Joint Studies Programs

As one of the important functions of an inter-university research institute, IMS facilitates joint studies programs for which funds are available to cover the costs of research expenses as well as the travel and accommodation expenses of individuals. Proposals from domestic scientists are reviewed and selected by an interuniversity committee.

(1) Special Projects

(a) Enhancing the Durability of Metal Complex–Carbon Electrodes in Electrochemical CO_2 Reduction in Water

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Carbon dioxide (CO_2) is an attractive carbon resource. Two-electron reduction of CO_2 yields industrially valuable products such as carbon monoxide (CO) and formic acid (HCO_2H). Among various approaches, electrochemical CO_2 reduction using water as the electron and proton source has gained increasing attention, with both solid metal electrodes and metal complex–based electrocatalysts being actively studied. Compared with solid metal electrodes, which typically require higher overpotentials and show lower product selectivity, metal complex–supported electrodes offer distinct advantages, including lower energy consumption, rational molecular-level design through the choice of metal centers and organic ligands, efficient electron transfer, and reduced catalyst loading.

A key challenge, however, lies in the stable immobilization of metal complexes on electrode surfaces. Structural degradation of complexes under applied potential or their detachment from the electrode surface leads to significant loss of CO_2 reduction activity. Enhancing the durability of such catalysts is therefore an urgent issue. In this study, we developed a robust metal complex–based electrode catalyst with high durability by anchoring a (PNNP)Ir complex onto a carbon paper (CP) support, yielding [(PNNP)Ir]/CP electrodes, as reported below.

We developed an iridium complex catalyst, Mes-IrPCY$_2$, bearing a tetradentate PNNP ligand, as a highly efficient photocatalyst for CO_2 reduction. This complex exhibits an exceptional turnover number (TON > 10,400), far exceeding conventional mononuclear self-sensitized systems. The PNNP ligand, composed of a bipyridine unit and two phosphine donors, allows systematic tuning of electronic and steric properties through ligand modification. In this study, we first advanced toward next-generation electrodes by immobilizing (PNNP)Ir complexes on carbon paper (CP). The electrodes, [(PNNP)Ir]/CP, were fabricated by coating the complexes with pyrrole polymer and carbon powder. Structural characterization of [Mes-IrPPh$_2$]/CP using SEM and EDS confirmed a homogeneous distribution of N, P, and Ir, with the complex concentrated on the CP surface. Electrochemical tests revealed that [Mes-IrPPh$_2$]/CP exhibited catalytic current at a low onset potential (E_{on} = −0.24 V vs. RHE), marking the first demonstration of such low-voltage activity for this class of molecularly engineered electrodes. These findings underscore the promise of PNNP–Ir complexes as durable, tunable platforms for efficient CO_2 electroreduction and artificial photosynthesis.

We further evaluated the electrochemical CO_2 reduction performance of the fabricated [(PNNP)Ir]/CP electrodes in aqueous media using a two-compartment electrolysis cell separated by a Nafion membrane, with a Pt anode and the CO_2 reduction cathode. In CO_2-saturated 0.5 M $KHCO_3$ electrolyte, application of −0.37 V vs. RHE for 3 h revealed that [Mes-IrPPh$_2$]/CP exhibited the highest activity. A total of 0.765 mmol of products (formate + CO) was generated from 2.86 μmol of catalyst, achieving a Faradaic efficiency of 86.4% for formate with a current density of 5.49 mA cm^{-2}. Remarkably, even at a lower applied potential of −0.27 V vs. RHE, the electrode maintained high efficiency, with Faradaic yields exceeding 95%. Long-term electrolysis at −0.37 V vs. RHE for 168 h produced 12.5 mmol of formate in a linear growth trend, demonstrating that the [Mes-IrPPh$_2$]/CP electrode catalyst possesses excellent durability under these conditions.

Then, we have also developed an interfacial measurement technique based on nonlinear spectroscopy, in which multiple femtosecond pulses are temporally and spatially overlapped to coherently excite interfacial responses. A key challenge at the outset was that interfacial signals were buried under overwhelming bulk contributions from the aqueous solution and electrode. Through systematic optimization of the measurement scheme, we successfully suppressed bulk-derived background signals by more than four orders of magnitude, thereby establishing a methodology that enables effective detection of signals originating exclusively from the electrode interface. Using this approach, we examined [Mes-IrPPh$_2$]/CP and CP electrode. The results revealed that the molecular response of interfacial water in the electric double layer was strongly modulated compared with bare CP electrodes, and that this modulation depended sensitively on the solution conditions (acidic, neutral, or basic).

In summary, this study established a novel class of CO_2 reduction electrode catalysts based on PNNP–Ir complexes, demonstrating their outstanding durability under both photo- and electrochemical conditions. The integration of in situ nonlinear spectroscopic feedback with catalyst design has enabled deeper understanding of interfacial processes and guided the development of electrodes with enhanced stability and performance. Building on these advances, the research has further evolved into a CREST co-creation project on catalytic upcycling of oxidized carbon resources, underscoring the broader significance of our work in paving the way toward sustainable carbon utilization technologies.

(b) Fabrication of Plasmon-Quantum Dots Hybrid Structures and Elucidation of Their Photoexcited State Dynamics by Ultrafast Nanoscale Microspectroscopy

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KAMADA, Kazuki (*Osaka Metropolitan Univ.*)

When semiconductor quantum dots (QDs) form a well-packed and highly ordered aggregates, new optoelectric functionalities (*e.g.* carrier transport property) appear due to the quantum chemical interactions between the QDs. These functionalities are promising to be applied for future QD-based solar cells. Furthermore, by integrating metal nanostructures exhibiting plasmonic responses as a substrate to support the QD assembly, the photofunctionalities drastically enhances through a strong interaction with the plasmonic field.

The aim of research is to understand the unique optoelectronic properties resulting from inter-QD and plasmon-QD interactions to achieve precise control of the photofuctionalities in the hybrid system. A research group at Osaka Metropolitan Univ. (Shibuta and Kamada) has precisely synthesized water-soluble QDs (e.g. CdTe and CdSe) with high optical absorption/luminescent properties at visible wavelength range. Short-chain ligands are chosen to stabilize the QDs while promoting stronger inter-QD coupling, enabling a well-packed QD layer to be assembled on a plasmonic substrate by solution-based layer-by-layer deposition (left in the Figure). The plasmonic properties of the plasmon-QD hybrid structure can be characterized by an upconversion fluorescence microscopy excited with a femtosecond laser (Kamada *et. al.*, submitted, bottom right of Figure 1.).

The plasmonically excited carrier/exciton dynamics in the system are then probed by ultrafast and ultrabroadband scanning near-field optical microscopy. This cutting-edge nanospectroscopy performed in IMS by Kumagai and Nishida begins to reveal the spatiotemporal dynamics of photo-excited carriers (upper right in Figure). The ultrafast phenomena in the plasmon-QD hybrid system will be theoretically addressed approach to understanding light-matter interaction in collaboration with Iwasa's group at Hokkaido Univ.).

This joint research will elucidate the physical mechanisms governing the distinctive optoelectronic properties of QD–plasmonic structures and establish rational design principles for high-efficiency optoelectronic devices and light-to-electricity conversion processes.

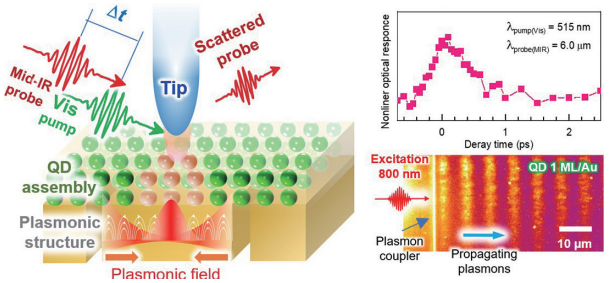

Figure 1. (left) Plasmon-QD hybrid structure and ultrafast and ultrabroadband scanning near-field optical microscopy. (bottom right) Optical imaging of plasmonic excitation. (upper right) Ultrafast response of the corresponding sample.

(2) Research Symposia

(From Oct. 2024 to Sep. 2025)

Dates	Theme	Chair
Oct. 30–31, 2024	Chemical Synthesis 2.0: Toward a New Paradigm in Chemical Synthesis through the Integration of Research Methods	**MOMIYAMA, Norie**
Dec. 17–18, 2024	Approaching Complex Systems ~To What Extent Can We Predict Materials Complexity?	**KITADA, Atsushi** **KERA, Satoshi**
Jan. 20, 2025	Recent Advancements and Functionalities in Electronic Ferroelectrics	**OKIMOTO, Yoichi** **KUMAGAI, Takashi**
Feb. 27–28, 2025	Spin Life Science Using Spin as a Probe: Aiming to Accelerate Interdisciplinary Research	**NAKAMURA, Toshikazu**
Mar. 10–12, 2025	Chirality-Related Dynamic Phenomena	**TOGAWA, Yoshihiko** **YAMAMOTO, Hiroshi**
Apr. 7– 8, 2025	Molecular Science in Tribology	**HIRAYAMA, Tomoko** **ONISHI, Hiroshi**
May 12–13, 2025	Symposium on Optical Materials and its Measurements in UVSOR (SOMU2025)	**KUSOSAWA, Shunsuke** **MATSUI, Fumihiko**

May 31–Jun. 1, 2025	Hierarchical Molecular Dynamics: Advanced Experiments and Theories	**KURAMOCHI, Hikaru**
Sep. 1, 2025	Morino Discussion	**MUNAKATA, Toshiaki** **KUMAGAI, Takashi**
Jun. 15, 2025	Advanced Workshop on Interdisciplinary Exchange in Molecular Science	**KURODA, Runa** **SUGIMOTO, Toshiki**
Aug. 18–20, 2025	The 23rd ESR Summer School —Interdisciplinary Approach for Electron Spin Science—	**IIZUKA, Naoko** **NAKAMURA, Toshikazu**
Jul. 27–31, 2025	Recent Advances and Perspectives of Interfacial Materials and Molecular Sciences lead by Next-Generation Laser Techniques and Computational Science	**MORITA, Akihiro** **SUGIMOTO, Toshiki**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2024–Mar. 2025		Apr. 2025–Sep. 2025		Total		
		Regular	ARIM	Regular	ARIM	Regular	ARIM	Sum
Special Projects		1		1		2		2
Research Symposia		5		4		9		9
Research Symposia for Young Researchers		0		2		2		2
Okazaki Conference		0		1		1		1
Cooperative Research		21	42	19	27	40	69	109
Use of Facility	Instrument Center		103		70		173	173
	Equipment Development Center	0	6	0	9	0	15	15
	UVSOR	102	1	106	1	208	2	210
Use of Facility Program of the Computer Center						429*		429*

* from April 2024 to March 2025