Joint Studies Programs

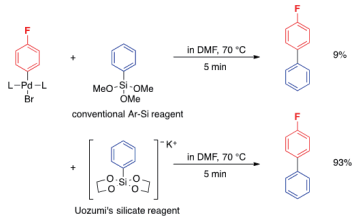
As one of the important functions of an inter-university research institute, IMS facilitates joint studies programs for which funds are available to cover the costs of research expenses as well as the travel and accommodation expenses of individuals. Proposals from domestic scientists are reviewed and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

(1) Special Projects

(a) *Operando* Structural Studies on the Reacting Species of the Cross-Coupling Catalysis

FUJIKAWA, Shigenori (*Kyushu Univ.*)
TAKAYA, Hikaru (*Teikyo Univ. Sci. and IMS (concurrent)*)
NAGASAKA, Masanari (*IMS*)
OKUMURA, Shintaro (*IMS*)
UOZUMI, Yasuhiro (*IMS*)

The palladium-catalyzed cross-coupling reactions have been recognized as the most powerful synthetic means of carbon–carbon bond formation. Coupling of aryl halides and organosilicon reagents, the so-called Hiyama coupling, is one of the representatives. Recently, Uozumi at IMS developed aryl silicate reagents which exhibited remarkably high reactivity toward the Hiyama coupling with aryl halides (Scheme 1). These observations prompted us to the joint project that examines the *operando* structural studies on the aryl silicates as well as conventional aryl silyl reagents under the actual coupling reaction conditions by *in situ* NEXAFS measurements. In the last year, we have measured the carbon K-edge NEXAFS spectrum of 100 mM trimethoxy(phenyl)silane (Ph-Si(OMe)$_3$) in tetrahydrofuran (THF) at BL3U of UVSOR-III Synchrotron, and the C–Si bond length of several organosilicon compounds were related to the reaction mechanism of Hiyama coupling reaction (by Okumura, Nagasaka, Uozumi). In this year, we have developed an ultrathin liquid cell that achieves the 2.6 mm optical length of argon gas (by Nagasaka, Takaya) including novel Si-free nanomembranes developed by Fujikawa (Figure 1). Figure 2 shows the soft X-ray transmission of the developed polymer film in the soft X-ray region from 50 eV to 560 eV. Since the polymer film includes the C=C and C=N groups, the sharp absorption peaks are observed at the C and N K-edges. Since the polymer film includes no Si atoms, there is no peaks at the Si L-edge (100 eV). Soft X-ray transmission of the polymer film shows a still high value below 200 eV, indicating the developed polymer film is suitable to measure XAS of liquid in the low-energy region. By using this measurement system, we will apply the Si L-edge NEXAFS measurements at BL3U of UVSOR-III in this year.



Scheme 1. The Hiyama Coupling Reactions with Uozumi's Aryl Silicate.

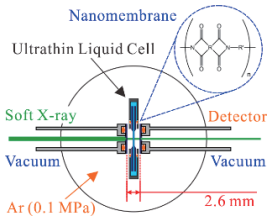


Figure 1. The schematic of an ultrathin liquid cell including Si-free nanomembranes.

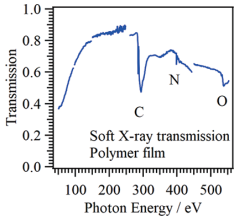


Figure 2. Soft X-ray transmission of the polymer film.

(b) Analysis and Elucidation of Deactivation Mechanism for High Durability of Metal Complex-Carbon Electrodes for Electroreduction of CO_2 in Water

SAITO, Susumu (*Nagoya Univ.*)
SATO, Shyunsuke (*Toyota Central R&D Labs., Inc.*)
SUGIMOTO, Toshiki (*IMS*)

In order to investigate the cause of the performance degradation of the cathode electrode during the ongoing electroreduction of CO_2 in water using a complex-carbon electrode,[1] *in-situ* observations of the cathode electrode are performed by nonlinear optical spectroscopy. In particular, we conducted *operando* measurement of second-harmonic generation (SHG) and third-harmonic generation (THG) using the home-made electrochemical spectroscopic cells and systems. Then, we found that the SHG signal is highly sensitive to microscopic structural changes and degradation of the electrode surfaces in response to the applied bias voltage, whereas the electronic non-resonant THG signal is almost unaffected by structural changes on the electrode surfaces. Using SHG, we succeeded in investigating not only the oxidation process of electrode, but also the adsorption of ion and the subsequent rearrangement of interfacial water molecules. Moreover, we have succeeded in newly developing highly sensitive coherent Raman spectroscopy technique. We are also applying this new method to the observation of working electrode surfaces under reaction conditions.

Reference

1) M. Yamauchi, H. Saito, T. Sugimoto, S. Mori and S. Saito, *Coord. Chem. Rev.* **472**, 214773 (2022).

(2) Research Symposia

(From Oct. 2022 to Sep. 2023)

Dates	Theme	Chair
Nov. 8, 2022	Resonant Soft X-Ray Scattering and Reflectivity: Nano/Mesoscale Structural Analysis of Soft Materials and Soft Matter	**ARAKI, Tohru** **KERA, Satoshi**
Nov. 28, 2022	Conference on Generation and Advanced Applications of Various Quantum Beams in UVSOR-III	**TAIRA, Yoshitaka**
Mar. 29–30, 2023	Understanding and Design of Biomolecular Machinery: Next Challenges of Molecular Engine	**UENO, Takafumi** **IINO, Ryota**
Jun. 14–15, 2023	Industry-Academia-Government-Citizens Collaboration for a Sustainable Society with Examples from Chemistry, Engineering, and Environmental Studies	**TOKORO, Chiaru** **OKAMOTO, Hiromi**
Jul. 29–30, 2023	Seeds and Needs for Tomorrow's Synchrotron Radiation Photoelectron Spectroscopy Research	**MATSUI, Fumihiko**
Aug. 31, 2023	Morino Discussion	**MUNAKATA, Toshiaki** **KURAMOCHI, Hikaru**
Sep. 13–14, 2023	Toward the Development of Ionic Liquid Informatics	**KITADA, Atsushi** **KERA, Satoshi**
Sep. 29, 2023	UVSOR–SPring8 Infrared Beamline Joint Users Meeting	**TANAKA, Kiyohisa**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2022–Mar. 2023		Apr. 2023–Sep. 2023		Total		
		Regular	ARIM	Regular	ARIM	Regular	ARIM	Sum
Special Projects		2		1		3		3
Research Symposia		3		5		8		8
Research Symposia for Young Researchers		0		0		0		0
Cooperative Research		25	25	17	22	42	47	89
Use of Facility	Instrument Center		75		70		145	145
	Equipment Development Center	0	7	0	5	0	12	12
	UVSOR	105	3	104	1	209	4	213
Use of Facility Program of the Computer Center						298*		298*

* from April 2022 to March 2023