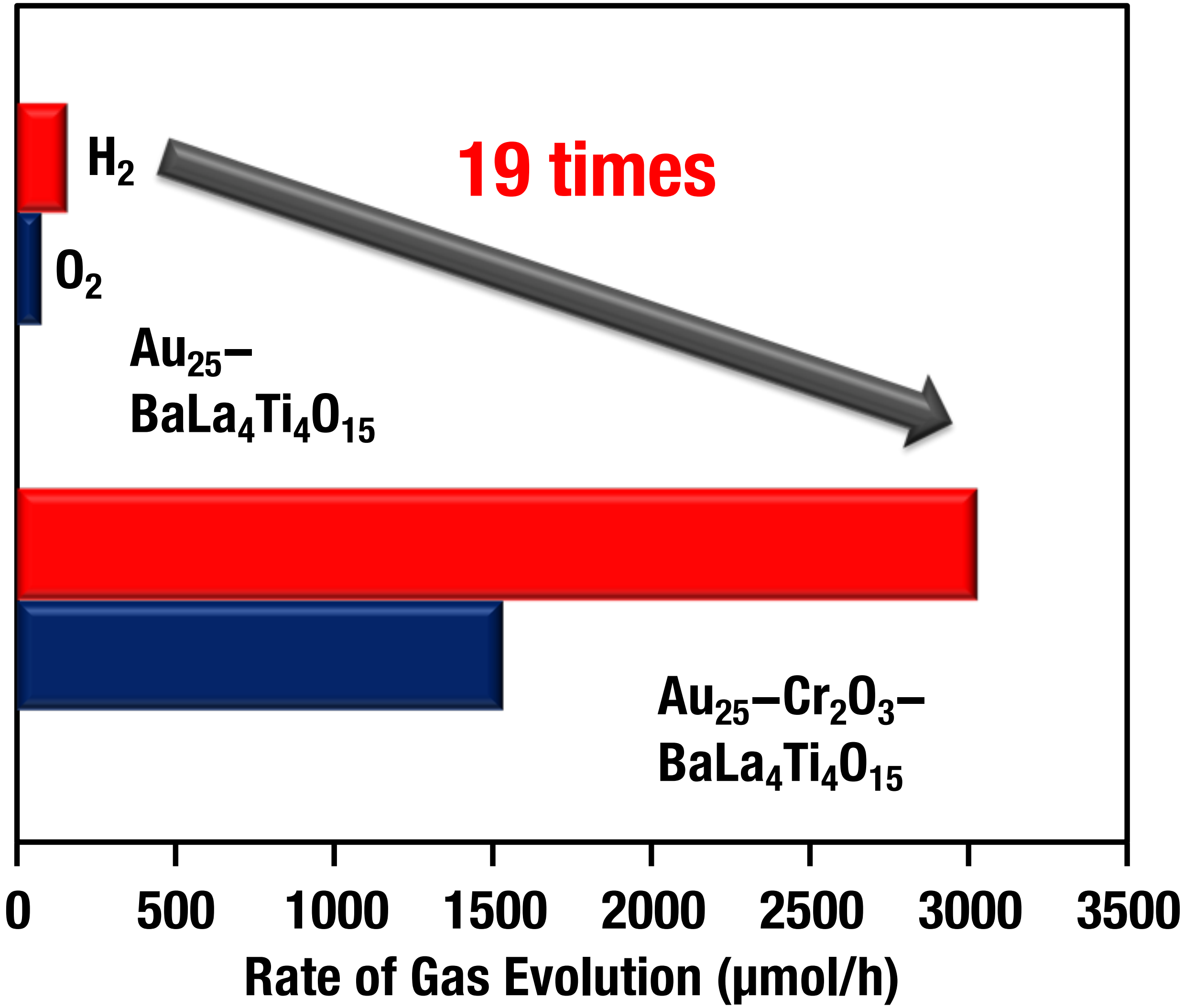
HR-TEM image



We have succeed in embedding cocatalyst in Cr_2O_3 while maintaining cluster size

Cr_2O_3膜形成後の光触媒の水分解活性

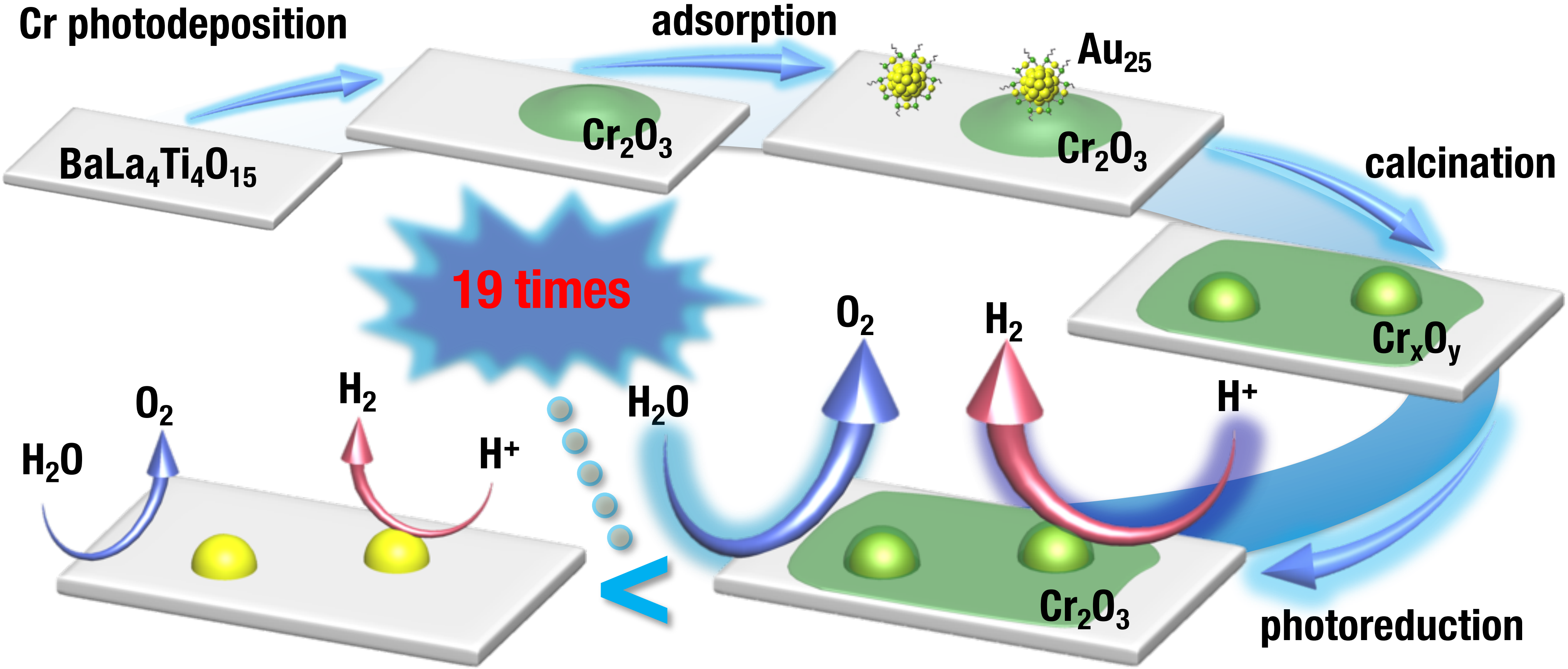




The photocatalytic activity was improved by about 19 times
by the formation of Cr2O3 shell

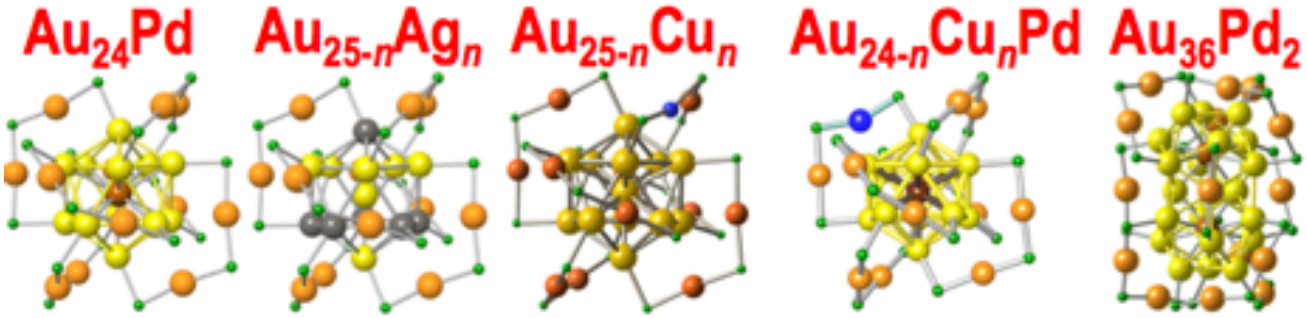
助触媒の微細化研究より得られた知見

J. Phys. Chem. C (2018).

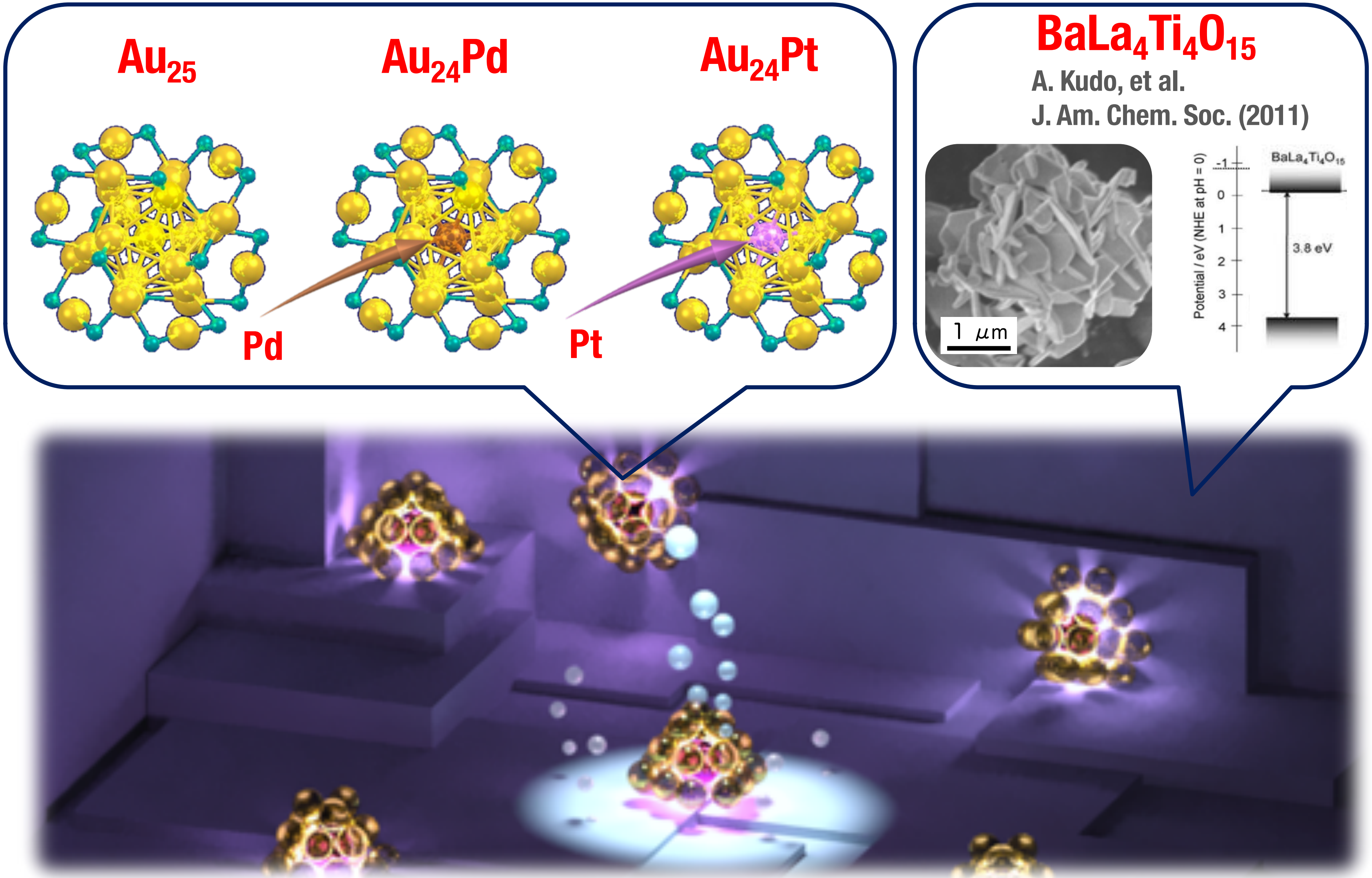


We have succeeded in creating highly activity water-splitting photocatalyst using characteristics of small gold cluster cocatalyst by establishing new method for the formation of Cr_2O_3 shell.

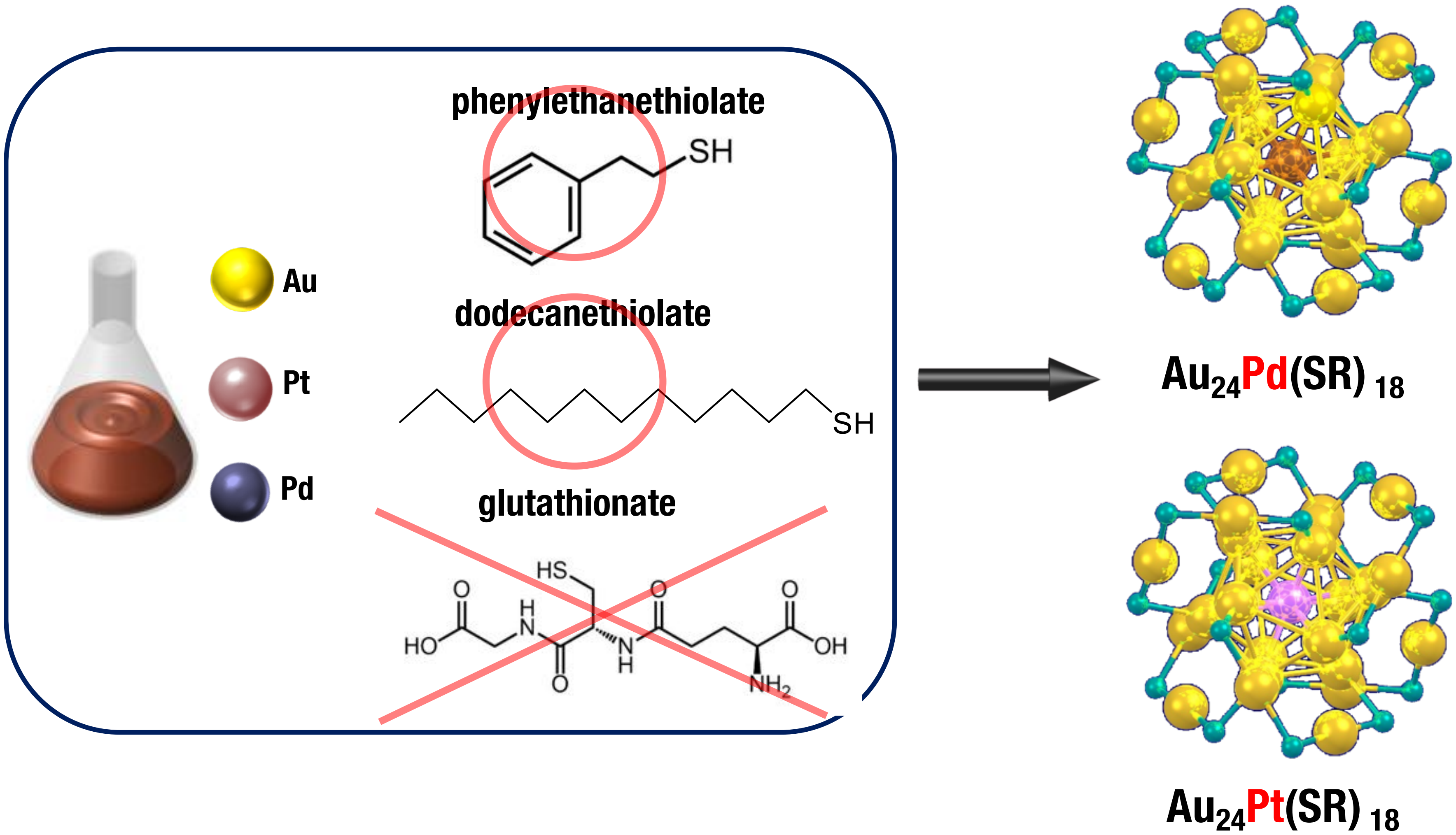
我々が合成に成功した合金クラスター



合金クラスターの助触媒利用

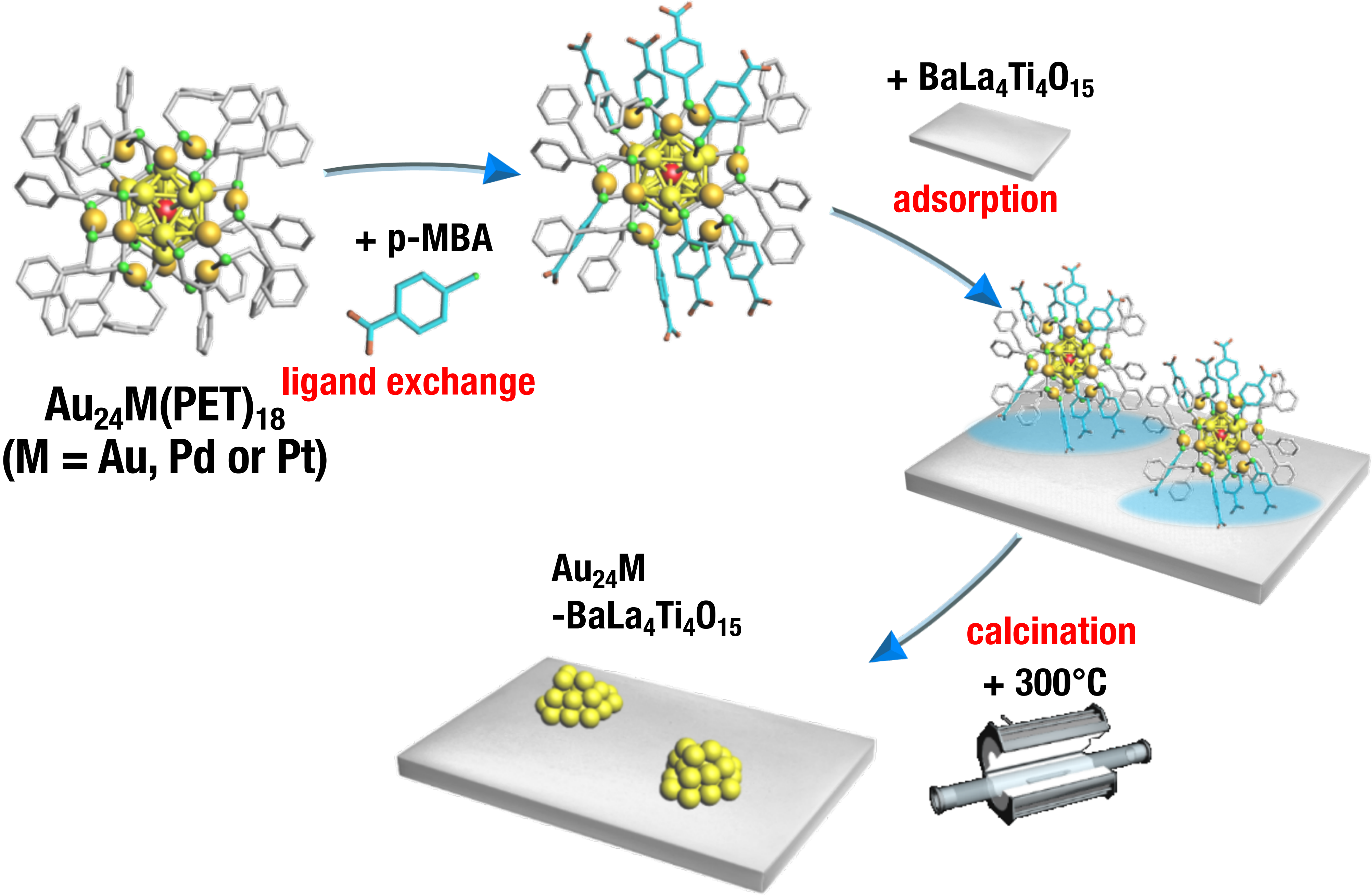


合金クラスターの合成



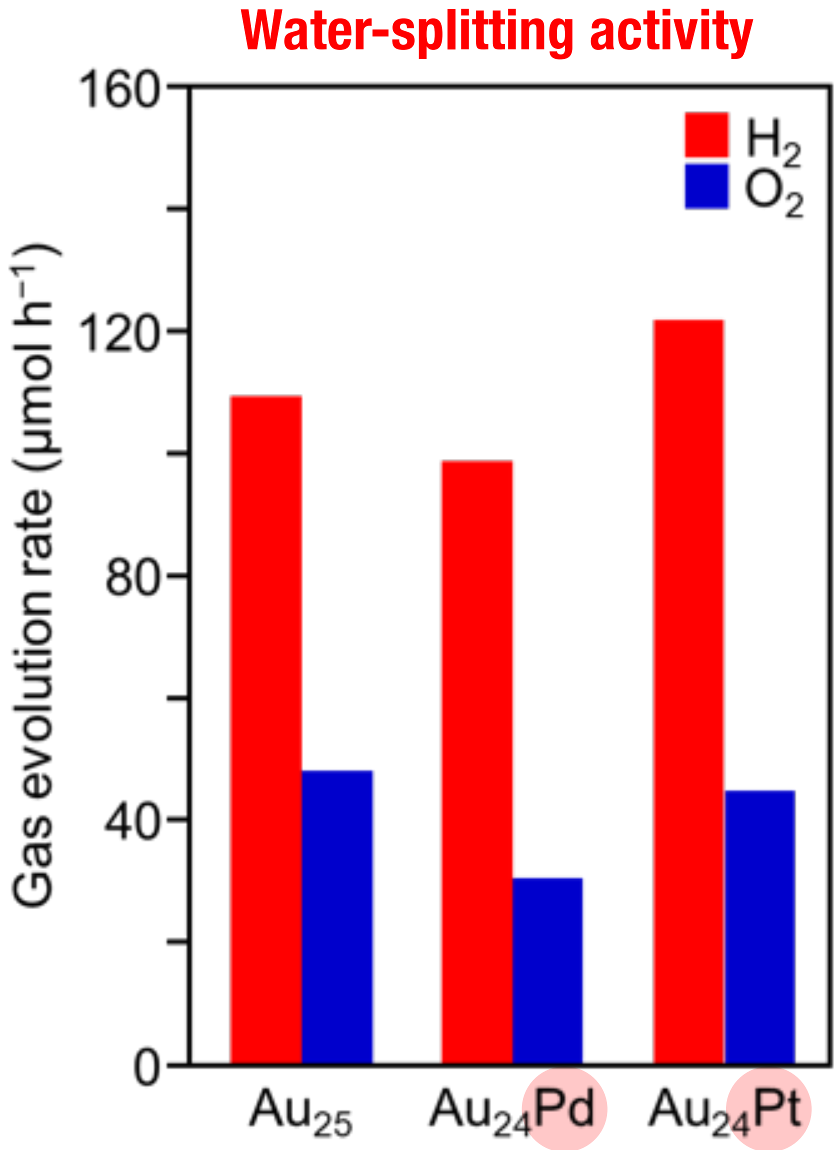
Alloy cluster can be synthesized using only hydrophilic ligands

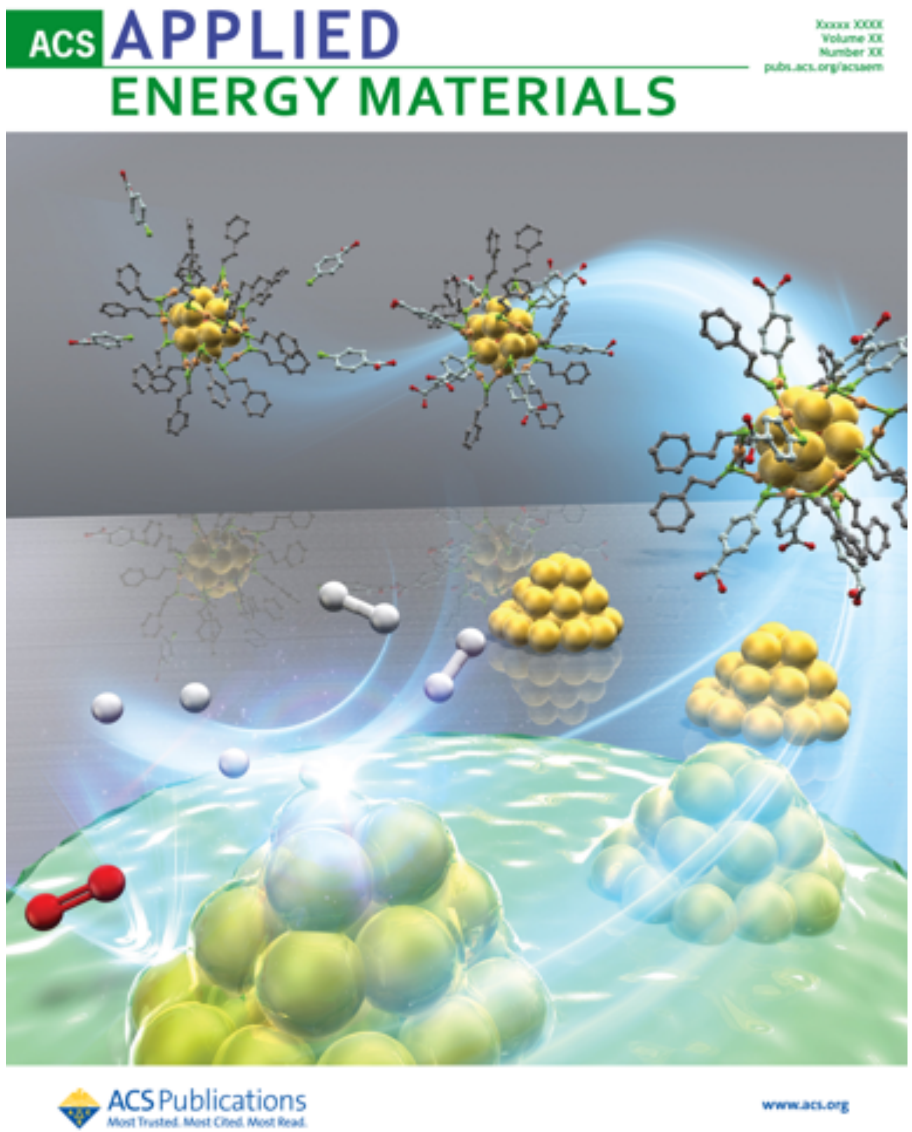
合金クラスターの担持


Au24M(PET)18
(M = Au, Pd or Pt)
+ p-MBA
ligand exchange
+ BaLa4Ti4O15
adsorption
calcination
+ 300°C
Au24M
-BaLa4Ti4O15

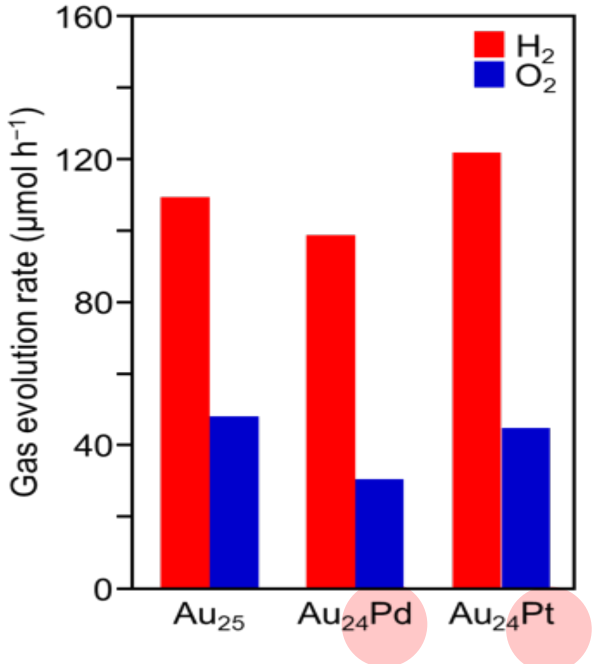
水分解活性

ACS Applied Energy Materials (2019).

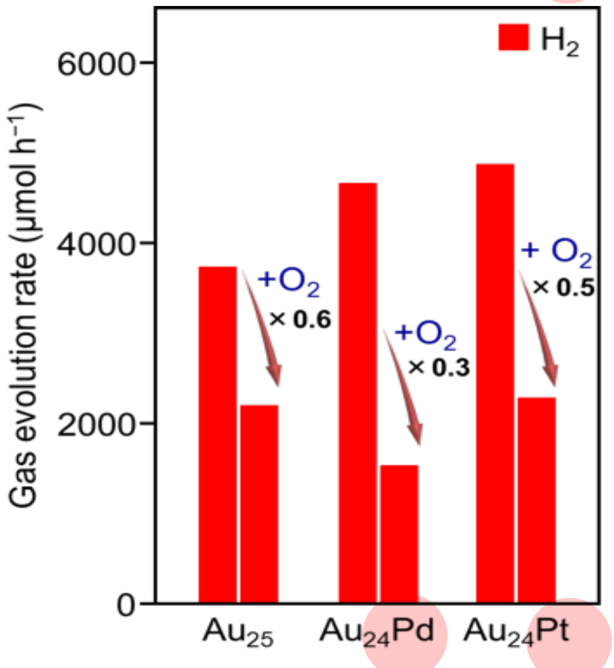




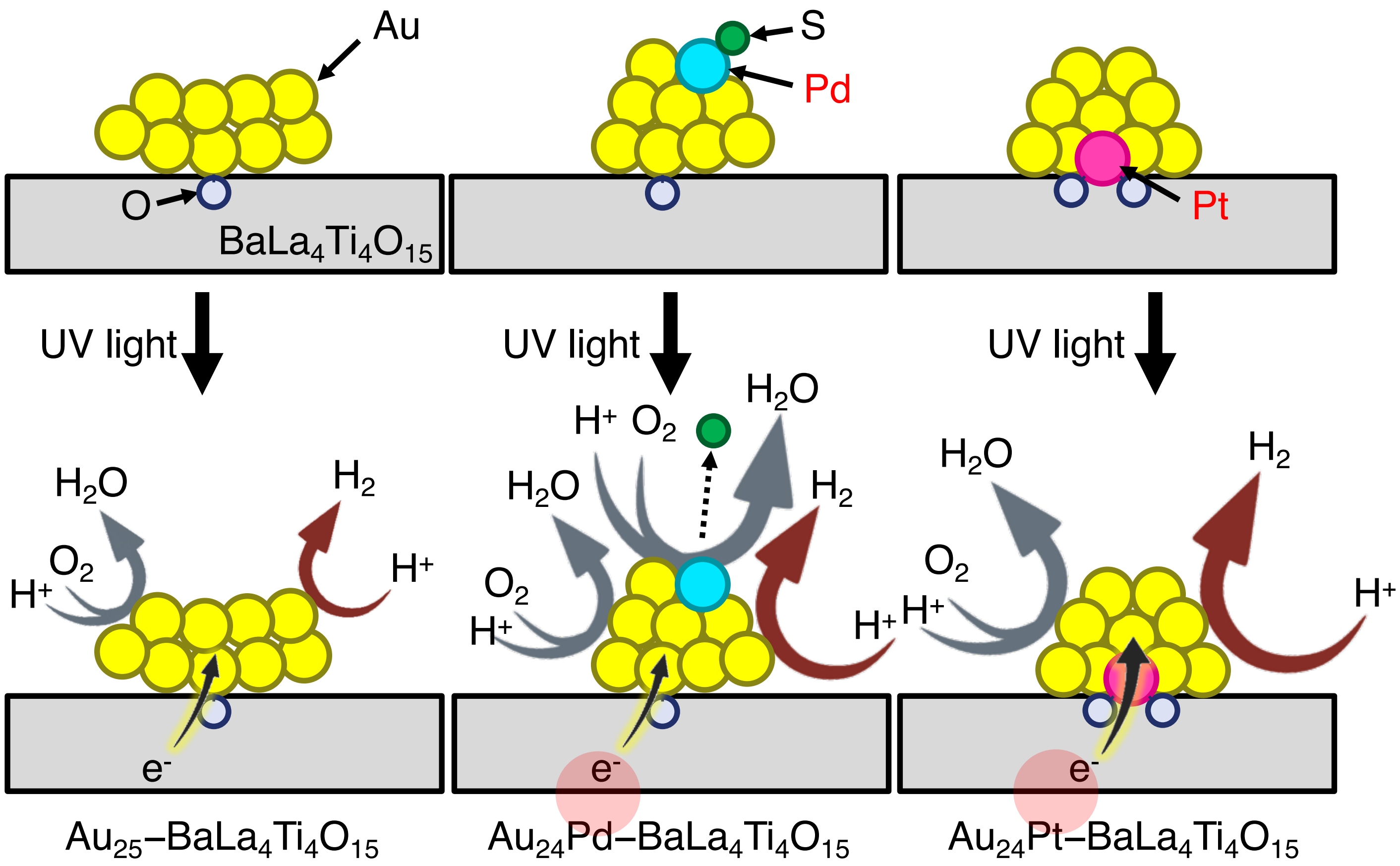
メカニズム



160
120
80
40
0
Gas evolution rate (μmol h⁻¹)
H2
O2
Au25
Au24Pd
Au24Pt



6000
4000
2000
0
Gas evolution rate (μmol h⁻¹)
H2
+O2
× 0.6
+O2
× 0.3
+ O2
× 0.5
Au25
Au24Pd
Au24Pt



Au
O
BaLa4Ti4O15
S
Pd
Pt
UV light
UV light
UV light
H2O
O2
H+
H2
H+
e-
H+ O2
H2O
H2O
H2
O2
H+
H+
e-
H2O
H2
O2
H+
H+
e-
Au25–BaLa4Ti4O15
Au24Pd–BaLa4Ti4O15
Au24Pt–BaLa4Ti4O15

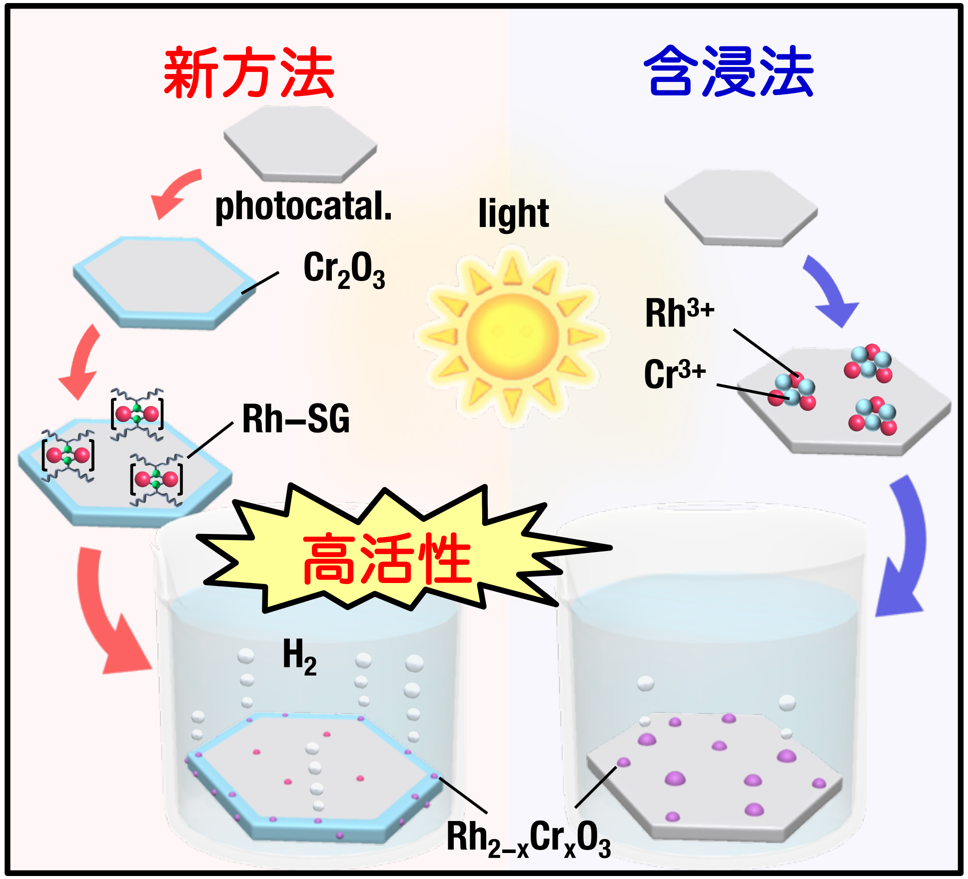
ロジウムの助触媒利用

- $(RhCr)_2O_3$粒子の助触媒利用
- 効果的担持法の確立

東京理科大学 総合研究機構
光触媒国際研究センター
Tokyo University of Science Photocatalysis International Research Center

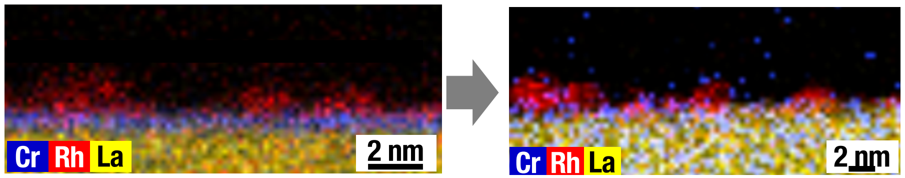
光合成分子機構の学理解明と
時空間制御による革新的光 ― 物質変換系の創製
I⁴LEC Innovations for Light-Energy Conversion

Angew. Chem., Int. Ed. in revision.

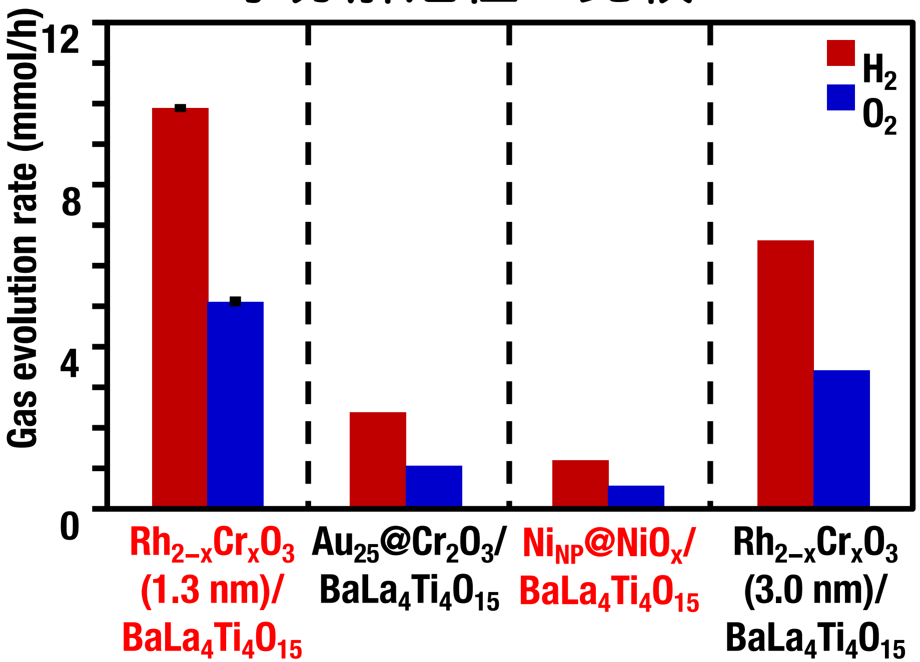


$BaLa_4T_4O_{15}$での過去最高の量子収率の実現

粒子生成メカニズムの解明



水分解活性の比較



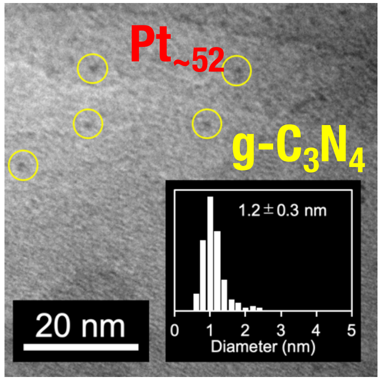
可視光応用水分解光触媒の高活性化

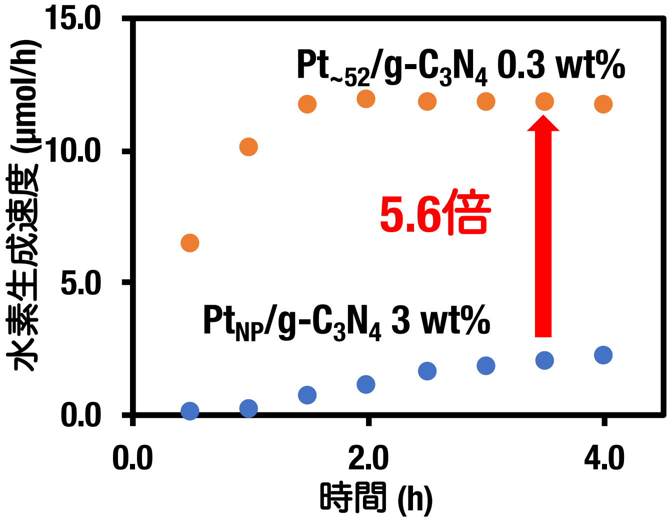
・最先端材料の高活性化
・適切元素クラスターの助触媒利用

東京理科大学 総合研究機構
光触媒国際研究センター
Tokyo University of Science Photocatalysis International Research Center

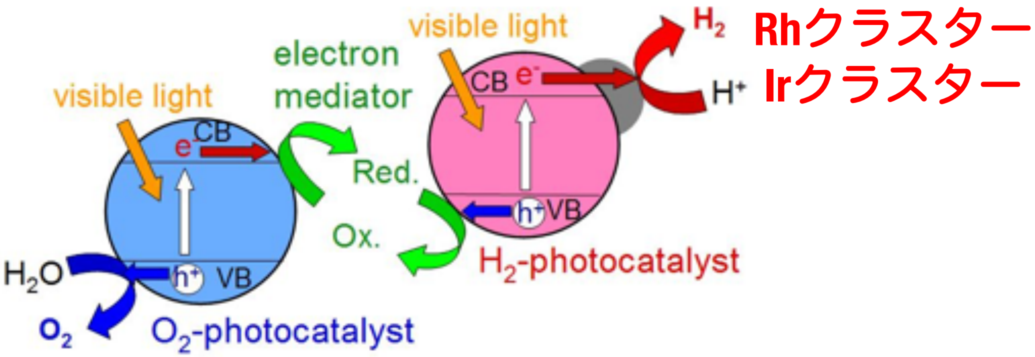
光合成分子機構の学理解明と
時空間制御による革新的光 ー 物質変換系の創製
I⁴LEC Innovations for Light-Energy Conversion

・一段階光触媒

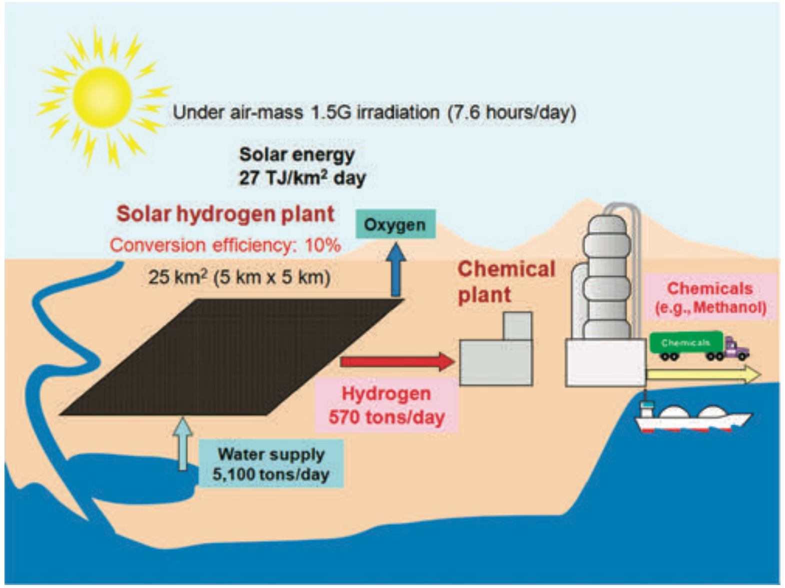




・二段階光触媒



K. Meda and K. Domen,
J. Phys. Chem. Lett. 2010



実用目処のSTH=10%を目指して

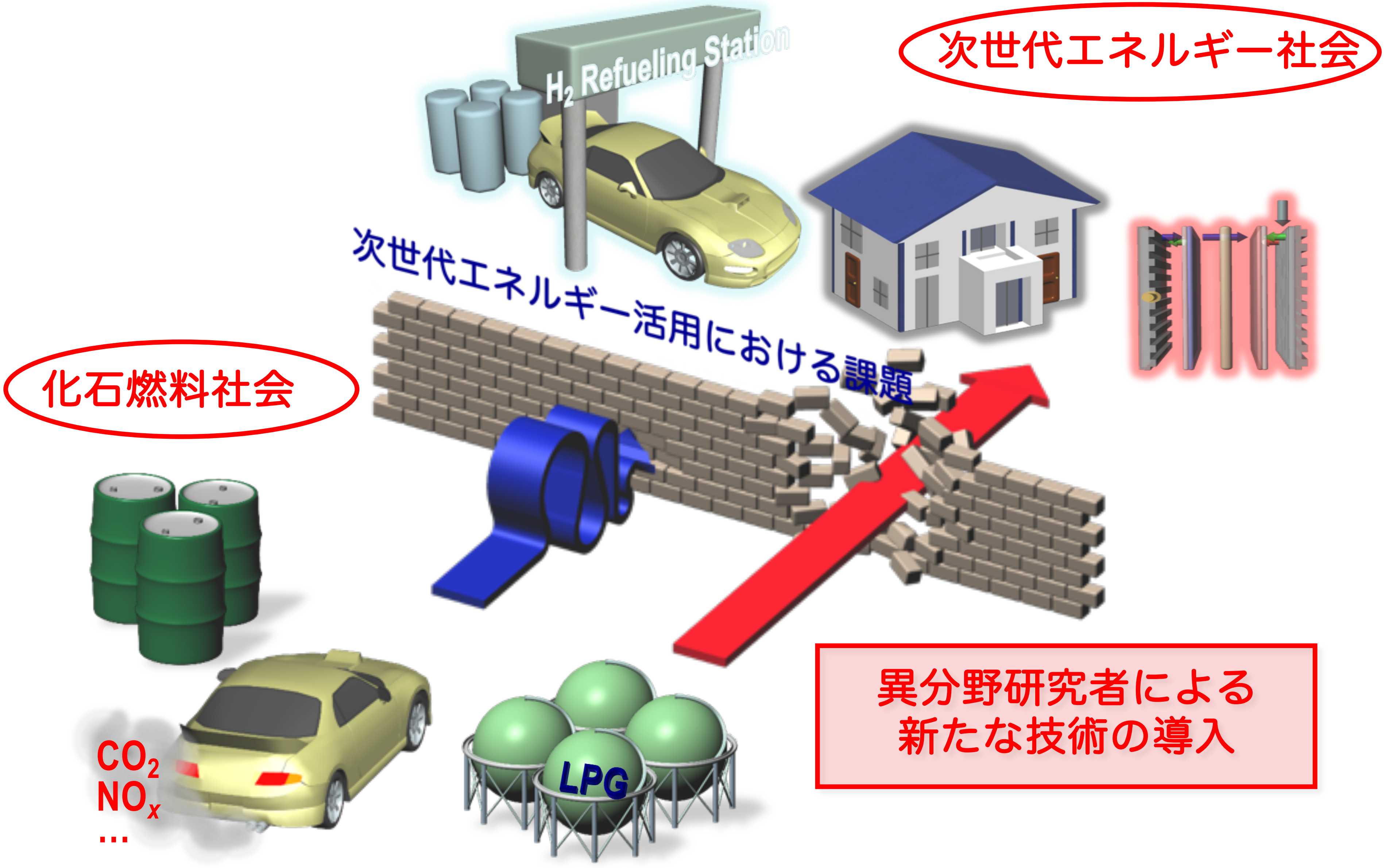
参考)

K. Domen, et al. Nat. Rev. 2017

GaN:Mg/InGaN:Mg AQY: 12.3%

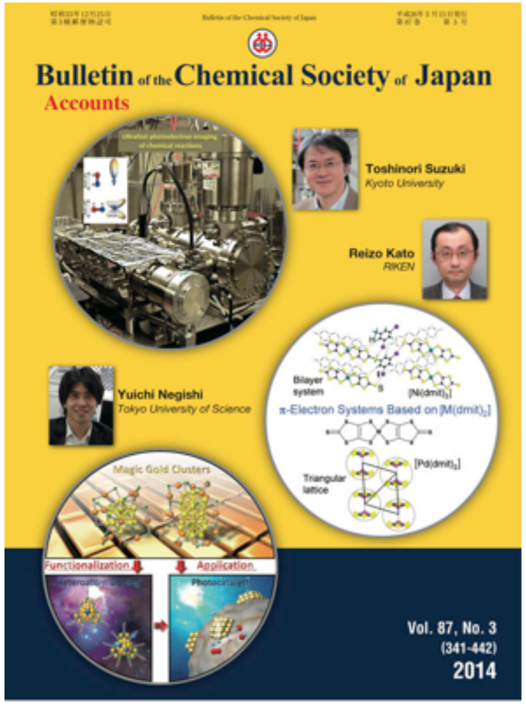
Rh/Cr_2O_3 400-475 nm, STH: 1.8%

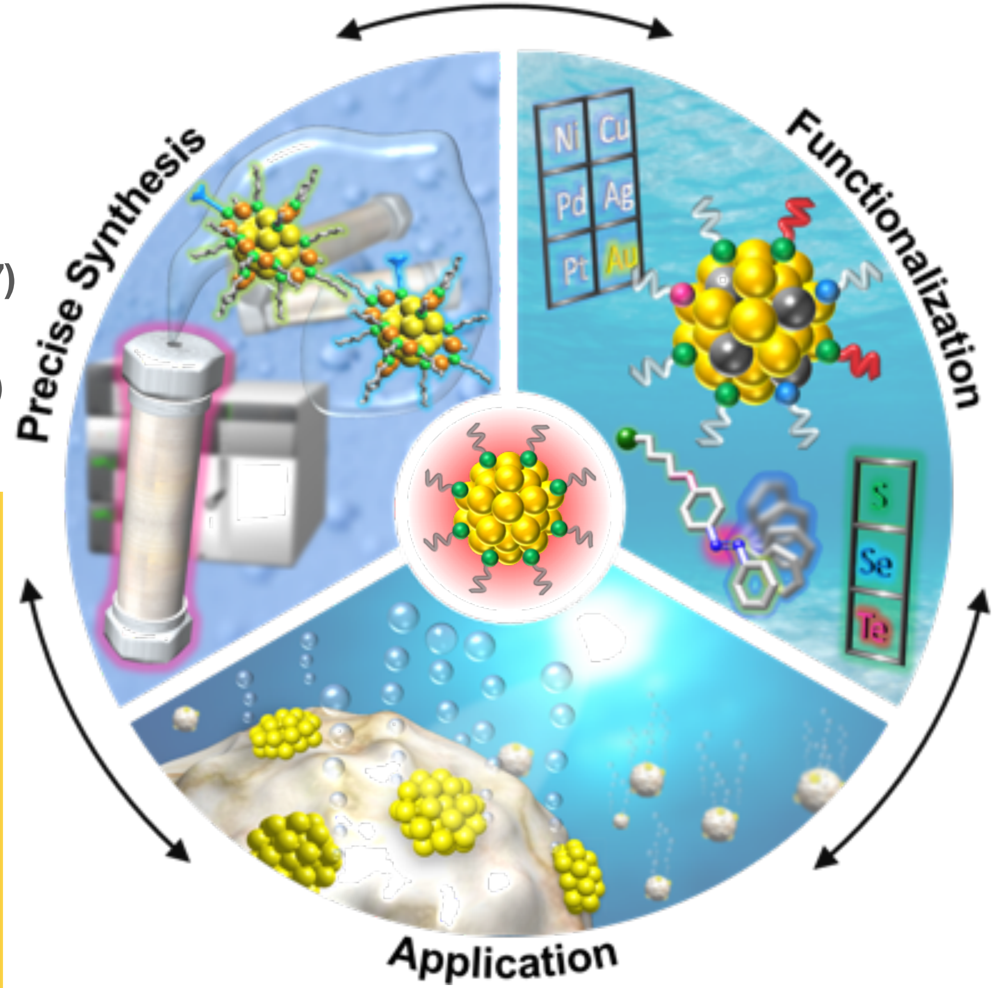
我々の期待


H2 Refueling Station
次世代エネルギー社会
次世代エネルギー活用における課題
化石燃料社会
CO2
NOx
…
LPG
異分野研究者による
新たな技術の導入

全体のまとめ

J. Phys. Chem. Lett. (2012)
J. Am. Chem. Soc. (2013)
Nanoscale (2014)
J. Am. Chem. Soc. (2015)
ACS Nano (2015)
PCCP (2016)
Ind. Eng. Chem. Res. (2017)
Nanoscale (2018)
J. Phys. Chem. Lett. (2012)



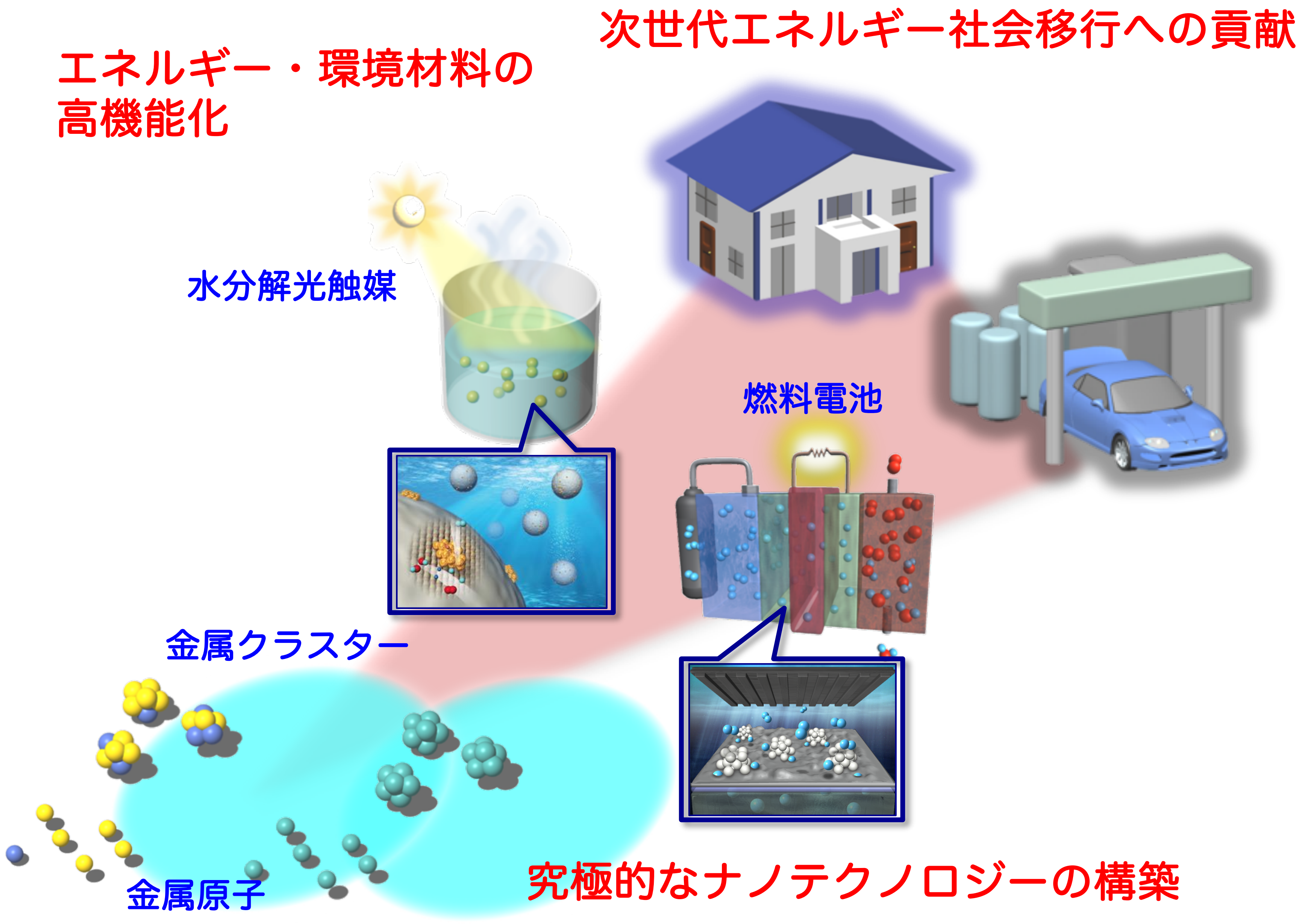


Nanoscale (2012).
PCCP (2010).
Chem. Commun. (2010).
Chem. Commun. (2012).
J. Phys. Chem. Lett. (2012).
J. Phys. Chem. Lett. (2012).
J. Phys. Chem. Lett. (2013).
Nanoscale (2013).
Nanoscale (2015).
Langmuir (Letters), (2011).
J. Phys. Chem. Lett. (2012).
Chem. Commun. (2013).
J. Phys. Chem. Lett. (2013).
J. Phys. Chem. Lett. (2014).
Dalton Trans. (2016)
J. Phys. Chem. C (2016).
J. Phys. Chem. Lett. (2018).
Nanoscale (2018).

Nanoscale (2013)
J. Phys. Chem. C (2015)
J. Mater. Appl. (2018)

J. Phys. Chem. C (2018)
Reference Module (2017)
Encyclopedia of Interfacial Chemistry (2018)

目指しているゴール

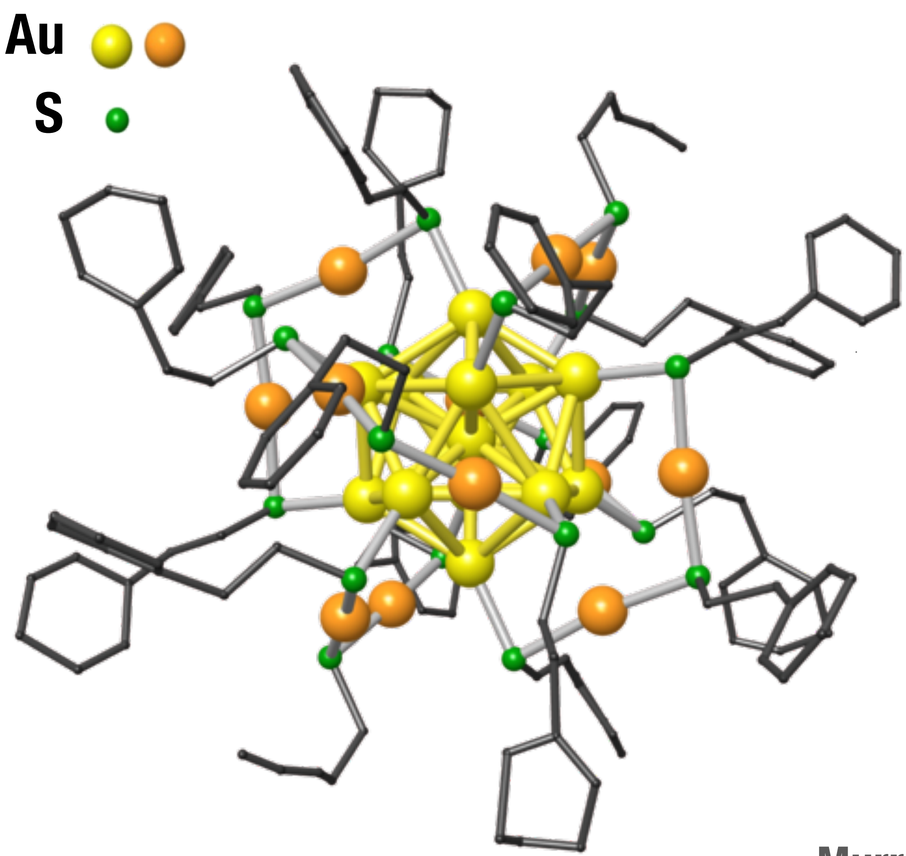


次世代エネルギー社会移行への貢献
エネルギー・環境材料の
高機能化
水分解光触媒
燃料電池
金属クラスター
金属原子
究極的なナノテクノロジーの構築

東京理科大学根岸研究室

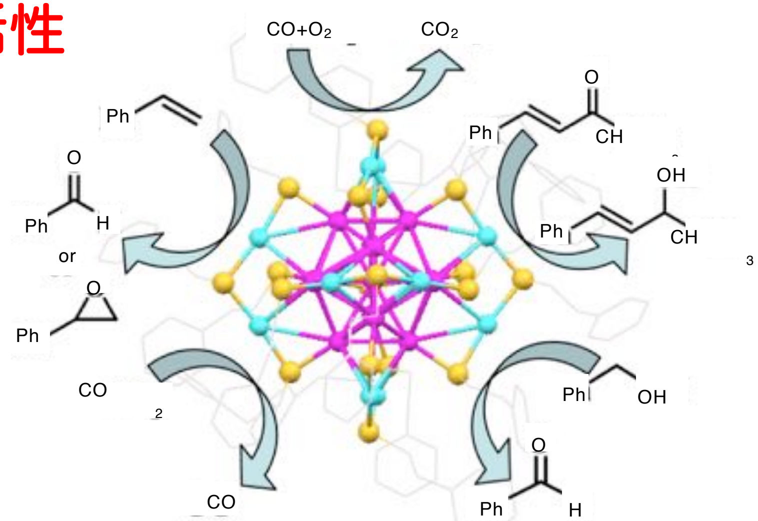
研究費謝辞：日本板硝子材料工学助成会

対象とする物質系

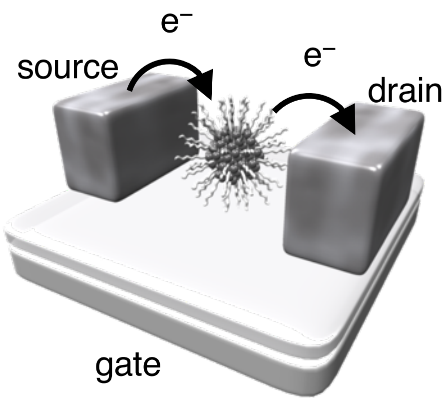


触媒活性

Jin et al.



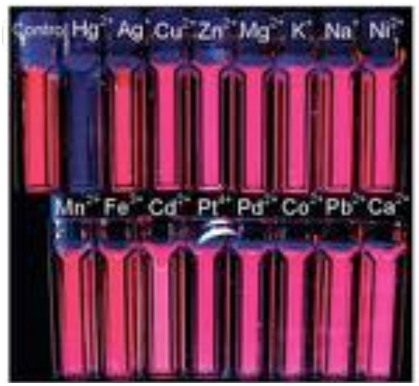
レドックス挙動



Murray et al.

可視発光

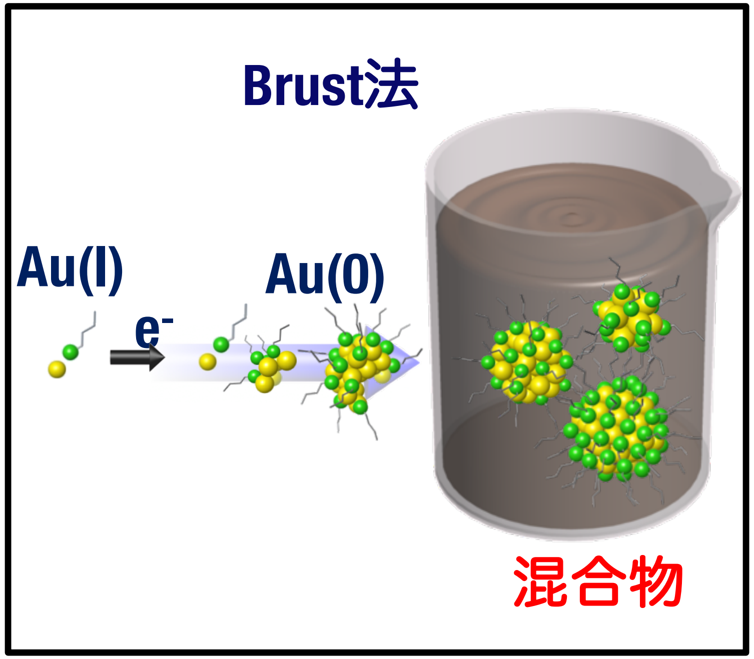
Xie et al.

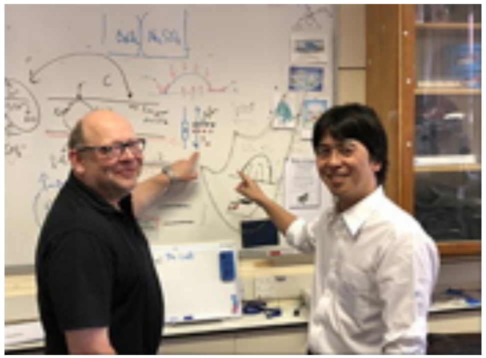


機能性ナノ物質としての高いポテンシャル

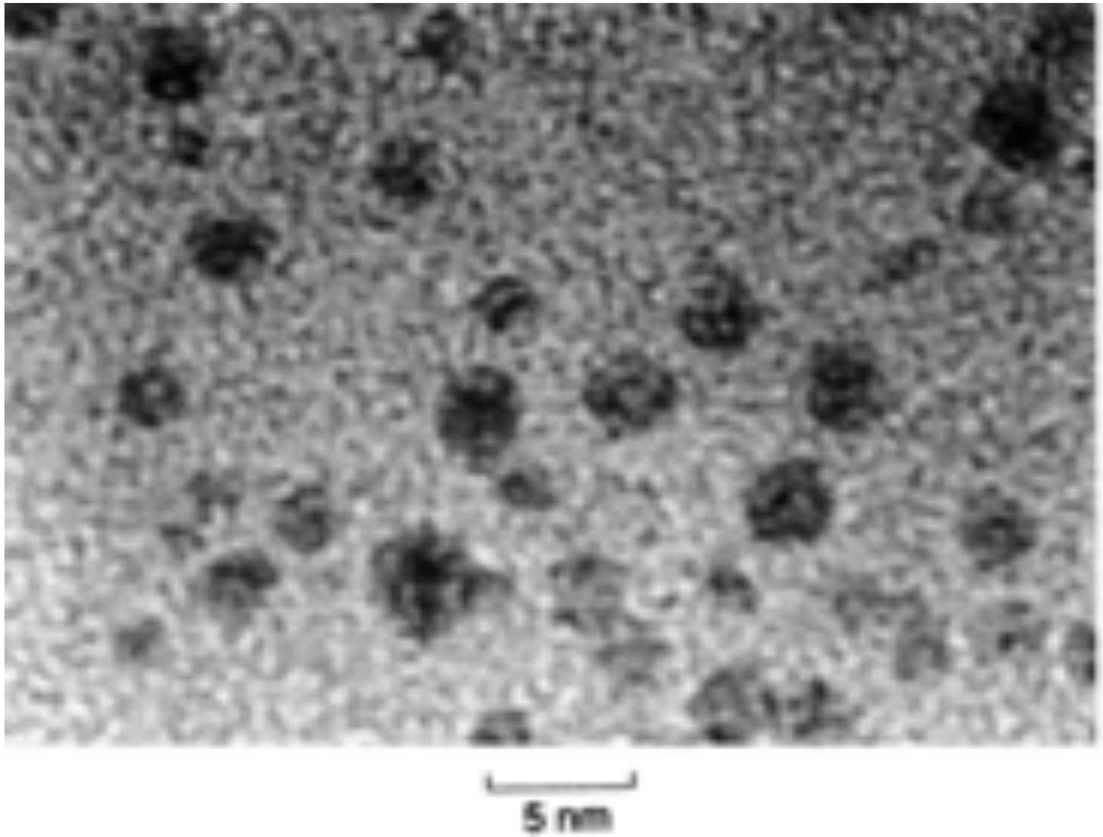
化学合成の可能な金属クラスター

チオラート保護金ナノクラスター





Brust教授
（リバプール大学）

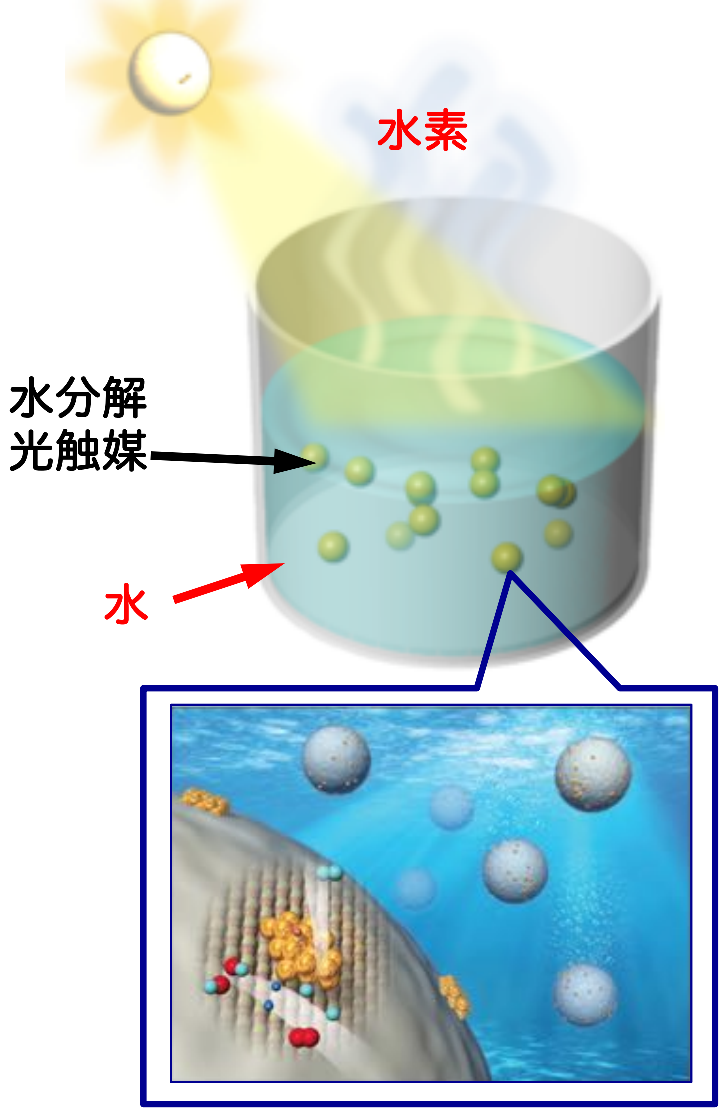


M. Brust,
J. Chem. Soc., Chem. Commun, 1994.

被引用数 6322 回

我々のエネルギー環境材料高機能化への取り組み

水分解光触媒



研究スタート: 光触媒研究部門

PIRC
東京理科大学 総合研究機構
光触媒国際研究センター
Tokyo University of Science Photocatalysis International Research Center

文部科学省認定
共同利用・共同研究拠点
光触媒研究推進拠点
認定期間　平成27年4月1日～平成33年3月31日

文部科学省科学研究費補助金　新学術領域研究　領域番号：2406（平成24～28年度）
人工光合成による太陽光エネルギーの物質変換：
実用化に向けての異分野融合
AnApple

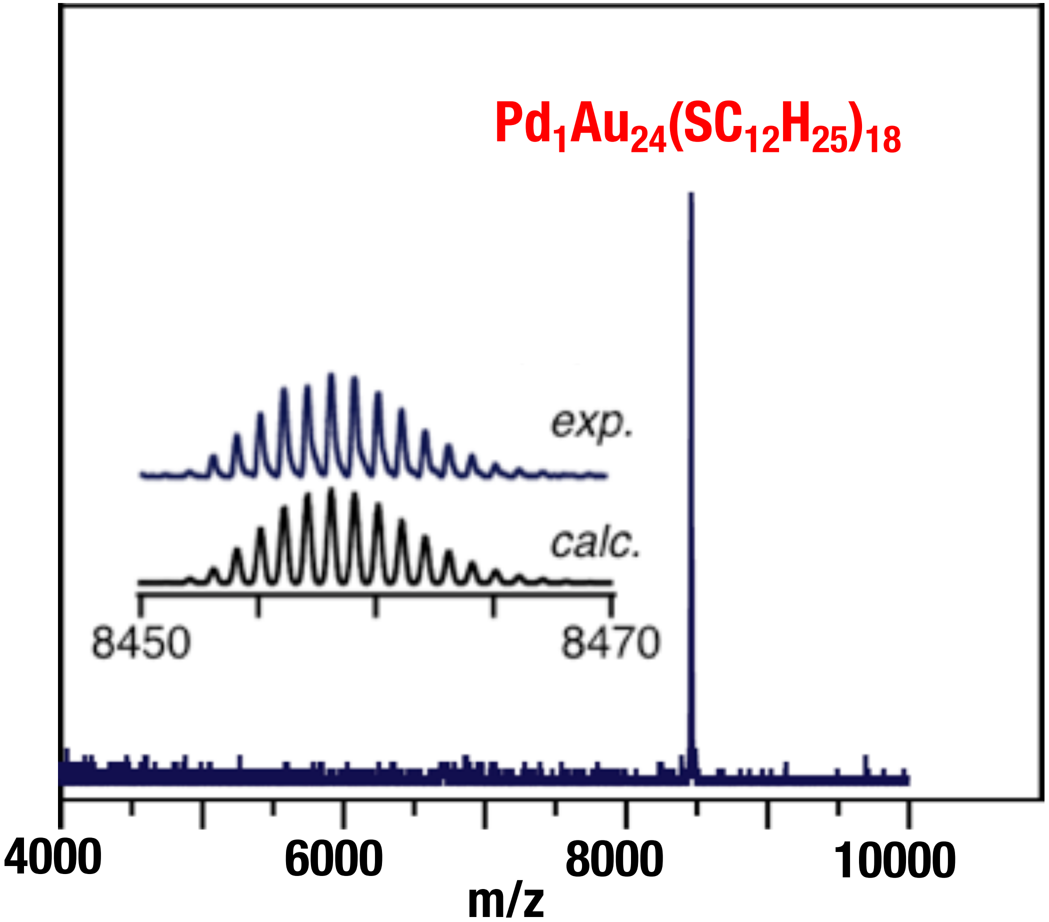
光合成分子機構の学理解明と
時空間制御による革新的光 ー 物質変換系の創製
I⁴LEC　Innovations for Light-Energy Conversion

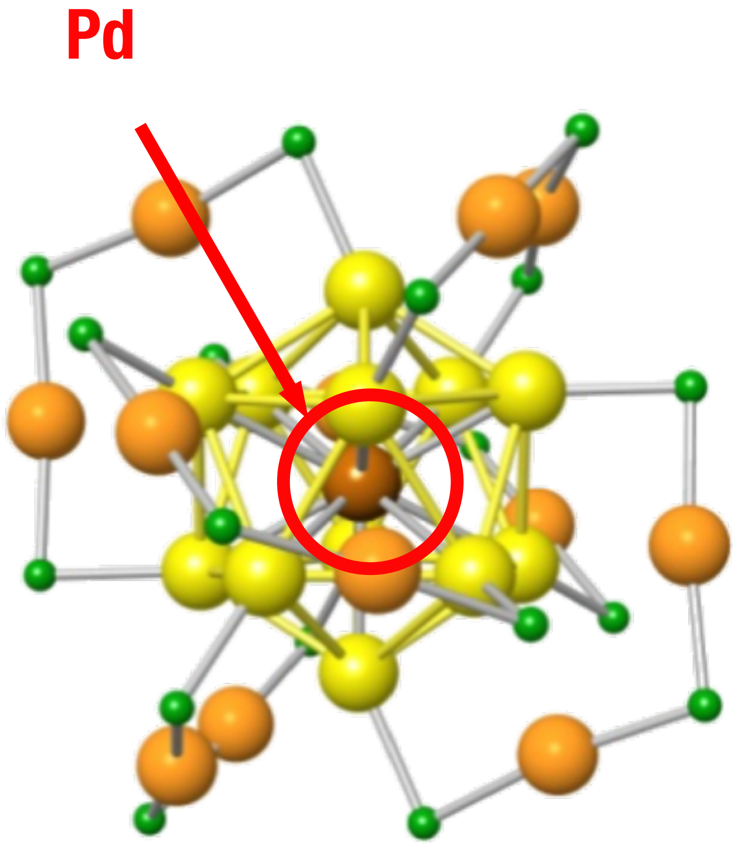
活性部位の厳密制御によるエネルギー・環境材料の高機能化へ

$Au_{24}Pd(SR)_{18}$の精密合成

Phys. Chem. Chem. Phys. (2010).
J. Chem. Chem. Lett. (2014).

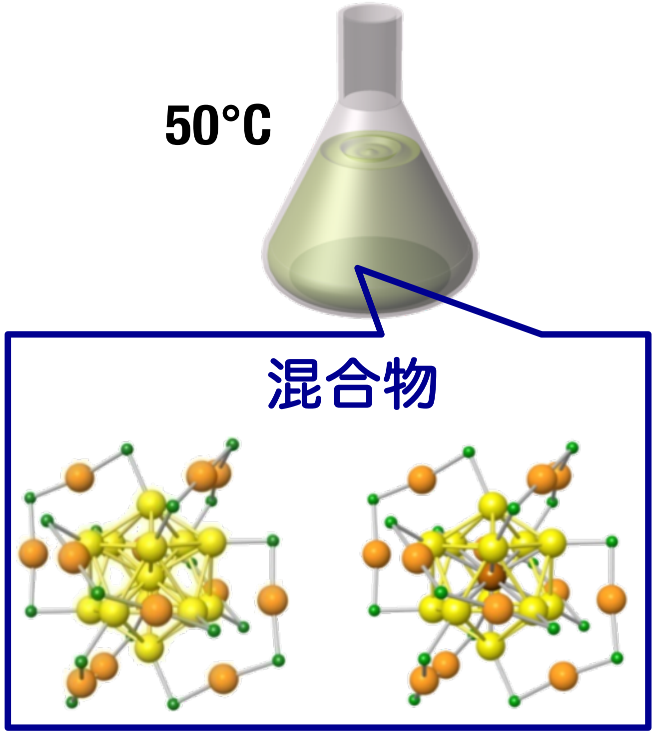
MALDI 質量スペクトル



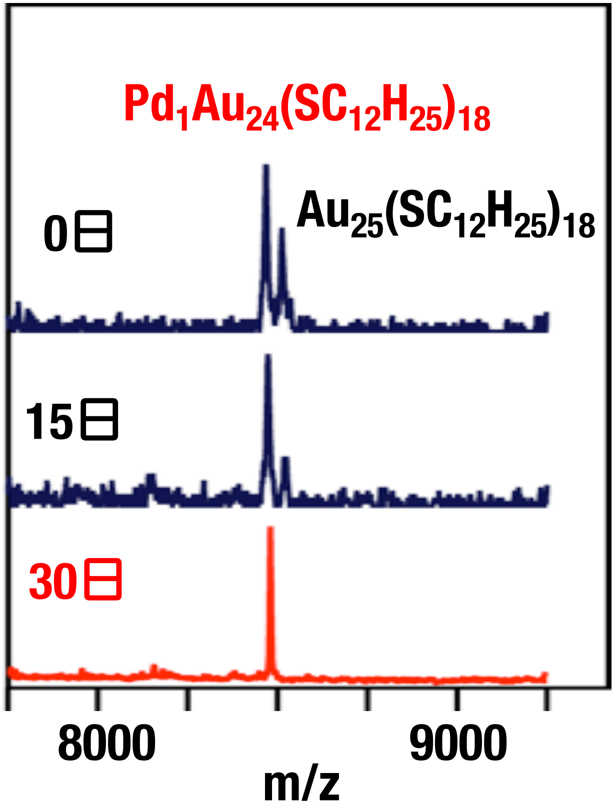


Pdドーピングの効果

Phys. Chem. Chem. Phys. (2010).　　Nanoscale (2013).



溶液中での存在比

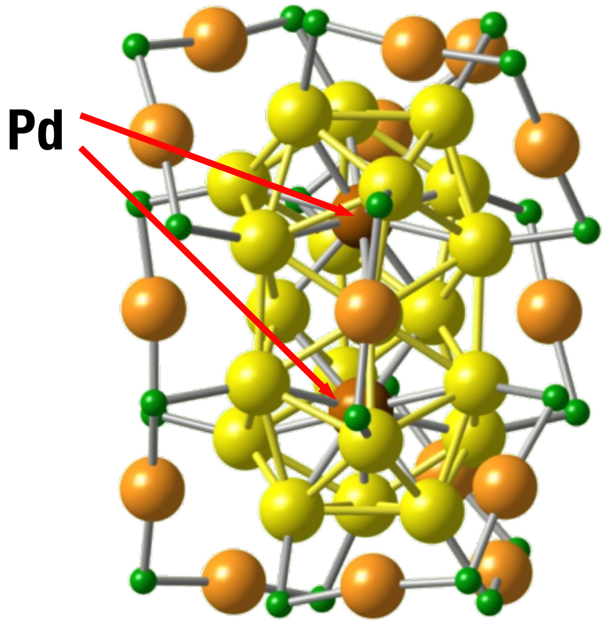


配位子交換反応性

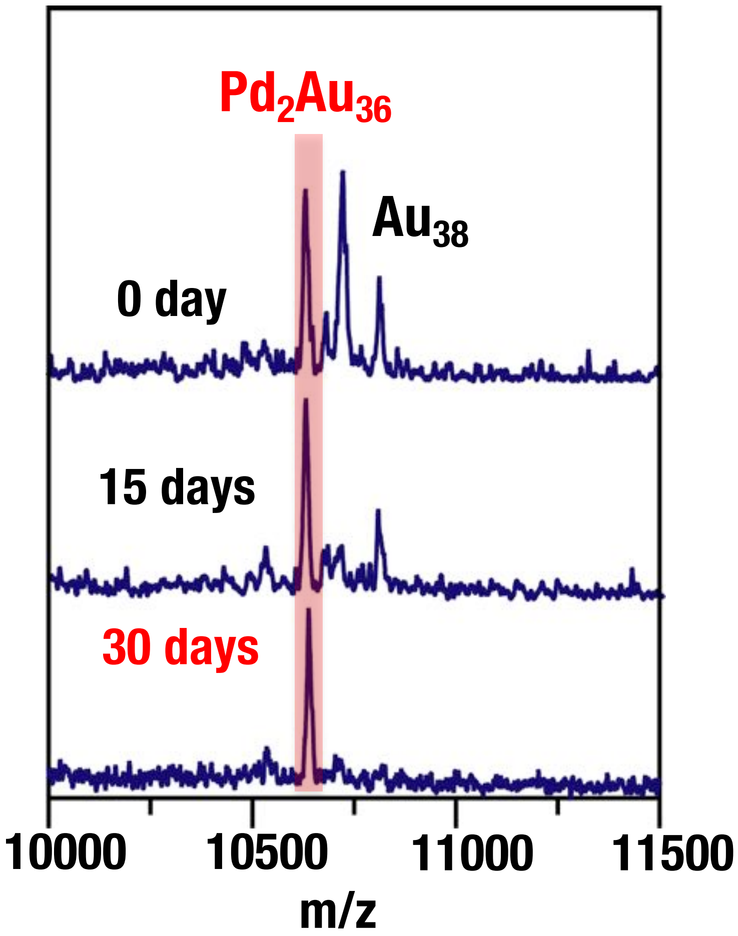
溶液中での安定性の向上

配位子交換反応性の向上

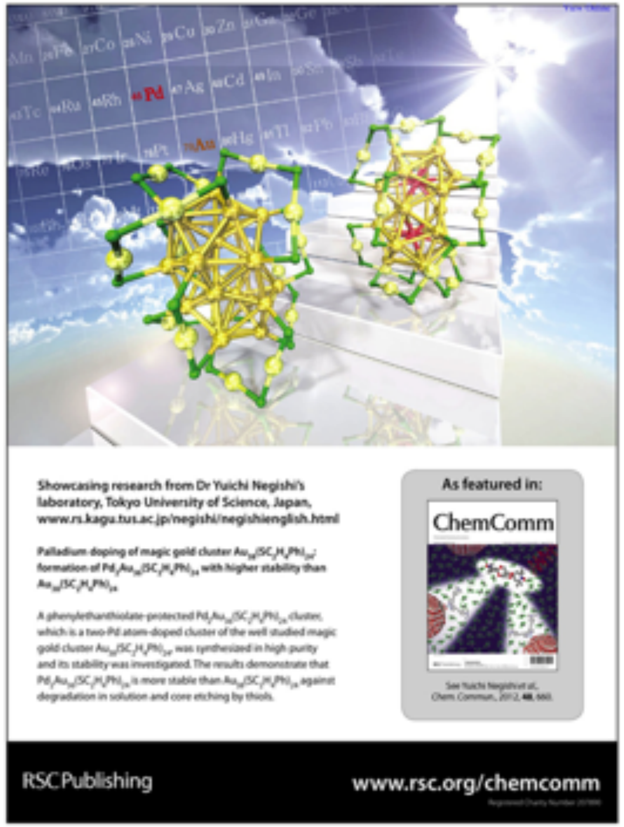
Pdドーピングの効果



comparison of stability
in solution



Chem. Commun. (2012).



より大きなクラスターに対しても安定性向上の効果あり

高機能化への手段

J. Phys. Chem. Lett. (Perspective). (2014)

官能基の制御

異原子ドーピング

金–配位子間結合の制御

慶應義塾大学理工学部化学科　茅・中嶋研究室時代

慶應義塾大学理工学部化学科　茅・中嶋研究室

茅・中嶋研究室でのクラスター研究

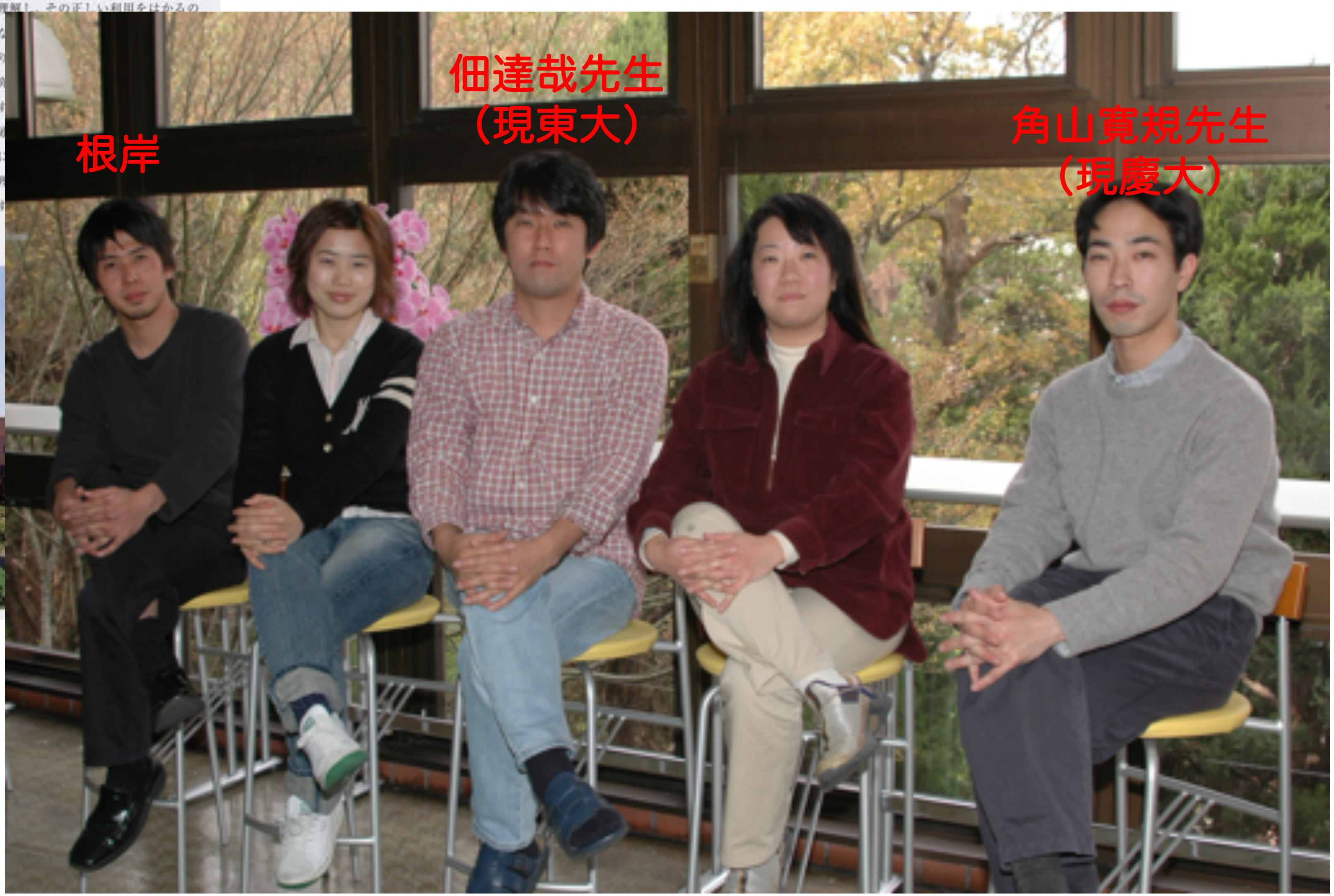
分子科学研究所佃グループ

分子科学研究所

分子科学の国際的研究センター

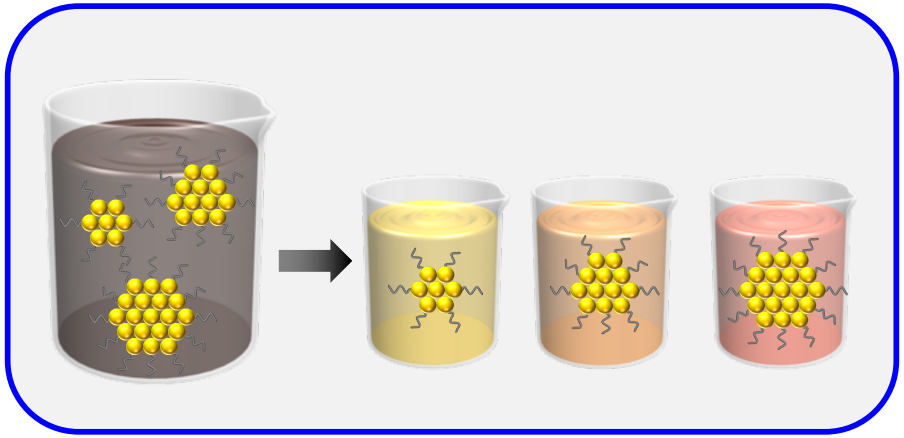
分子科学研究所は、物質の基礎である分子の構造とその機能に関する実験的研究並びに理論的研究を行うとともに、化学と物理学の境界にある分子科学の研究を推進するための中核として、広く研究者の共同利用に供することを目的として設立された大学共同利用機関です。物質観の基礎を培う研究機関として広く物質科学の諸分野に共通の知識と方法論を提供しています。限られた資源のなかで、生産と消費の上に成り立つ物質文明が健全

に保持されるためには、諸物質の機能を深く理解し、その正しい利用をはかるの

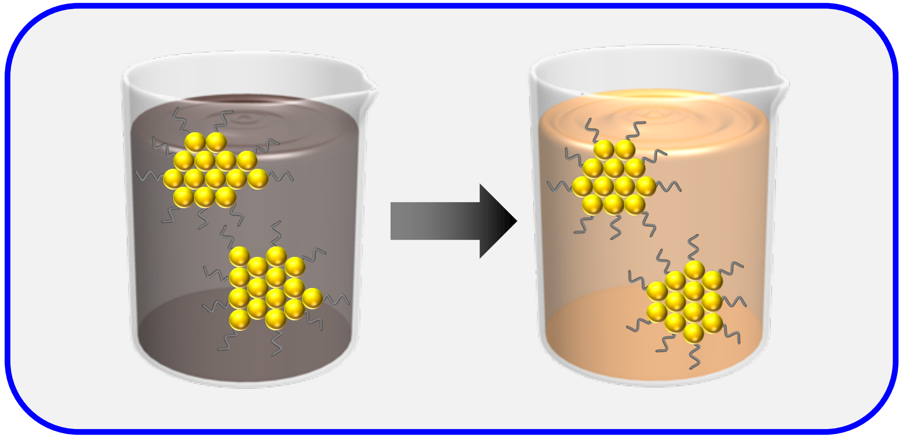


精密合成法

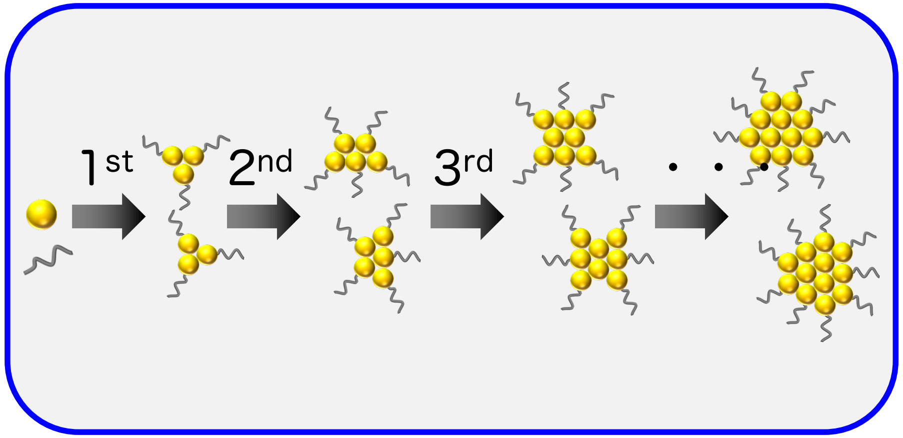
①高分解能分離



②サイズ収束



③成長速度制御



④配位子交換