Academic Program [Oral B] | 08. Catalysts and Catalysis：Oral B

Wed. Mar 26, 2025 1:00 PM - 3:30 PM JST | Wed. Mar 26, 2025 4:00 AM - 6:30 AM UTC
[C]C403(C403, Bldg. 2, Area 2 [4F])

[[C]C403-1pm] 08. Catalysts and Catalysis

Chair: Shoji Iguchi, Hajime Suzuki

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[[C]C403-1pm-01]

Improvement of photoelectrochemical hydrogen evolution activity by flux synthesis of near-infrared responsive $Cu_2Sn_{0.38}Ge_{0.62}S_3$ crystalline particles

〇Yosuke Kageshima[1], Tatsuya Kanazawa[1], Katsuya Teshima[1], Kazunari Domen[1,2], Hiromasa Nishikiori[1] (1. Shinshu Univ., 2. The Univ. of Tokyo)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[[C]C403-1pm-02]

Site-selective photodeposition of gold nanoparticles on the edges of ZnO nanowires

〇Yaozong Yan[1], Hisayoshi Kobayashi[2], Hiroaki Tada[3], Tetsuro Soejima[4] (1. Graduate School of Science and Engineering, Kindai University, 2. Emeritus Professor of Kyoto Institute of Technology, 3. Institutes of Innovation for Future Society, Nagoya University, 4. Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[[C]C403-1pm-03]

The Effect of Aromatic Hydrocarbons on the Visible-Light Induced Photo-oxidation of Dibenzothiophene for Desulfurization from Fuels

〇Takahiro Yamauchi[1], Taka-Aki Shinozaki[1], Yohan Ko[1], Akina Yoshizawa[1], Eiji Yamamoto[1], Haruno Murayama[2], Makoto Tokunaga[1] (1. Department of Chemistry, Graduate School of Science, Kyushu University, 2. Department of Applied Chemistry and Bioscience, Faculty of Engineering, Kanagawa Institute of Technology)

Japanese
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[[C]C403-1pm-04]

A Study on Electronic Structure and Performance of $SrTiO_3$:Rh,La Gains by Photoelectron Spectroscopy and Kelvin Probe Method

〇Tadaaki Tani[1], Yuichi Yamaguchi[2], Yoshiyuki Nakajima[3], Takayuki Uchida[4], Taisei Nishimi[5], Akihiko Kudo[2] (1. The Society of Photography and Imaging of Japan, 2. Tokyo University of sience, 3. Riken Keiki Company, Ltd., 4. Tokyo Polytechnic University, 5. Japan Technological Research Association of Artificial Photosynthetic Chemical Process)

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

Break

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[[C]C403-1pm-05]

【Withdrawn】Visible Light-Driven Photocatalytic CO_2 Reduction Using Hybrids Consisting of Iron(III) Porphyrin and Conjugated Polymer Semiconductors.

🏷 Japanese
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC

[[C]C403-1pm-06]

Raman spectroscopic observation of oxygen evolution reaction of Ni-Fe based electrode

Kenko Tsuchimoto[1], ○Tomohiro Fukushima[2,3], Masaki Itatani[2], Kei Murakoshi[2] (1. Graduate School of Chemical Sciences and Engineering, Hokkadio University, 2. Department of Chemistry, Faculty of Science, Hokkadido University, 3. JST-PRESTO)

🏷 Japanese
3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC

[[C]C403-1pm-07]

Theoretical investigation for the effects of surface reduction and water adsorption on the catalytic CO oxidation mechanisms over Au/ZnO catalyst.

○Tomohisa Yonemori[1], Takashi Kawakami[1], Shusuke Yamanaka[1], Mitsutaka Okumura[1] (1. Osaka University)

近赤外光応答 $Cu_2Sn_{0.38}Ge_{0.62}S_3$ 結晶微粒子のフラックス合成による光電気化学的水素生成活性の向上

（信州大 [1]・東大 [2]）〇影島洋介 [1]・金澤辰哉 [1]・手嶋勝弥 [1]・堂免一成 [1,2]・錦織広昌 [1]

Improvement of photoelectrochemical hydrogen evolution activity by flux synthesis of near-infrared responsive $Cu_2Sn_{0.38}Ge_{0.62}S_3$ crystalline particles ([1]*Shinshu University*, [2]*The University of Tokyo*) 〇Yosuke Kageshima,[1] Tatsuya Kanazawa,[1] Katsuya Teshima,[1] Kazunari Domen,[1,2] Hiromasa Nishikiori[1]

We have demonstrated photoelectrochemical (PEC) hydrogen evolution from water using $Cu_2Sn_xGe_{1-x}S_3$ (CTGS) particulate photocathodes.[1] These materials possess tunable bandgap energies according to the Sn/Ge ratio, and respond to long wavelength light up to the near-infrared region. However, the CTGS particles synthesized via a conventional solid-state reaction (SSR) had undefined morphologies with wide size distributions ranging from the submicron to micron order. Thus, there should be a room for improvement in PEC performance of CTGS photocathodes by improving crystal qualities. In this study, high-quality CTGS (x = 0.38) crystalline particles were grown through a flux method. CTGS synthesized via a flux method showed higher photocurrent than the SSR specimen at whole potential region (Fig. 1). Especially for the case of LiCl-RbCl flux, the photocurrent at 0 V_{RHE} reached to as high as −9 mA cm^{-2}, which was approximately 3 times larger than the SSR specimen. In the presentation, detailed characterization of the synthesized materials will also be discussed.

Keywords : Photocatalysts; Photocathodes; Hydrogen Evolution; Sulfide; Flux Synthesis

これまでに、$Cu_2Sn_xGe_{1-x}S_3$ (CTGS) 粉末光カソードを用いた水からの光電気化学的な水素生成を報告してきた [1]。この材料群は、Sn/Ge 比に応じてバンドギャップを制御可能であり、近赤外領域までの長波長光に応答する。しかし、一般的な固相反応 (SSR) によって合成された CTGS は不定形の粒子形態であり、サブミクロンからミクロンオーダーの広い粒度分布を示す。そのため、結晶品質の改善による CTGS 光カソードの光電気化学特性の改善の余地が残る。本研究では、高品質な CTGS 結晶微粒子 (x = 0.38) をフラックス法によって合成した。フラックス法によって合成された CTGS は、全ての電位域で SSR 試料よりも高い光電流を示した (Fig. 1)。特に LiCl-RbCl フラックスを用いた場合、0 V_{RHE} における光電流は約 −9 mA cm^{-2} に達した。これは、SSR 試料の約 3 倍に相当する。発表では、合成した材料の詳細なキャラクタリゼーションについても議論する。

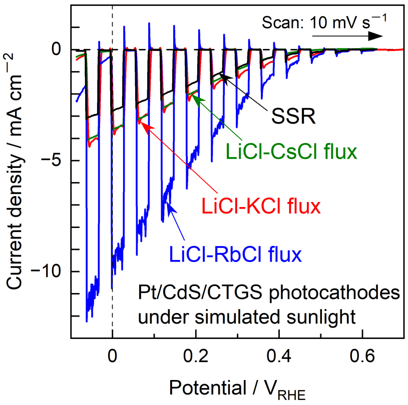


Fig. 1. Current-potential curves obtained from CTGS synthesized via SSR or flux method.

1) Y. Kageshima, *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 5698−5708.

Site-selective photodeposition of gold nanoparticles on the edges of ZnO nanowires

([1]*Graduate School of Science and Engineering, Kindai University,* [2]*Emeritus Professor of Kyoto Institute of Technology,* [3]*Institutes of Innovation for Future Society, Nagoya University,* [4]*Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University*)○Yaozong Yan,[1] Hisayoshi Kobayashi,[2] Hiroaki Tada,[3] Tetsuro Soejima[4]

Keywords: Photodeposition, Gold nanoparticles, ZnO nanowire

Selective modification of chemically active sites on supports, such as steps, edges, and corners, with metal nanoparticles (NPs) is a challenging topic in the fields of catalysis and photocatalysis. Focusing on the support, rapid progress is currently being made in the synthesis of MO nanocrystals (NCs) with well-defined facets. Their edges and corners can be viewed as surface defects consisting of linear arrays of chemically active atoms with a high degree of coordinative unsaturation. Therefore, selective and dense formation of metal NPs on chemically active edges and corners should be effective for improving catalytic and photocatalytic activities. However, the formation of site-selective, high-density metal NPs on a support has not yet been achieved. Radial ZnO mesocrystals (rad-ZnO MC) (Fig 1a) composed of hexagonal nanowires (NWs) with {10-10} sidewalls were synthesized by a simple solution-phase method.[1] Here we show that Au NPs are densely aligned along the edges of ZnO NWs by photodeposition from an O_2 free aqueous methanol solution of $HAuCl_4$, even though the Au complexes are uniformly adsorbed across the entire surface of the ZnO NWs (Fig 1b). Based on the results of experiments and density functional theory calculations, we proposed a reaction mechanism of the site-selective photodeposition involving the reduction of the Au complex by the excited electrons instantly relaxed at the edge sites followed by the crystal growth. This study encourages us to apply the site-selective photodeposition to other faceted semiconductor nanocrystals and to contribute to the improvement in their catalytic and photocatalytic activities.

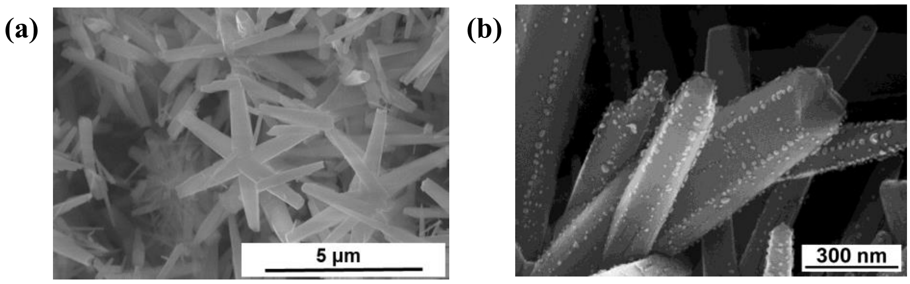


Fig. 1 (a) SEM image of rad-ZnO MC. (b) SEM image of Au nanoparticle-loaded rad-ZnO MC prepared by the photodeposition

1) Y. Yan et al., *CrystEngComm*. **2023**, *25*, 5796 – 5801.

2) Strasser, P et al., *Chem. Soc. Rev.* ***2018****, 47, 715-735.*

燃料からの脱硫を目的としたジベンゾチオフェンの可視光酸化反応における共存芳香族炭化水素の効果

（九大院理[1]・神奈川工科大[2]）○山内 崇弘[1]・篠﨑 貴旭[1]・高 ヨハン[1]・吉澤 明菜[1]・山本 英治[1]・村山 美乃[2]・徳永 信[1]

The Effect of Aromatic Hydrocarbons on the Visible-Light Induced Photo-oxidation of Dibenzothiophene for Desulfurization from Fuels

([1]*Department of Chemistry, Graduate School of Science, Kyushu University*, [2]*Department of Applied Chemistry and Bioscience, Faculty of Engineering, Kanagawa Institute of Technology*) ○Takahiro Yamauchi[1], Taka-Aki Shinozaki[1], Yohan Ko[1], Akina Yoshizawa[1], Eiji Yamamoto[1], Haruno Murayama[2], Makoto Tokunaga[1]

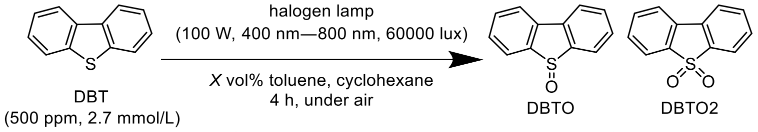
Photocatalytic oxidative desulfurization has attracted attention as a practical desulfurization method under mild conditions. On the other hand, it has been reported that the interaction of titanium dioxide with toluene and other aromatic compounds lengthens light absorption wavelength of catalyst 1), 2). In this study, we investigated visible light responsibility of titanium dioxide and catalytic reaction mechanism of photo-oxidation of dibenzothiophene (DBT).

The model fuel was prepared by dissolving DBT in cyclohexane containing 5 vol% toluene. Titanium dioxide (87.8 mg) was added to a quartz tube along with the model fuel (3 mL). Then, the reaction proceeded under irradiation of a halogen lamp for 4 h with stirring. As a result, DBT was hardly oxidized under the toluene (0 vol%) condition, which confirmed that the decrease in DBT was mainly due to adsorption on the catalyst. However, the addition of toluene increased DBTO and DBTO2 yields, suggesting that toluene in the model fuel contributes to catalyst activation.

Keywords : Oxidative desulfurization, Titanium dioxide, Photocatalyst, Dibenzothiophene, Visible-light irradiation

光触媒を用いた酸化的脱硫法は温和な条件下で実施可能な手法として注目されている。一方、酸化チタンはトルエンなど芳香族化合物との相互作用により、その光吸収波長が長波長化することが報告されている 1), 2)。本研究ではジベンゾチオフェン (DBT) の光酸化脱硫において、トルエンなど芳香族化合物を含む反応系中での酸化チタンの可視光応答性や触媒作用機構に関する詳細な検討を行った。

モデル燃料はトルエン (*X* vol%) を含むシクロヘキサンに DBT を溶解させて調製した。そして石英製試験管にモデル燃料 (3 mL) とともに酸化チタン (87.8 mg) を入れ、撹拌しながらハロゲンランプを 4 時間照射して反応検討を行った。結果として、まずトルエン未添加の場合は、ほとんど DBT の酸化が進行しておらず、主に触媒への吸着による DBT の減少が確認された。しかしモデル燃料へのトルエン添加により、酸化反応の進行と DBTO、DBTO2 収率の増大が見られ、系中のトルエンが触媒の活性化に寄与することを示唆する結果が得られた。



X (vol%)	DBT転化率 (%)	DBTO収率 (%)	DBTO2収率 (%)
0	58	15	3
5	>99	21	36
10	>99	15	54

図　系中のトルエン濃度検討

1) K. Imai *et al.*, *Appl. Catat. B,* **2024**, 346, 123745
2) T. Kamegawa *et al.*, *ACS Appl. Mater. Interfaces*, **2012**, 4, 6635-6639

光電子分光とケルビンプローブ法による $SrTiO_3$:Rh,La 粒子の電子構造と性能の研究

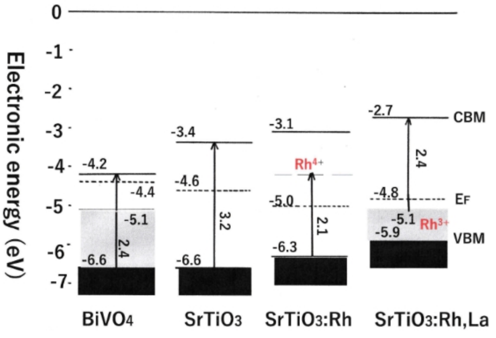
（日本写真学会[1]・東京理科大理[2]・理研計器[3]・東京工芸大工[4]・人工光合成化学プロセス技術研究組合[5]）○谷 忠昭[1]・山口 友一[2]・中島 嘉之[3]・内田孝幸[4]・西見 大成[5]・工藤 昭彦[2]

A Study on Electronic Structure and Performance of $SrTiO_3$:Rh,La Grains by Photoelectron Spectroscopy and Kelvin Probe Method

([1]*Society of Photography and Imaging of Japan,* [2]*Tokyo University of Science,* [3]*Riken Keiki Co., Ltd.,* [4]*Tokyo Polytechnic University,* [5]*ARPChem.*) ○Tadaaki Tani,[1] Yuichi Yamaguchi,[2] Yoshiyuki Nakajima,[3] Takayuki Uchida,[4] Taisei Nishimi,[5] Akihiko Kudo[2]

Although STH conversion efficiency of overall water splitting (OWS) by Z-scheme system with $SrTiO_3$:Rh,La achieved 1.1%, it is still far from its practical target (>5%). Since the idea to attribute the cause of its low efficiency to the enhancement of recombination by defects could not be supported by physical properties of $SrTiO_3$[1)], this study was undertaken to measure the electronic structure of $SrTiO_3$:Rh,La grains in order to seek for the cause of its low efficiency and guideline for its improvement by means of photoelectron spectroscopy and Kelvin probe method instead of Mott-Schottky plot, which was judged to be inadequate for photocatalysts grains. It was revealed that, by doping of Rh and La, the conduction and valence bands raised, and the Fermi level deepened, becoming to be suitable for hydrogen evolution. The obtained result has indicated the possibility that the cause of the low efficiency of OWS by photocatalysts with longer wavelength at their absorption edge results from their electronic structures, and that the efficiency can be improved by controlling their electronic structure.

Keywords : Photocatalyst; Overall Water Splitting; $SrTiO_3$; Electronic Structure; Photoelectron Spectroscopy; Kelvin Probe



CBM; conduction band minimum
VBM; valence band maximum
E_F; Fermi level

光触媒粒子による水の全光分解（OWS）に Z スキームで $SrTiO_3$:Rh,La を用いて最高 STH 変換効率 1.1%に達したが、実用水準（>5%）にはまだ距離がある。非効率の原因は、欠陥による再結合の促進では物性と相容れないので[1)]電子構造に求めた。Mott-Schottky プロットの光触媒への適用が不適当との指摘を受け、理研計器社製大気中光電子収量分光と Kelvin probe 法を併用して $SrTiO_3$:Rh,La 粒子の電子構造を測定した。その結果、Rh と La のドープで $SrTiO_3$ はその価電子帯と伝導帯が高くなるとともにフェルミ準位が下がり、吸収端波長(λ)を長くしつつ水素発生に適した電子構造となり変換効率が向上したことが分かった。この結果はλを長くした場合の低効率の原因が電子構造であり、それを制御して変換効率を高める可能性を示唆していた。

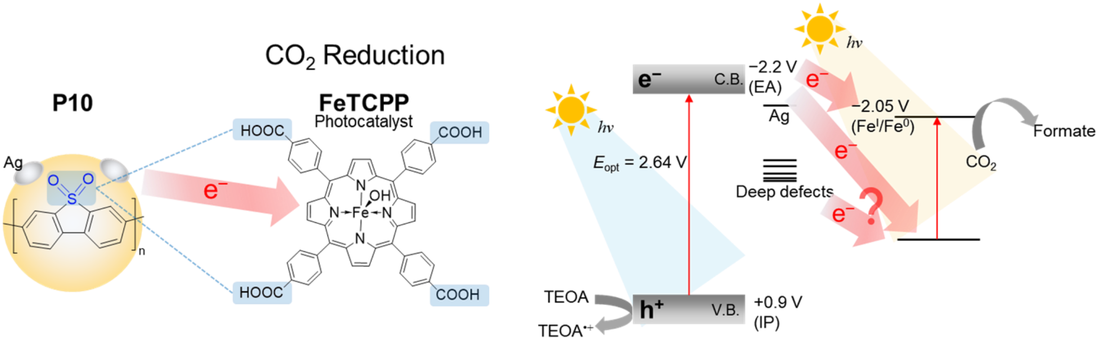
1) T. Tani, Y. Yamaguchi, T. Nishimi, T. Uchida, A. Kudo, *Phys. Chem. Chem. Phys.*, **2023**, 25, 11418-11428.

Visible Light-Driven Photocatalytic CO_2 Reduction Using Hybrids Consisting of Iron(III) Porphyrin and Conjugated Polymer Semiconductors

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University,* [2]*Department of Pure and Applied Chemistry, University of Strathclyde,* [3]*School of Science, Institute of Science of Tokyo*) ○Sunghan Choi[1], Ewan McQueen[2], Kei Kamogawa[3], Kisuke Nakao[1], Sebastian Sprick[2], Osamu Ishitani[1]

Keywords: Artificial Photosynthesis; Fe-Porphyrin; Congugated Polymer Semiconductors; CO_2 Reduction; Photocatlayst

In the previous report, we described hybrid photocatalysts consisting of a conjugated polymer semiconductor (CPS) and a supramolecular photocatalyst with high CO_2-to-HCOOH conversion efficiency. In this study, we utilized the same poly(dibenzo[*b,d*]thiophene sulfone) [P10] as the CPS, which, according to density functional theory (DFT) calculations, has a sufficiently negative reduction potential to facilitate electron transfer to other catalysts. To promote the use of earth-abundant transition metals, we introduced an iron-based porphyrin (FeTCPP) as the central catalytic component. This system exhibited significant CO_2-to-HCOOH conversion efficiency under dual-wavelength irradiation. Simultaneous excitation at 470 nm and 590 nm greatly enhanced the photocatalytic efficiency compared to single-wavelength excitation at 470 nm. After 110 hours of photolysis, the FeTCPP/Ag/P10 hybrid photocatalyst produced 192 μmol of HCOOH, achieving a high turnover number (TON_{HCOOH}) of 9645 in a DMA/TEOA mixture solution.



1) E. Mcqueen; N, Sakakibara, *Chem. Sci.* **2024**, *15*, 18146.

Raman 分光計測による Ni-Fe 電極の酸素発生反応中間体解析

（北大院総化 [1]・北大院理 [2]・JST-さきがけ [3]）土本 兼廣 [1]・○福島 知宏 [2,3]・板谷 昌輝 [2]・村越 敬 [2]

Raman Spectroscopic Observation of Oxygen Evolution Reaction of Ni-Fe-based Electrode

([1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [2]*Department of Chemistry, Faculty of Science, Hokkaido University,* [3]*JST-PRESTO*) Kenko Tsuchimoto,[1]○ Tomohiro Fukushima,[2,3] Masaki Itatani,[2] Kei Murakoshi[2]

Oxygen evolution reaction is the slow reaction even with the state-of-the-art catalysts. We utilized the Ni-Fe electrode as a model system to investigate the reaction intermediate from in-situ Raman spectroscopy. Ni-Fe electrode was electrodeposited and showing superior OER activity than Ni electrode. Raman spectroscopy revealed that the reaction intermediate in the OER catalysis. Raman imaging can detect the catalytic active site in heterogenous electrode.

Keywords : Oxygen evolution reaction, Raman spectroscopy, Reaction intermediates.

【序論】酸素発生反応（OER）はプロトン共役電子移動を伴う4電子移動反応であり、多くの中間体が存在する。 Raman 分光法を用いた中間体観測により、多電子移動の素過程を追跡することが可能となる。[1] 本研究では Ni に Fe がドープされた Ni-Fe 電極の OER 挙動を Raman イメージング計測により解析したので報告する。

【実験】 FTO 基板上に Ni を 40 nm 電子線蒸着することで Ni / FTO 電極を作製した。 Ni / FTO 電極上に 100 mM $Fe(NO_3)_3$ 水溶液を用いて、Ni と Fe 酸化物を電極表面に還元析出させることで作製した。Ni-Fe 電極基板を作用極、 Pt を対極、 Ag / AgCl を参照極として、3 極式電気化学セルを構築した。電解質水溶液には 0.3 M NaOH + 0.7 M $NaClO_4$ (pH = 13) を用いて *in-situ* Raman イメージング計測を行った。

【結果と考察】電気化学電位の上昇に伴い、480 cm^{-1} 、560 cm^{-1} および 1000 cm^{-1} から 1100 cm^{-1} の領域に Raman 信号が観測され、それぞれ OER 中間体である Ni-OH 伸縮および Ni-OOH 伸縮および NiO-O に帰属された (Figure (a))。Ni-Fe 電極は Ni 電極と比較して 50 mV 程度の過電圧の低減、Tafel 勾配も 75 mV/decade から 45 mV/decade へと改善が観測され、OER 活性の増大が観測された。Raman イメージング計測を行ったところ、酸化状態の進行した特異的な触媒サイトが観測され (Figure (b))、系を特徴づける触媒サイトが特定された。

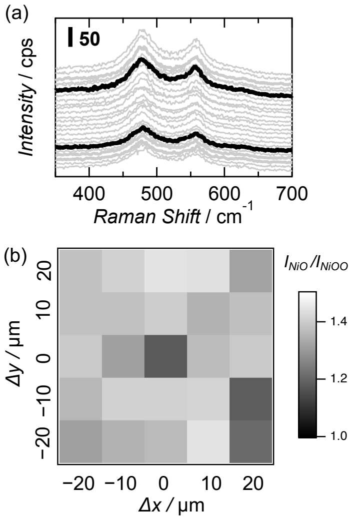


Figure. (a) Raman spectra of Ni-Fe based electrode in 0.3 M NaOH and 0.7 M $NaClO_4$ electrolyte at 1.6 V vs. RHE. Top bold trace represents Δ*x*, Δ*y* = 0 µm and 20 µm. Bottom bold trace represents the spectra at Δ*x*, Δ*y* = 20 µm and −10 µm. (b) Raman imaging of the intensity ratio between Ni-O and Ni-OOH.Excitation wavelength 633 nm. Laser Intensity 1 mW. Exposure time 8 s. Objective lens ×100.

【参考文献】[1] T. Fukushima, K. Tsuchimoto, K. Murakoshi *et al.*, *J. Phys. Chem. C*, **2024**, *128*, *47*, 20156.

表面の還元状態や水分子被覆が Au/ZnO 触媒の CO 酸化機構に与える影響に関する理論的研究

（阪大院理）○米森 朋久・川上 貴資・山中 秀介・奥村 光隆

Theoretical investigation for the effects of surface reduction and water adsorption on the catalytic CO oxidation mechanisms over Au/ZnO catalyst. (*Graduate School of Science, Osaka University*) ○ Tomohisa Yonemori, Takashi Kawakami, Shusuke Yamanaka, Mitsutaka Okumura

Au nanocluster supported on reducible metal oxides such as TiO_2 and ZnO is well known to exhibit high catalytic activity of CO oxidation even at low temperatures below 0℃. There have been a lot of theoretical studies on its catalytic activity of Au/TiO_2, however, the reaction mechanism over Au/ZnO are unclear. We investigated the reaction mechanism of CO oxidation over Au/ZnO paying much attention to the effects of surface reduction and the role of adsorbed H_2O molecules using density functional theory calculations.

Activation barriers of the reaction between CO and active oxygen species on each surface state are summarized in Table 1. These results indicate that this catalytic reaction possibly proceeds at low temperatures in the absence of H_2O molecules due to the high reducibility of the support, and that surface reduction facilitates the catalytic activity.

Keywords : Au Catalyst; DFT; CO oxidation; Active Oxygen; Non-Stoichiometric Surface

金の微粒子を TiO_2 や ZnO といった高い還元性を有する金属酸化物上に高分散で担持すると、0℃以下の低温領域でも非常に高い CO 酸化活性を示すことが知られている。これまでに TiO_2 上に担持した金ナノ粒子触媒(Au/TiO_2)による反応機構が理論的に調べられてきたが、類似の触媒活性を示す Au/ZnO 上での反応機構に関する理論的研究は多くない。本研究では低温領域でも進行し得る Au/ZnO による CO 酸化機構を、触媒表面の還元状態や水分子被覆の影響に注目して密度汎関数計算により調査し、本触媒反応機構の総合的な議論を行った。

Table 1.に各触媒表面(両論比表面、還元表面、水分子被覆表面)で活性酸素種と CO が表面錯形成する過程の活性化障壁、及び生成する活性酸素種を示した。ここから、担体の高い還元性により水分子の有無に関わらず低温領域でも高い活性を示し得ること、還元表面上で触媒活性がより向上することが示唆される。当日の発表では欠損表面の生成・消失機構、水分子存在下での反応機構に関する仮説に関しても議論する。

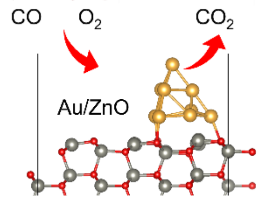


Figure 1. Catalytic CO oxidation over Au/ZnO.

Table 1. Activation barriers (E_{act}) of the reaction between CO and active oxygen species on each catalyst surface.

Catalyst Surface	E_{act} (eV)	Active Species
Stoichiometric	0.24	O_2^{2-}
Reduced (O defect)	0.14	O_2^{2-}
Reduced (Hydrogenated)	0.18	O_2^{2-}
H_2O-covered	0.26	OOH^-