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

Fri. Mar 20, 2026 9:00 AM - 11:30 AM JST | Fri. Mar 20, 2026 12:00 AM - 2:30 AM UTC | E1123 (1123, Bldg. 11 [2F])

[E1123-4am] Oral B

Chair: Takafumi Yatabe, Makoto Tokunaga

Japanese
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC

[E1123-4am-01] Intramolecular Hydride Transfer Racemization Coupled with Enzymatic Kinetic Resolution Enables Asymmetric Syntheses of Chiral Caged Compounds

○Simon Joynson Cooper[1], Tsuyoshi Mita[1], Hiroki Hayashi[1] (1. Hokkaido University)

English
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC

[E1123-4am-02] A convenient approach for the generation of *N*-stabilized oxyallyl cation and its [4+3] cycloaddition reaction

○Sangita Karanjit[1], Aoi Minamide[1], Ryota Sato[1], Kosuke Namba[1] (1. Tokushima University)

Japanese
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC

[E1123-4am-03] Selective desulfurative silylation of sulfides using hydrosilanes by Au–Pd nanoparticle catalysts

○So Hiramoto[1], Takafumi Yatabe[1], Takehiro Matsuyama[1], Kazuya Yamaguchi[1] (1. The University of Tokyo)

English
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC

[E1123-4am-04] Selective Synthesis of *m*-Phenylenediamine Derivatives through Catalytic Dehydrogenative Aromatization

○Heizo Kimura[1], Takafumi Yatabe[1], Soichi Kikkawa[2], Seiji Yamazoe[2], Daisuke Takei, Kazuya Yamaguchi[1] (1. The University of Tokyo, 2. Tokyo Metropolitan University)

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

Break

English
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC

[E1123-4am-05] Highly Active Supported Au Catalysts Derived from Au Precursors for Various Catalytic Reactions

○Yuxue Cao[1], Akina Yoshizawa[1], Yuji Masaki[1], Tomohiro Fukae[1], Haruno Murayama[2], Tetsuo Honma[3], Akihiro Nakayama[1], Eiji Yamamoto[1], Takashi Sato[4], Yousuke Suzuki[4], Makoto Tokunaga[1] (1. Kyushu University, 2. Kanagawa Institute of Technology, 3. JASRI, 4. Mitsubishi Chemical Corporation)

English
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC

[E1123-4am-06] Photocatalytic decomposition of perfluoroalkyl compounds using silver-loaded titanium dioxide

○Yuto Toyota[1], Rahat Javaid[2], Jochen Lauterbach[2], Yoichi Kobatashi[1,3] (1. Coll. of Life Sciences, Ritsumeikan Univ., 2. Molinaroli Coll. of Rng. Comput., Univ. of South Carolina, 3. PRESTO, JST)

Japanese
11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC

[E1123-4am-07] Simultaneous synthesis of hydrogen and conductive polymers using photo-redox cascade catalyst

○Atsushi Kobayashi[1] (1. Hokkaido University)

分子内ヒドリド移動によるラセミ化と酵素による速度論的光学分割を組み合わせたキラルカゴ型分子の不斉合成

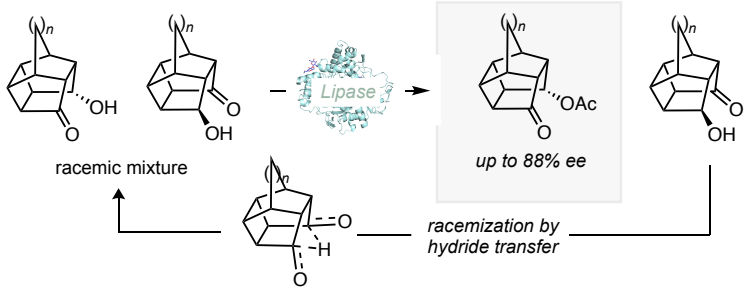
（北大 WPI-ICReDD[1]）○Simon Cooper[1]・美多 剛[1]・林 裕樹[1]

Intramolecular Hydride Transfer Racemization Coupled with Enzymatic Kinetic Resolution Enables Asymmetric Syntheses of Caged Compounds ([1]*WPI-ICReDD, Hokkaido Univ.*) ○ Simon J. Cooper,[1] Tsuyoshi Mita,[1] Hiroki Hayashi[1]

Lipases have a well-established utility in organic synthesis. Lipase-catalyzed dynamic kinetic resolutions, which couple enantioselective enzymatic acylation with starting material racemization, have led to methods that can access a variety of enantioenriched compounds without the yield threshold of 50% imposed by a traditional KR. The expansion of the DKR field in enzymatic and non-enzymatic contexts has been fueled in part by the application of underexplored racemization modalities. Inspired by works from Watt and co-workers (*vide infra*),[1] we targeted intramolecular hydride transfer in caged hydroxyketones as a racemization strategy. This process has been shown in a variety of caged/bicyclic systems, though its application in a synthetic context has yet to be demonstrated. We found that when coupled with a fungal lipase-catalyzed KR, intramolecular hydride transfer racemization regenerates the active reactant enantiomer, allowing for yields exceeding 80% with 94:6 er after three cycles.
Keywords: *Enzymatic Catalysis, Lipase, Racemization, Asymmetric Synthesis*

リパーゼは、有機化合物の速度論的光学分割に有効な酵素触媒として、幅広く利用されてきた。このリパーゼの触媒作用を原料分子のラセミ化と組み合わせることで、動的速度論的光学分割（dynamic kinetic resolution, DKR）が可能となり、これまで検討されてこなかったラセミ化を応用することで DKR 手法のさらなる拡張が期待される。

今回我々は、Watt らによる研究を参考にして[1]、カゴ型ヒドロキシケトンの分子内ヒドリド移動によるラセミ化とリパーゼのエナンチオ選択的アシル化と組み合わせた不斉合成手法の開発に成功した。本反応で得られるキラル多環式カゴ型化合物は、ユニークなケージ構造を有し、創薬研究で活用されている。特に本研究では、既存の低分子性不斉求核触媒ではキラル認識が困難な基質に対して、真菌由来リパーゼが優れたキラル識別力を発揮することを見出すことに成功した。

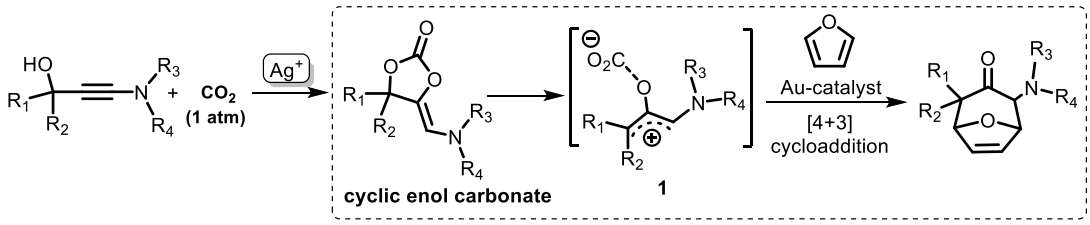


1) Prior reports of intramolecular hydride-transfer racemization. *J. Chem. Soc., Perkin Trans. 2*, **1976**, 1549-1553, *J. Chem. Soc., Perkin Trans. 2*, **1981**, 175-184, *Tetrahedron Lett.*, **1982**, *23*, 975-978.

A convenient approach for the generation of N-stabilized oxyallyl cation and its [4+3] cycloaddition reaction

([1]*Graduate School of Pharmaceutical Science, Tokushima University*)
○Sangita Karanjit[1], Aoi Minamide[1], Ryota Sato[1], Kosuke Namba[1]
Keywords: Oxyallyl cation, cycloaddition reaction

Oxyallyl cations are widely used as intermediates in organic synthesis, such as [4+3] or [3+2] cycloaddition reaction which is a very important and powerful approach for constructing ring systems. Conventionally, oxyallyl cations are generated from α-halo or sulfonyl-substituted ketones or enol ethers which readily react with conjugated dienes or electron rich olefins. With the pioneering work by Murai et al.[1] which opened up the access to the oxyallyl cation from a new source i.e., cyclic enol carbonates, several catalytic transformations via oxyallyl cation intermediate to form C-C bond has been reported.[2] However, there are no reports for the [4+3] cycloaddition reaction via generation of heteroatom-stabilized oxyallyl cation from cyclic enol carbonate. Herein, we presented Au-catalyzed [4+3] cycloaddition reaction of N-stabilized oxyallyl cation **1** with furan via decarboxylation of cyclic carbonates which forms the cyclopentenone core skeleton in many natural products. The cyclic enol carbonates which are the starting material for this decarboxylative transformation were easily prepared from the Ag-catalyzed reaction of CO_2 with propargyl alcohol in good yields using our reusable heterogeneous silver catalyst immobilized on silica support[3] ($Im^+Cl^-@SiO_2$). This decarboxylation strategy is simple, mild, efficient, and green route which involves the elimination of CO_2 as the driving force to generate oxyallyl cation in-situ for the [4+3] cycloaddition reaction to be applied in the construction of bicyclic key intermediates containing cyclopentenone.



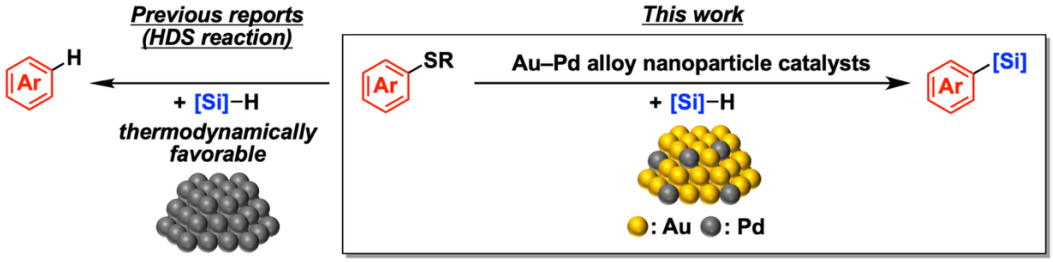
1. K. Ohe, H. Matsuda, T. Ishihara, S. Ogoshi, N. Chatani, S. Murai *J. Org. Chem.* **1993**, *58*, 1173.
2. a) W. Chai, Q. Zhou, W. Ai, Y. Zheng, T. Qin, X. Xu, W. Zi *J. Am. Chem. Soc.* **2021**, *143*, 3595. b) Y. Zheng, T. Qin, W. Zi *J. Am. Chem. Soc*. **2021**, *143*, 1038.
3. S. Karanjit, E. Tanaka, L. K. Shrestha, A. Nakayama, K. Ariga, and K. Namba, *Catal. Sci. Technol.* **2022**, *12*, 3778.

Au–Pd ナノ粒子触媒によるヒドロシランを用いたスルフィドの選択的脱硫黄型シリル化反応

（東大院工 [1]）○平本 創 [1]・谷田部 孝文 [1]・松山 剛大 [1]・山口 和也 [1]
Selective Desulfurative Silylation of Sulfides Using Hydrosilanes by Au–Pd Nanoparticle Catalysts ([1]*School of Engineering, The University of Tokyo*) ○So Hiramoto,[1] Takafumi Yatabe,[1] Takehiro Matsuyama,[1] Kazuya Yamaguchi[1]

Sulfides are ubiquitous in natural products, pharmaceuticals, agrochemicals, and functional materials. The desulfurative silylation of sulfides into organosilicon compounds, which are also widely utilized in various fields such as electronic materials, coatings, and pharmaceuticals, is an important transformation but limited to a report using silylboranes. Thus, the development of desulfurative silylation using hydrosilanes, readily available silylating reagents, is desired. However, when hydrosilanes are employed, the thermodynamically favored hydrodesulfurization (HDS) of sulfides generally proceeds preferentially rather than the desired silylation. In this study, we achieved the highly challenging selectivity switch by Au–Pd alloy nanoparticle catalysts with high Au/Pd ratios and developed the first selective desulfurative silylation of sulfides via C(sp^2)–S bond cleavage with hydrosilanes.
Keywords : Au–Pd Nanoparticle Catalyst; Sulfides; Desulfurative Silylation Reaction; Hydrosilanes; Selectivity Switch

スルフィドは天然に広く存在するほか、医農薬品、機能性材料など、様々な用途で利用されている [1)]。スルフィドの脱硫黄型シリル化反応は、電子材料、塗料、医薬品などの分野で広く用いられる有機ケイ素化合物 [2)]をスルフィドから直接合成する有用な反応であるが、シリル化剤としてシリルボランを用いた報告 [3)]が一報存在するのみであり、入手容易なヒドロシランを用いた反応の開発が望まれる。しかしながら、ヒドロシランをシリル化剤に用いた場合には、目的のシリル化反応よりも熱力学的に有利な C(sp^2)–S 結合切断を経る水素化脱硫反応が優先的に進行し、実際にこれまで選択的水素化脱硫反応 (HDS) のみが複数報告されている [4)]。本研究では、種々の検討の結果、Pd に対して過剰量の Au を合金化した Au–Pd ナノ粒子触媒により、初のヒドロシランを用いたスルフィドの C(sp^2)–S 結合切断を経る選択的脱硫黄型シリル化反応を開発した。



1) F. Pana, Z. J. Shi, *ACS Catal*. **2014**, *4*, 280. 2) H. Bock, *Angew. Chem. Int. Ed.* **1989**, *28*, 1627. 3) S. Chen, X. Guo *et al.*, *Angew. Chem. Int. Ed.* **2023**, *62,* e202303470. 4) a) M.-K. Chung, M. Schlaf, *J. Am. Chem. Soc.* **2004**, *126*, 7386. b) N. Barbero, R. Martin, *Org. Lett.* **2012**, *14*, 796.

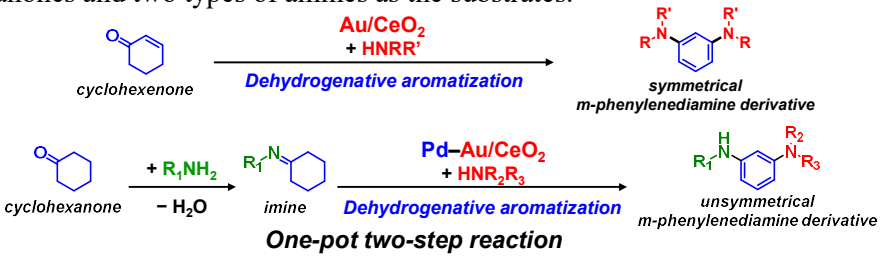
Selective Synthesis of *m*-Phenylenediamine Derivatives through Catalytic Dehydrogenative Aromatization

([1]*School of Engineering, The University of Tokyo*, [2]*Graduate School of Science, Tokyo Metropolitan University*) ○Heizo Kimura,[1] Takafumi Yatabe,[1] Soichi Kikkawa,[2] Seiji Yamazoe,[2] Daisuke Takei,[1] Kazuya Yamaguchi[1]

Keywords: dehydrogenative aromatization; Au nanoparticle catalysts; palladium catalysts; aerobic oxidation; *m*-phenylenediamine

Dehydrogenative aromatization is an environmentally friendly reaction that enables the synthesis of various aromatic compounds from cyclohexanones, which are relatively easy to functionalize regioselectively.[1] However, the synthesis of *m*-phenylenediamine derivatives via dehydrogenative aromatization, in which two amine nucleophiles can be introduced simultaneously at the *m*-position, has not been achieved because it was difficult to control the product selectivity due to irreversible formation of byproducts such as phenols and anilines. Here, we have achieved the selective synthesis of symmetric *m*-phenylenediamine derivatives through dehydrogenative aromatization using cyclohexenones and secondary amines as the substrates, using a CeO_2-supported Au nanoparticle (Au/CeO_2) catalyst for the first time.[2] Furthermore, detailed analysis revealed that the key points of this reaction are: (i) specific multi-site adsorption of the intermediates onto Au nanoparticles, (ii) promotion of O_2 utilization by the CeO_2 support, (iii) facilitation of 1,2/1,4-addition of secondary amines to cyclohexenones on the CeO_2 support.

However, this reaction system presented two issues: (i) it could not be applied to the synthesis of unsymmetrical *m*-phenylenediamine derivatives using two types of amines as the nucleophiles, and (ii) cyclohexenones were more difficult to obtain and synthesize than cyclohexanones. In this study, further investigation revealed that these issues could be resolved by employing a composite catalyst system combining Au/CeO_2 with Pd exhibiting α,β-dehydrogenation activity.[3] This approach enabled the selective one-pot two-step synthesis of *m*-phenylenediamine derivatives, including the unsymmetrical ones, using cyclohexanones and two types of amines as the substrates.



1) Y. Izawa, C. Zheng, S. S. Stahl, *Angew. Chem. Int. Ed.* **2013**, *52*, 3672. 2) H. Kimura, T. Yatabe, K. Yamaguchi, *J. Am. Chem. Soc.* **2025**, *147*, 27238. 3) a) D. Takei, T. Yatabe, X. Jin, T. Yabe, N. Mizuno, K. Yamaguchi, *ACS Catal.* **2020**, *10*, 5057. b) D. Takei, T. Yatabe, T. Yabe, R. Miyazaki, J. Hasegawa, K. Yamaguchi, *JACS Au* **2022**, *2*, 394.

Highly Active Supported Au Catalysts Derived from Novel Au Precursors for Various Catalytic Reactions

([1]*Graduate School of Science, Kyushu University*, [2]*Faculty of Engineering, Kanagawa Institute of Technology*, [3]*Japan Synchrotron Radiation Research Institute (JASRI)*, [4]*Mitsubishi Chemical Corporation*) ○Yuxue Cao,[1] Akina Yoshizawa,[1] Yuji Masaki,[1] Tomohiro Fukae,[1] Haruno Murayama,[2] Tetsuo Honma,[3] Akihiro Nakayama,[1] Eiji Yamamoto,[1] Takashi Sato,[4] Yousuke Suzuki,[4] Makoto Tokunaga[1]

Keywords: Supported Au Catalysts; Impregnation Method; Au Precursors; Catalytic Reactions

Gold nanoparticles (Au NPs) are efficient catalysts for various transformations.[1] While the deposition–precipitation (DP) method affords even distribution, it requires large solvent volumes, increasing cost and environmental impact. The impregnation (IP) method is more scalable but often suffers from Au NPs aggregation due to chloride ions. A highly stable, chloride-free *N*-heterocyclic carbene (NHC)–Au precursor was previously reported by our group; however, its reduction at 300 ℃ was incomplete, leaving organic residues that negatively affected catalytic activity.[2]

To overcome these issues, we developed chloride-free and fully reducible NHC-Au and pyridine-Au precursors. Au/ZrO_2 catalysts prepared from Au precursors was identified based on transmission electron microscopy (TEM) analysis. Thermogravimetric–differential thermal analysis (TG–DTA) and in-situ X-ray absorption fine structure (XAFS) measurements confirmed that decomposition of the precursors and the complete reduction of Au occurred at around 300 ℃.

We subsequently evaluated the catalytic activity of this class of catalysts in several transformations, including the 1,3-rearrangement of allylic esters, the cyclization of hex-5-ynoic acid, and the Claisen rearrangement, all of which afforded moderate to excellent yields.

1) Huang, Q.-A.; Cao, Y.; Satou, K.; Murayama, H.; Yoshizawa, A.; Yamamoto, E.; Nakayama, A.; Ishida, T.; Kitagawa, Y.; Ishimaru, Y.; Okumura, M.; Honma, T.; Suzuki, Y.; Tokunaga, M. *Appl. Catal. B: Environ. Energy.* **2025**, 373, 125351.2) Huang, Q.-A.; Takaki, M.; Murayama, H.; Yoshizawa, A.; Yamamoto, E.; Dien, L. X.; Ishida, T.; Honma, T.; Tzouras, N. V.; Scattolin, T.; Nolan, S. P.; Tokunaga, M. *Mol. Catal.* **2023**, 549, 113460.

Photocatalytic decomposition of perfluoroalkyl compounds using silver-loaded titanium dioxide

([1]*College of Life Sciences, Ritsumeikan University*, [2]*Department of Computer Science and Engineering, University of South Carolina*, [3]*PRESTO JST*) ○Yuto Toyota,[1] JAVAID Rahat[2]; LAUTERBACH Jochen[2]; KOBAYASHI, Yoichi[1,3]

Keywords: Photocatalysis; Perfluoroalkyl substance; Perfluorooctanesulfonic acid; Metal-loaded semiconductor; Silver-loaded titanium dioxide

Perfluoroalkyl substances (PFASs) are widely used due to their thermal stability and chemical resistance; however, the strong carbon–fluorine (C–F) bonds also make them environmentally persistent and bioaccumulative, motivating the development of degradation strategies under mild conditions. We previously demonstrated the conversion of PFASs to fluoride ions using cadmium sulfide nanocrystals under continuous 405 nm irradiation.[1] However, this approach raises concerns about toxic Cd release.

In this study, we aimed to develop a more environmentally benign method for the degradation of PFAS by employing low-toxicity materials. We selected silver-loaded titanium dioxide (Ag/TiO_2) as the photocatalyst owing to its excellent chemical stability, low toxicity, and low cost. Under 365 nm LED irradiation, Ag/TiO_2 efficiently degraded perfluorooctanesulfonic acid (PFOS, Fig. 1a), one of the most chemically persistent PFASs. The reaction was conducted in water by dissolving the potassium salt of PFOS and adding triethanolamine as a hole scavenger, with the catalyst suspended in the solution. Before light irradiation, 20% of the PFOS in the solution was found to be adsorbed on the surface of Ag/TiO_2. Upon light irradiation, fluoride ions were generated. Fluoride ion generation indicates the cleavage of C–F bonds. After 4 hours of 365 nm UV-light irradiation, 99% of PFOS was degraded, and approximately 46% of its 17 C–F bonds were cleaved (Fig. 1b). These results indicate that Ag/TiO_2 readily adsorbs PFOS and efficiently generates fluoride ions upon light irradiation.

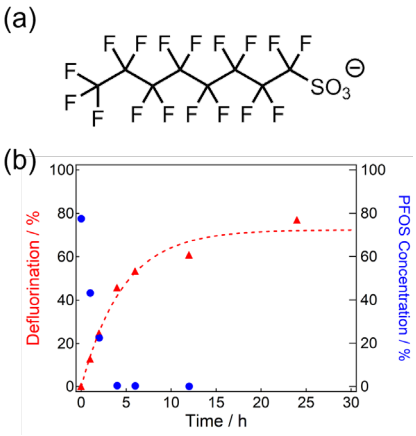


Figure 1. a) Molecular structure of PFOS anion and b) PFOS degradation under 365 nm UV irradiation (760 mW, 0.76 W/cm^2) using 1 wt% Ag/TiO_2.

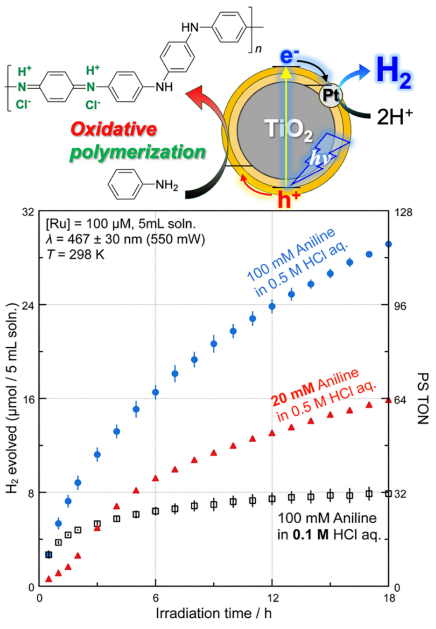
1) Y. Arima, Y. Okayasu, D. Yoshioka, Y. Nagai, Y. Kobayashi, *Angew. Chem. Int. Ed.* **2024**, *63*, e202408687.

光レドックスカスケード触媒による水素･導電性高分子の同時合成

（北大院理）○小林 厚志
Simultaneous Synthesis of Hydrogen and Conductive polymers using Photo-redox Cascade Catalyst (*Faculty of Science, Hokkaido University*) Atsushi Kobayashi

Photocatalytic coproduction of hydrogen and valuable chemicals by using solar light energy is a promising approach to contribute sustainable hydrogen society. We have previously developed photo-redox cascade catalyst (PRCC) systems by loading two different Ru(II) sensitizers onto Pt-supported TiO_2 nanoparticles, successfully linking various substrate oxidation reactions with visible-light-driven hydrogen production. In this work, to further extend the possibility of PRCC system, we present here a photocatalytic coproduction of hydrogen and electro-conductive polyaniline polymers in 0.1 M aniline hydrochloric acid (0.5 M) aqueous solution under blue light irradiation. The H_2 production activity of this PRCC system was found to depend strongly on the polyaniline formation condition (*e.g.* aniline and HCl concentrations).
Keywords : Photocatalyst; Hydrogen Production; Oxidative Polymerization

持続可能な水素社会実現に向けて、水素と化成品を同時に作り出す光触媒反応が注目を集めている。これまでに我々は 2 種類の Ru(II)錯体色素を Pt 担持 TiO_2 ナノ粒子表面へ階層的に固定化した光レドックスカスケード触媒(PRCC)を開発し、様々な基質酸化反応と可視光水素生成反応を連動させてきた。[1] 本研究では PRCC 系の可能性をさらに追求すべく、可視光水素生成反応に組み合わせる反応として、PRCC ナノ粒子の酸化反応活性を促進し得る導電性高分子の酸化重合生成を選択した。



0.5 M 塩酸水溶液に PRCC ナノ粒子（Ru 色素濃度 100 μM）とアニリン（100 mM）を加え、Ar 脱気後に青色光を照射したところ、水素が生成し、光照射 18 時間後の Ru 色素当りの触媒回転数（PS TON）は 116 と見積もられた（右図）。導電性ポリアニリンに特徴的な黒緑色沈殿が生成したことや、塩酸を 0.1 M に希釈すると光照射 1 時間以降の水素生成量が激減したこと、アニリン濃度を 20 mM に希釈した場合には光照射 1 時間以降に水素生成反応が加速したことなどを考慮すると、PRCC ナノ粒子による光水素生成反応とアニリンの酸化重合が同時進行し、PRCC ナノ粒子の光触媒活性がポリアニリン生成過程に強く依存していることが示唆された。詳細は当日報告する。

1) A. Kobayashi, *ChemSusChem* **2025**, *18*, e202400688.