

# The 2nd CSLT-CSJ Joint Symposium 2021

## –Catalyst for Energy Conversion and Storage–

Date : on 21st March 2021(Sun) 1:00PM- 3:40PM



### 【Program】

13:00-

#### Opening Remarks

- Executive Manager Prof. Mitsuo Sawamoto
  - President of Chemical Society Located in Taipei
- Prof. Chain-Shu Hsu

(Chair: Prof. Masanori Sakamoto, Kyoto University)

13:05-

Metal-complex/Semiconductor Hybrid Photocatalysts and Photoelectrodes for Visible-light CO<sub>2</sub> Reduction

(Tokyo Institute of Technology) Prof. Kazuhiko Maeda

13:30-

Computational Modeling for CO<sub>2</sub> Electrochemical Reduction on Cu-based Materials

(National Taiwan Normal Univ.) Prof. Ming-Kang (Brad) Tsai

(Chair: Prof. Kazuhiko Maeda, Tokyo Institute of Technology)

13:55-

Development of Function-Integrated Catalytic System for Small Molecule Conversion

(Osaka University) Prof. Mio Kondo

14:20-

Operando Understanding the Catalytic Centers in Ambient Condition

(National Taiwan Normal University) Prof. Hao-Ming Chen

(Chair: Prof. Mio Kondo, Osaka University)

14:45-

Plasmonic p-n Junction for Infrared Light to Chemical Energy Conversion

(Kyoto University) Prof. Masanori Sakamoto

15:10-

Bridging Energy and Chemistry via Nanoarchitectonic Engineering at Atomic Scale

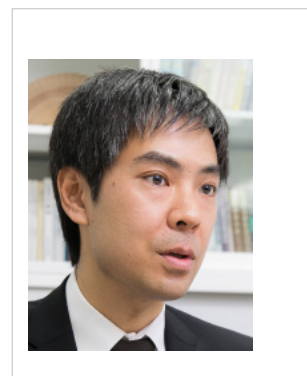
(National Synchrotron Radiation Research Center) Prof. Chun-Hong Kuo

15:35-

Closing Remarks Prof. Ryu Abe (Kyoto University)

## Kazuhiko Maeda

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### ➤ Educational Background

2003 B.Sc., Tokyo University of Science, Japan  
2005 M.Sc., Tokyo Institute of Technology (supervisor: Prof. Michikazu Hara)  
2007 Doctor of Engineering, The University of Tokyo (supervisor: Prof. Kazunari Domen)

### ➤ Professional Career

2007.4–2009.3; JSPS Research Fellow (DC2, PD)  
2007.10–2008.3; Post-doc at The University of Tokyo (Prof. Kazunari Domen)  
2008.4–2009.3; Post-doc at The Penn State University (Prof. Thomas E. Mallouk)  
2009.4–2012.7; Assistant Professor, The University of Tokyo  
2010.10–2014.3; PRESTO/JST researcher  
2012.8–present; Associate Professor, Tokyo Institute of Technology

### ➤ Research Interests

- 1) Heterogeneous photocatalysis for light to chemical energy conversion, with a focus on water splitting and CO<sub>2</sub> fixation
- 2) Synthesis and functions of mixed anion compounds

### ➤ Selected Awards

2012; 6th PCCP Prize for Outstanding Achievement of Young Scientists, Royal Society of Chemistry  
2013; The Chemical Society of Japan Award for Young Chemists  
2016; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, Japan: The Young Scientists' Prize  
2016; The 13th JSPS Prize  
2018; Highly Cited Researcher 2018  
2019; Highly Cited Researcher 2019

### ➤ Recent Publications

1. "Nature-Inspired, Highly Durable CO<sub>2</sub> Reduction System Consisting of a Binuclear Ruthenium(II) Complex and an Organic Semiconductor Using Visible Light", R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani, K. Maeda. *J. Am. Chem. Soc.* **2016**, *138*, 5159.
2. "Robust Binding between Carbon Nitride Nanosheets and a Binuclear Ruthenium(II) Complex Enabling Durable, Selective CO<sub>2</sub> Reduction under Visible Light in Aqueous Solution", R. Kuriki, M. Yamamoto, K. Higuchi, Y. Yamamoto, M. Akatsuka, D. Lu, S. Yagi, T. Yoshida, O. Ishitani, K. Maeda. *Angew. Chem., Int. Ed.* **2017**, *56*, 4867.
3. "A Stable, Narrow-Gap Oxyfluoride Photocatalyst for Visible-Light Hydrogen Evolution and Carbon Dioxide Reduction", R. Kuriki, T. Ichibha, K. Hongo, D. Lu, R. Maezono, H. Kageyama, O. Ishitani, K. Oka, K. Maeda. *J. Am. Chem. Soc.* **2018**, *140*, 6648.
4. "Solar-Driven Photoelectrochemical Water Oxidation over an n-Type Lead-Titanium Oxyfluoride Anode", N. Hirayama, H. Nakata, H. Wakayama, S. Nishioka, T. Kanazawa, R. Kamata, Y. Ebato, K. Kato, H. Kumagai, A. Yamakata, K. Oka, K. Maeda. *J. Am. Chem. Soc.* **2019**, *141*, 17158.

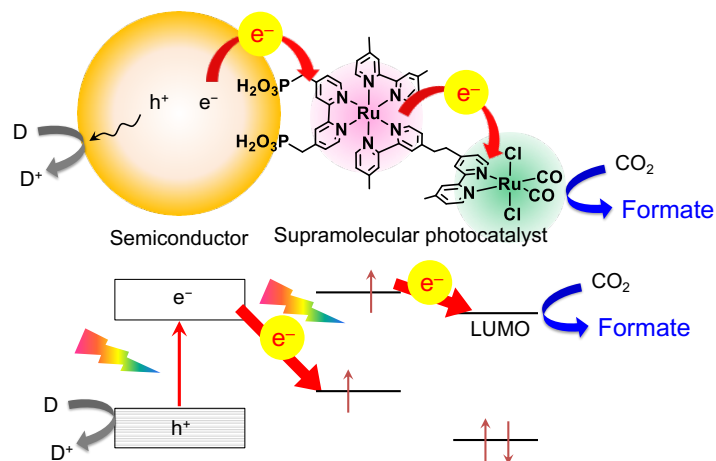
## Metal-complex/semiconductor hybrid photocatalysts and photoelectrodes for visible-light CO<sub>2</sub> reduction

Kazuhiko Maeda

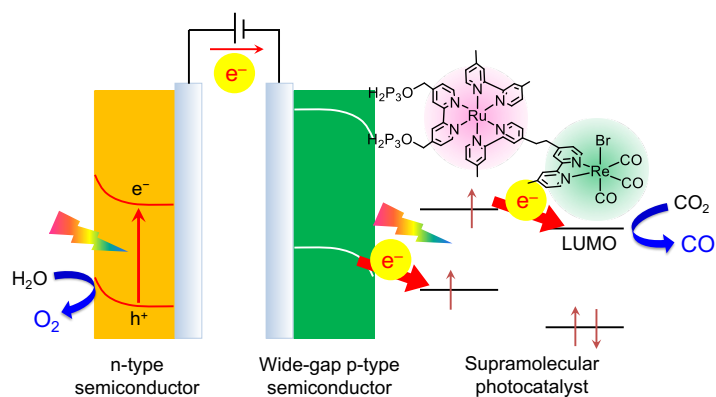
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CO<sub>2</sub> reduction into carbon feedstocks using a heterogeneous photocatalyst is an attractive means of addressing the problems of global warming and the depletion of fossil fuels. Of particular importance is the development of a photosystem workable under visible light, which accounts for the main component of solar spectrum, toward artificial photosynthesis. Hybrid systems constructed with a metal complex and a semiconductor are promising because of the excellent electrochemical (and/or photocatalytic) ability of metal complexes for CO<sub>2</sub> reduction and the high efficiency of semiconductors for water oxidation to form molecular O<sub>2</sub>.<sup>1</sup> In this talk, recent progress on the development of hybrid photocatalysts and photoelectrodes for CO<sub>2</sub> reduction will be presented.

For example, we have developed a new system for CO<sub>2</sub> reduction using a visible-light-responsive semiconductor and a binuclear metal complex having a redox photosensitizer and a catalytic unit (Fig. 1). This hybrid was capable of reducing CO<sub>2</sub> into HCOOH (or CO) according to two-step photoexcitation of the semiconductor and the photosensitizer unit of the metal complex. On the other hand, neither semiconductor nor metal complex alone showed activity under the same reaction conditions. It was found that semiconductors of TaON, CaTaO<sub>2</sub>N, Y<sub>2</sub>Ta<sub>2</sub>O<sub>5</sub>N<sub>2</sub>, C<sub>3</sub>N<sub>4</sub>, Ta<sub>3</sub>N<sub>5</sub>, Li<sub>2</sub>LaTa<sub>2</sub>O<sub>6</sub>N, GaN:ZnO solid solution, and Pb<sub>2</sub>Ti<sub>2</sub>O<sub>5.4</sub>F<sub>1.2</sub> became active component for this system driven by visible light (> 400 nm) in combination with a suitable binuclear metal complex. This metal-complex/semiconductor hybrid system could be also applied to a photoelectrochemical cell to simultaneously reduce CO<sub>2</sub> to CO and oxidize H<sub>2</sub>O into O<sub>2</sub> under visible light in the presence of a small external bias (Fig. 2).



**Fig. 1.** Z-scheme CO<sub>2</sub> reduction using a semiconductor and a binuclear metal complex having photosensitizing and catalytic units. The binuclear Ru(II) complex shown here is known to work as an efficient homogeneous photocatalyst to produce HCOOH.



**Fig. 2.** Photoelectrochemical CO<sub>2</sub> reduction and water oxidation using a molecular photocathode and an n-type semiconductor photoanode.

## Ming-Kang (Brad) Tsai

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### ➤ Educational Background

1997 B.Sc., Department of Applied Chemistry,  
National Chiao Tung University, TW

2005 Doctor of Chemistry, College of Science, University of Pittsburgh, US (supervisor: Prof. Kenneth Jordan)

### ➤ Professional Career

2005 Postdoctoral Researcher, Pacific Northwest National Laboratory, US

2007 Research Associate, Brookhaven National Laboratory, US

2010 Assistant professor, National Taiwan Normal University, TW

2015 Associate professor, National Taiwan Normal University, TW

2019 Full Professor, National Taiwan Normal University, TW

### ➤ Research Interests

- 1) Computational Inorganic Chemistry in Renewable Energy Catalysis
- 2) Multiscale Modelling Method Development
- 3) Chemical Informatics in Materials and Molecule Design

### ➤ Awards

2017 Innovation-Oriented Trilateral Research Fund for Young Investigators of NTU System

2019 Innovation-Oriented Trilateral Research Fund for Young Investigators of NTU System

### ➤ Recent Publications

1. "Enhancing C-C Bond Formation by the Surface Strain: Investigating the C2 and C3 Intermediate Formation on the Strained Cu Surfaces", Yu-Te Chan, I-Shou Huang, and Ming-Kang Tsai.\* *Phys. Chem. Chem. Phys.* **2019**, *21*, 22704 (cover highlight).
2. "Harnessing Dielectric Confinement on Tin Perovskites to Achieve Emission Quantum Yield up to 21%", Jin-Tai Lin, Chen-Cheng Liao, Chia-Shuo Hsu, Deng-Gao Chen, Hao Ming Chen,\* Ming-Kang Tsai,\* Pi-Tai Chou,\* and Ching-Wen Chiu.\* *J. Am. Chem. Soc.* **2019**, *141*, 10324.
3. "Identification of Stabilizing High-valent Active Sites by Operando High-energy Resolution Fluorescence-detected X-ray Absorption Spectroscopy for High Efficient Water Oxidation", Sung-Fu Hung, Yu-Te Chan, Chun-Chih Chang, Ming-Kang Tsai,\* Yen-Fa Liao, Nozomu Hiraoka, Chia-Shuo Hsu, and Hao Ming Chen,\* *J. Am. Chem. Soc.* **2018**, *140*, 17263.
4. "A Computational Exploration on CO<sub>2</sub> Reduction via CO Dimerization on Mixed-Valence Copper Oxide Surface", Chun-Chih Chang, Elise Y. Li,\* and Ming-Kang Tsai,\* *Phys. Chem. Chem. Phys.* **2018**, *20*, 16906 (cover highlight).
5. "Interplay between Polarizability and Hydrogen Bond Network of Water: Reparametrizing the Flexible Single-Point-Charge Water Model by the Nonlinear Adaptive Force Matching Approach", I-Shou Huang and Ming-Kang Tsai.\* *J. Phys. Chem. A* **2018**, *122*, 4654.

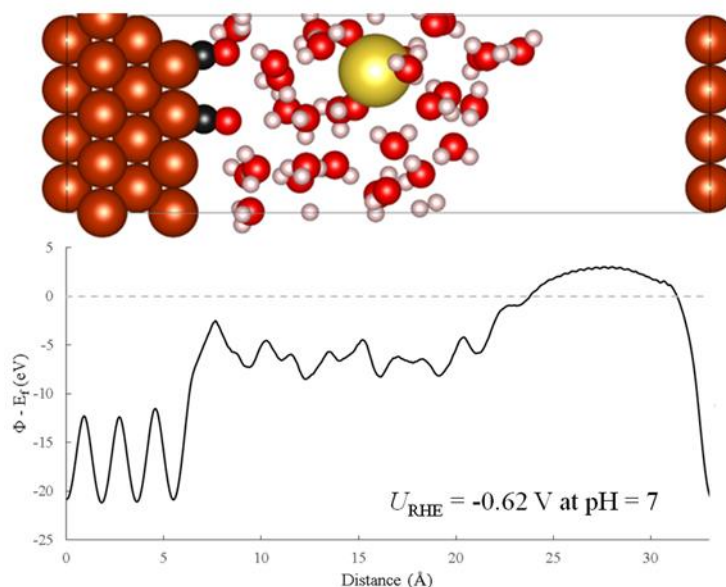
# Computational Modeling for CO<sub>2</sub> Electrochemical Reduction on Cu-based Materials

Ming-Kang (Brad) Tsai<sup>a</sup>

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Electrochemical reduction of CO<sub>2</sub> into liquid fuel is an ultimate-and-ideal cycle for realizing the catalytic application of the renewable energy storage. With preparing the Cu catalyst from the reduction of copper oxide, as known as OD-Cu, Li et al. observed a wide range of single- and multiple-carbon hydrocarbon products from CO reduction reaction (CORR), in order to preclude the complex reduced-intermediate absorption kinetics on Cu surfaces [Nature 2014]. Toward the purpose of understanding the rate-determining step of C–C bond formation, Nørskov and co-workers calculated CO••CO dimerization barrier on several Cu surfaces with the presence of a proton and explicit water molecules, and the barrier was predicted to be experimentally accessible around 0.5 eV [Surface Science 2016].

In this talk, our computational efforts in understanding the important factors to enhance the C–C bond coupling process will be reported, e.g. solvation, mixed-valence surface and surface stains. The corresponding experimental observations related to the aforementioned factors will be also discussed. In addition to the CO<sub>2</sub> electrochemical reduction reactivity predicted by the selected slab models, the integration of modelling methodology combining Density Functional Theory (DFT), molecular mechanics (MM), and electric field will also be demonstrated.



**Figure 1.** The schematic representation for modelling CO••CO coupling on Cu electrode surface.



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### ➤ Educational Background

2003 B.Sc., The University of Tokyo (supervisor: Prof. Hiroshi Nishihara)  
2005 M.Sc., Graduate School of Science, XXX University (supervisor: Prof. Hiroshi Nishihara)  
2008 Doctor of Science, Graduate School of Science, XXX University (supervisor: Prof. Hiroshi Nishihara)

### ➤ Professional Career

2008 JSPS Reserch Fellow (PD), Kyoto University  
2011 Post-doctoral Researcher, JST ERATO Kitagawa Integrated Pores Project  
2011 Assistant Professor, Institute for Molecular Science  
2012 JST ACT-C Researcher  
2019 Associate Professor, Osaka University

### ➤ Research Interests

- 1) Coordination Chemistry
- 2) Small Molecule Conversion

### ➤ Awards

2018 7th NINS Young Researcher Award  
2018 CSJ Female Chemist Encouragement Award  
2016 Morita Science Research Award  
2012 5th Shiseido Female Researcher Science Grant

### ➤ Recent Publications

1. "Pentanuclear Iron Catalysts for Water Oxidation: Substituents Provide Two Routes to Control Onset Potentials ", Vijayendran K. K. Praneeth, Mio Kondo, Masaya Okamura, Takuya Akai, Hitoshi Izu, and Shigeyuki Masaoka. *Chem. Sci.*, **2019**, 10, 4628.
2. "Function-integrated Ru catalyst for photochemical CO<sub>2</sub> reduction ", Sze Koon Lee, Mio Kondo, Masaya Okamura, Takafumi Enomoto, Go Nakamura, and Shigeyuki Masaoka. *J. Am. Chem. Soc.* **2018**, 140, 16899.
3. "Development of a framework catalyst for photocatalytic hydrogen evolution", Pondchanok Chinapang, Masaya Okamura, Takahiro Itoh, Mio Kondo, and Shigeyuki Masaoka. *Chem. Commun.*, **2018**, 54, 1174. (Selected as a Back Cover Picture).
4. "A pentanuclear iron catalyst designed for water oxidation", Masaya Okamura, Mio Kondo, Reiko Kuga, Yuki Kurashige, Takeshi Yanai, Shinya Hayami, Vijayendran K. K. Praneeth, Masaki Yoshida, Ko Yoneda, Satoshi Kawata, and Shigeyuki Masaoka. *Nature*, **2016**, 530, 465.

# Development of Function-Integrated Catalytic System for Small Molecule Conversion

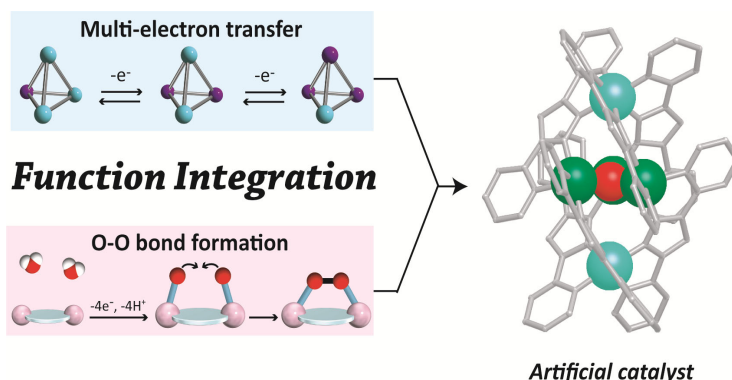
Mio Kondo

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Development of catalysts for small molecule conversion reactions has drawn tremendous attention recently because of the urgent need to solve the world's energy and environmental problems. In particular, the catalysts that can produce sustainable fuels and chemicals from abundant sources are highly required. In this study, we aimed to develop novel catalytic systems for molecule conversion reactions based on function integration into metal complexes. The following two topics will be presented in the talk.

## 1. Function-Integrated Catalyst for Water Oxidation

The water oxidation reaction ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ) is an essential reaction to provide the protons and electrons requisite to generate chemical fuels. We assumed that efficient water oxidation catalyst can be constructed by integrating following two key features; (i) multinuclear structures to promote multi-electron transfer and (ii) two adjacent water-activation sites to promote intramolecular O-O bond formation (**Figure 1**). Based on the

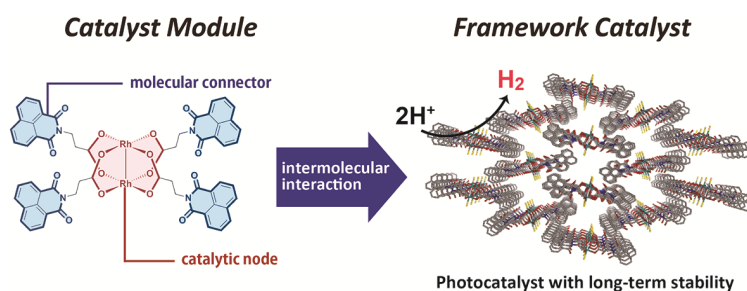


**Figure 1.** Strategy to design a function -integrated catalyst for water oxidation.

strategy, we employed a pentanuclear iron complex with adjacent open-coordination sites. Electrochemical analysis revealed that the pentairon complex can serve as a highly active water oxidation catalyst with the turnover frequency of  $1,900 \text{ s}^{-1}$ .

## 2. Function-Integrated Catalyst for Photocatalytic Hydrogen Evolution

In this study, we aimed to develop novel molecular-based catalytic systems, in which the advantageous features of homogeneous and heterogeneous systems are integrated. In our system, a discrete catalyst module, which has a metal-complex-based catalytic centre and intermolecular interaction sites, can be assembled into an ordered structure via non-covalent interactions to afford a heterogeneous framework catalyst (**Figure 2**). A Rh(II) dimer complex-based catalyst module was self-assembled by simple recrystallization to afford a framework catalyst. The photocatalytic studies of the framework catalyst that the framework can promote photocatalytic  $\text{H}_2$  evolution with the long-lived activity and was reused without considerable loss of catalytic activity.



**Figure 2.** Function-integrated system for hydrogen production.

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### Career and Service:

B.S., 2002, Department of Chemistry, National Taiwan University.

M.S., 2004, Department of Chemistry, National Taiwan University.

Ph.D., 2008, Department of Chemistry, National Taiwan University.

Postdoctoral Fellow, 2009-2012, Department of Chemistry and Physics, National Taiwan University.

Postdoctoral Fellow, 2012-2013, Department of Chemistry, UC Berkeley.

Assistant Professor, 2013-2018, Department of Chemistry, National Taiwan University.

Associate Professor, 2018-present, Department of Chemistry, National Taiwan University.

### Honor and Awards:

2020- Highly Cited Researchers, Web of Science

2019- Outstanding Research Award, Ministry of Science and Technology, Taiwan

2019- Lectureship Award for Asian and Oceanian Photochemist Sponsored by Eikohsha, The Japanese Photochemistry Association, Japan

2018- JACS Young Investigators, ACS virtual issue

2018- Young Scholar Innovation Award, Foundation of the Advancement of Outstanding Scholarship, Taiwan

2018- Excellent Teaching Award, National Taiwan University

2018- The Academia Sinica Research Award for Junior Research Investigators, Academia Sinica

2018- The Excellent Paper Award, Catalysis Society of Taiwan

2017- Dr. Ta-You Wu Memorial Award, Ministry of Science and Technology, Taiwan

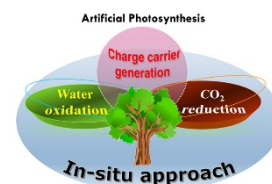
2017- Outstanding Young Chemist Award, Chinese Chemical Society Located in Taipei

### Research Interests:

In situ/Operando methodology development.

(Photo)electrochemistry for artificial photosynthesis.

Synthesis and applications of Inorganic materials



### Selected Publications:

1. Shaowen Cao, Han Li, Tong Tong, Hsiao-Chien Chen, Anchi Yu, Jiaguo Yu,\* Hao Ming Chen\*, "Single-Atom Engineering of Directional Charge Transfer Channels and Active Sites for Photocatalytic Hydrogen Evolution" *Adv. Funct. Mater.* **2018**, 28, 1802169.
2. Bo Weng, Kang-Qiang Lu, Zichao Tang, Hao Ming Chen\*, Yi-Jun Xu\*, "Stabilizing Ultrasmall Au Clusters for Enhanced Photoredox Catalysis" *Nature Commun.* **2018**, 9, 1543.
3. Min-Yi Chen, Jin-Tai Lin, Chia-Shuo Hsu, Chung-Kai Chang, Ching-Wen Chiu\*, Hao Ming Chen\*, Pi-Tai Chou\*, "The Strongly Coupled Tin-Halide Perovskites to Modulate the Light Emission: Tunable 550-640 nm Light Emission (FWHM 36-80 nm) with a Quantum Yield of up to 6.4%" *Adv. Mater.* **2018**, 30, 1706592.
4. Sung-Fu Hung, Ying-Ya Hsu, Chia-Jui Chang, Chia-Shuo Hsu, Nian-Tzu Suen, Ting-Shan Chan, Hao Ming Chen\*, "Unraveling Geometrical Site Confinement in High-efficient Iron-doped Electrocatalysts toward Oxygen Evolution Reaction" *Adv. Energy Mater.* **2018**, 8, 1701686.
5. Sheng-Chih Lin, Chia-Shuo Hsu, Shih-Yun Chiu, Tzu-Yu Liao, Hao Ming Chen\*, "Edgeless Ag-Pt Bimetallic Nanocages : In Situ Monitor Plasmon-induced Suppression of Hydrogen Peroxide Formation" *J. Am. Chem. Soc.* **2017**, 139, 2224-2233. (Featured in the 2018 *JACS* Young Investigators Issue)
6. Nian-Tzu Suen, Sung-Fu Hung, Quan Quan, Nan Zhang, Yi-Jun Xu\*, Hao Ming Chen\*, "Electrocatalysis for oxygen evolution reaction: recent development and future perspective" *Chem. Soc. Rev.* **2017**, 46, 337-365. (Cover highlight)
7. Bo-An Chen, Jin-Tai Lin, Nian-Tzu Suen, Che-Wei Tsao, Tzu-Chi Chu, Ying-Ya Hsu, Ting-Shan Chan, Yi-Tsu Chan, Jye-Shane Yang, Ching-Wen Chiu, Hao Ming Chen\*, "In Situ Identification of Photo- and Moisture-Dependent Phase Evolution of Perovskite Solar Cell" *ACS Energy Lett.* **2017**, 2, 342-348.
8. Sung-Fu Hung, Fang-Xing Xiao, Ying-Ya Hsu, Nian-Tzu Suen, Hong-Bin Yang, Hao Ming Chen\*, Bin Liu\*, "Iridium Oxide-Assisted Plasmon-Induced Hot Carriers: Improvement on Kinetics and Thermodynamics of Hot Carriers" *Adv. Energy Mater.* **2016**, 6, 1501339. (Cover highlight)
9. Hsin-Yi Wang, Sung-Fu Hung, Han-Yi Chen, Ting-Shan Chan, Hao Ming Chen\*, Bin Liu\*, "In Operando Identification of Geometrical-Site-Dependent Water Oxidation Activity of Spinel Co<sub>3</sub>O<sub>4</sub>" *J. Am. Chem. Soc.* **2016**, 138, 36-39.p
10. Ching-Wei Tung, Ying-Ya Hsu, Yen-Ping Shen, Yixin Zheng, Ting-Shan Chan, Hwo-Shuenn Sheu, Yuan-Chung Cheng, Hao Ming Chen\*, "Reversible Adapting Layer Produces Robust Single-crystal Electrocatalyst for Oxygen Evolution", *Nature Commun.* **2015**, 6, 8106.



# *Openando* Understanding the Catalytic Centers in Ambient Condition

**Hao Ming Chen\***

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## **ABSTRACT**

Electrochemical reduction of CO<sub>2</sub> is heavily pursued as a potential solution of CO<sub>2</sub> recycling and realizes the high-density renewable energy storage. Among numerous types of catalysts, copper-based catalysts have been shown to perform interesting nature toward hydrocarbon products. Nevertheless, achieving practical CO<sub>2</sub>RR selectivity toward desired products on the state-of-the-art copper-based catalysts is still facing great challenges. The great challenge for promoting the CO<sub>2</sub>RR selectivity may arise to a fact that this electrochemical process is a multiple proton-electron-transfer step and highly surface-sensitive, implying that the surface state of electrocatalyst may be dynamic and unpredictable under practical situations. By employing the comprehensive in-situ techniques we developed during past few years, we have demonstrated the first empirical demonstration to track the dynamic structural reconstruction/transformation in a model bimetallic system, which establishes a good understanding of the correlation between catalyst surface structure and catalytic selectivity. Furthermore, we also realized a very important achievement to develop an operando seconds-resolved X-ray absorption spectroscopy to uncover the chemical state evolution of working catalysts. It's well-known that a chemical reaction driven by applied potential is extremely fast, which is difficult to track the electrochemistry with acceptable temporal-resolution. This work is able to offer scientific insights into the roles metal states serve in chemical reaction in electrolyte.

## **Bio**

Hao Ming Chen received his B.Sc. and M.Sc from National Taiwan University in 2002 and 2004, and his Ph.D. in Chemistry from National Taiwan University in 2008, and then he was a postdoctoral fellow at Department of Physics in National Taiwan University and University of California (Berkeley) with Prof. Peidong Yang. He joined the Department of Chemistry at National Taiwan University in the summer of 2013 and was promoted to associate professor in 2018. He is the recipient of numerous awards including Outstanding Research Award (Ministry of Science and Technology, Taiwan), Lectureship Award for Asian and Oceanian Photochemist Sponsored by Eikohsha (The Japanese Photochemistry Association), *JACS* Young Investigators (ACS virtual issue), Young Scholar Innovation Award (the Foundation of the Advancement of Outstanding Scholarship), the Academia Sinica Research Award for Junior Research Investigators, the Dr. Ta-You Wu Memorial Award (the Ministry of Science and Technology), and the Outstanding Young Chemist Award (Chinese Chemical Society Located in Taipei). His current research interests include the developments of *in-situ/Operando* methodology toward the liquid/solid interfacial study, synthesis of metallic nanocrystals and semiconductor nanomaterials for solar energy conversion.

## NAME

Masanori Sakamoto

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Website:

<http://www.scl.kyoto-u.ac.jp/~teranisi/>



## Education:

April 1996 – March 2000: Kyusyu University, Fukuoka (Bachelor majoring in chemistry)

April 2001 – March 2003: Kyusyu University, Fukuoka (Master majoring in chemistry)

April 2003 – July 2005: Osaka University, Osaka (Doctor majoring in applied chemistry)

## Professional Experience:

August 2005 – October 2009: The Institute of Scientific and Industrial Research, Osaka University, Assistant professor

November 2009 – March 2011: Graduate School of Pure and Applied Sciences, University of Tsukuba, Assistant professor

April 2011 – January 2016: Institute for Chemical Research, Kyoto University, Assistant professor

February 2016 –present: Institute for Chemical Research, Kyoto University, Associate professor

## Awards:

Japanese Photochemistry Association Prize for Young Scientist for 2015

## Research Interests:

Photochemistry, Nanocrystal, Ligand functionalized nanocrystal, Nanoparticle suprastructure

## Selected Publications:

(1) Z. Lian, M. Sakamoto, Y. Kobayashi, N. Tamai, J. Ma, T. Sakurai, S. Seki, T. Nakagawa, M. Lai, M. Haruta, H. Kurata, T. Teranishi, *ACS Nano*, **2019**, 137, 8356-8363

(2) T. Kawawaki, M. Sakamoto, T. Nakagawa, and T. Teranishi, *J. Am. Chem. Soc.* **2019**, 141, 8402-8406.

(3) Z. Lian, M. Sakamoto, J. J. M. Vequizo, C. S. K. Ranasinghe, A. Yamakata, T. Nagai, K. Kimoto, Y. Kobayashi, N. Tamai, and T. Teranishi, *J. Am. Chem. Soc.* **2019**, 141, 2446-2450.

(4) M. Sakamoto, T. Kawawaki, M. Kimura, T. Yoshinaga, J. J. M. Vequizo, H. Mitsunaga, C. S. Ranasinghe, A. Yamakata, H. Matsuzaki, A. Furube, and T. Teranishi, *Nat. Commun.* **2019**, 10, 406.

(5) Z. Lian, M. Sakamoto, H. Matsunaga, J. J. M. Vequizo, A. Yamakata, M. Haruta, H. Kurata, and T. Teranishi, *Nat. Commun.* **2018**, 9, 2314.

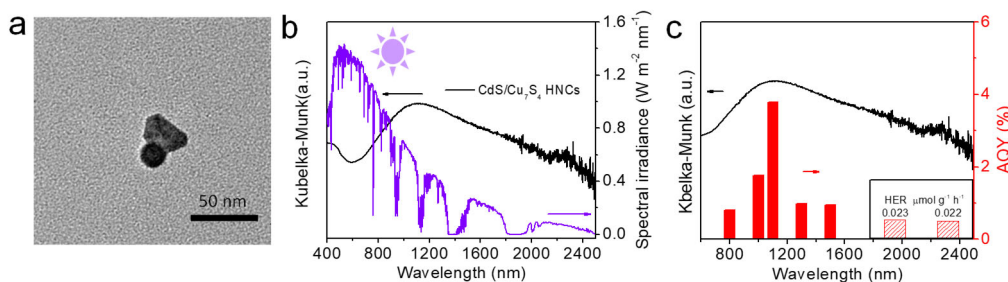
# Plasmonic p–n Junction for Infrared Light to Chemical Energy Conversion

(<sup>1</sup>*Institute for Chemical Research, Kyoto University*) ○Masanori Sakamoto<sup>1</sup>

**Keywords:** Nanocrystal; Localized surface plasmon resonance; Photocatalyst; Hydrogen evolution

The parts of the solar spectrum used for solar energy conversion, including photosynthesis and artificial photosynthesis, are limited to the ultraviolet (UV), visible, and a limited region of near infrared (NIR) light (700–1000 nm). IR light, which accounts for almost half of all solar energy, particularly IR light at wavelengths longer than 1000 nm, including shortwave IR (SWIR: 1400–3000 nm), represents a vast source of untapped energy. Developing artificial IR light-to-energy conversion systems would open up this resource for applications.

Here, we synthesized an IR-responsive plasmonic energy conversion system composed of CdS/plasmonic Cu<sub>7</sub>S<sub>4</sub> heterostructured nanocrystals (HNCs), which achieved highly efficient photocatalytic H<sub>2</sub> evolution (Figure 1a). Cu<sub>7</sub>S<sub>4</sub> NCs, which exhibit localized surface plasmon resonance (LSPR) in IR region, can be applied to harvesting solar energy in the IR region (Figure 1b). The CdS/Cu<sub>7</sub>S<sub>4</sub> HNCs exhibited an exceedingly high apparent quantum yield (AQY) of 3.8% at 1100 nm, which exceeds the current record for photocatalytic H<sub>2</sub> evolution under IR-light irradiation (Figure 1c). Furthermore, we demonstrated that our novel HNCs can convert energy from the solar spectrum up to the longest wavelengths (i.e., 2000–2500 nm). Our spectroscopic investigations using femtosecond-laser flash photolysis revealed that the high catalytic activity of our system was related to efficient hot electron injection and long-lived charge separation (> 273 μs) at the p–n heterojunction of the CdS/Cu<sub>7</sub>S<sub>4</sub> HNCs. The present work should encourage further development of solar fuel generation systems driven by these previously untapped solar energy resources.



**Figure 1.** (a) TEM image of Cu<sub>7</sub>S<sub>4</sub>/CdS HNCs. (b) Solar spectrum (purple line), and diffuse reflectance spectrum of Cu<sub>7</sub>S<sub>4</sub>/CdS HNCs (black line). (c) Apparent quantum yield (AQY) of HER activity of Cu<sub>7</sub>S<sub>4</sub>/CdS HNCs.

1) Z. Lian, M. Sakamoto, J. J. M. Vequizo, C. S. K. Ranasinghe, A. Yamakata, T. Nagai, K. Kimoto, Y. Kobayashi, N. Tamai, and T. Teranishi *J. Am. Chem. Soc.* **2019**, *141*, 2446–2450.

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### ➤ Educational Background

1998 B.Sc., National Cheng-Kung University, Taiwan

2002 M.Sc., National Tsing Hua University (supervisor: Prof. Michael H. Huang)

2009 Doctor of Philosophy, Graduate School of Science, National Tsing-Hua University  
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### ➤ Professional Career

2009 Postdoctoral Research Fellow, Department of Chemistry, National Tsing Hua University, Taiwan

2010 Postdoctoral Research Fellow, Department of Chemistry, Boston College, USA

2012 Postdoctoral Research Fellow, Department of Chemistry, UC Berkeley, USA

2013 Assistant Research Fellow, Institute of Chemistry, Academia Sinica, Taiwan

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### ➤ Research Interests

1) Nanosynthesis

2) Nanocatalysis

### ➤ Awards

2019 Ta-You Wu Memorial Award, Ministry of Science and Technology, Taiwan

2018 Excellent Young Chemist Award, Chinese Chemical Society Located in Taipei, Taiwan

2018 Best Presentation in Division of Catalysis Science and Technology, 256th ACS National Meeting

### ➤ Recent Publications

1. “Au-BINOL Hybrid Nanocatalysts: Insights into the Structure-Based Enhancement of Catalytic and Photocatalytic Performance”, Patlolla, S. R.; Kao, C.-R.; Chen, G.-W.; Huang, Y.-C.; Chuang, Y.-C.; Sneed, B. T.; Chou, W.-C.; Ong, T.-G.\*; Dong, C.-L.\*; Kuo, C.-H.\*, *Ind. Eng. Chem. Res.* **2019**, 58, 5479-5489.
2. “Fabrication of Bimetallic Au-Pd-Au Nanobricks as An Archetype of Robust Nanoplasmonic Sensor”, Ng, K. C.; Lin, F.-C.; Yang, P.-W.; Chuang, Y.-C.; Chang, C.-K.; Yeh, A.-H.; Kuo, C.-S.; Kao, C.-R.; Liu, C.-C.; Jeng, U.-S.; Huang, J.-S.\*; Kuo C.-H.\*, *Chem. Mater.* **2018**, 30, 204-213.
3. “Spiny Rhombic Dodecahedral CuPt Nanoframes with Enhanced Catalytic Performance Synthesized from Cu Nanocube Templates”, Lyu, L.-M.; Kao, Y.-C.; Cullen, D. A.; Sneed, B. T.; Chuang, Y.-C.; Kuo C.-H.\*, *Chem. Mater.* **2017**, 29, 5681-5692.
4. “Turning the Halide Switch in the Synthesis of Au-Pd Alloy and Core-Shell Nanoicosahedra with Terraced Shells: Performance in Electrochemical and Plasmon-Enhanced Catalysis”, Hsu, S.-C.; Chuang, Y.-C.; Sneed, B. T.; Cullen, D. A.; Chiu, T.-W.; Kuo C.-H.\*, *Nano Lett.* **2016**, 16, 5514.

# Bridging Energy and Chemistry via Nanoarchitectonic Engineering at Atomic Scale

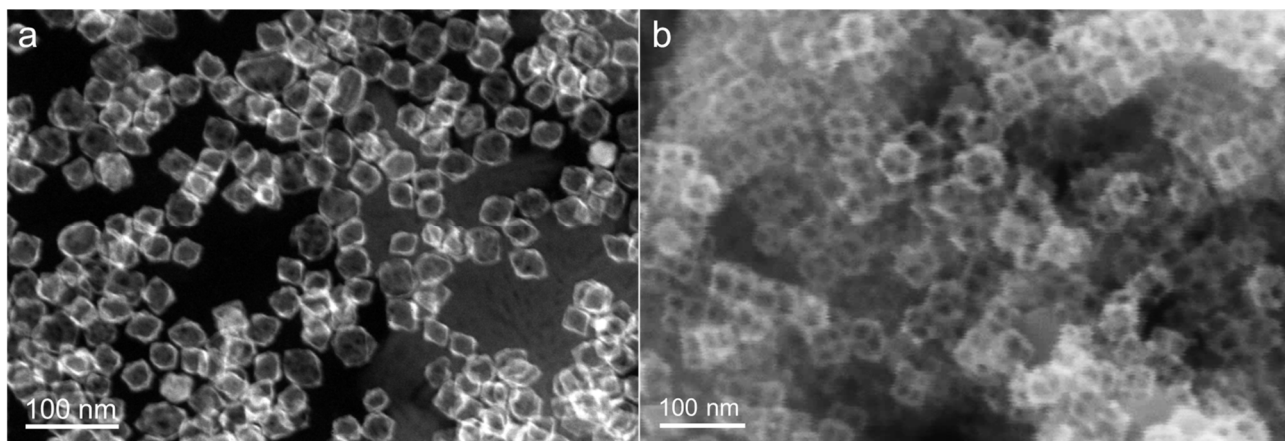
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Building bimetallic surfaces on nanocrystals renders them superior catalysts for energy-conversion reactions by virtue of the electronic effect. In addition, integration of plasmonics and catalysis in bimetallic nanocrystals provides more benefits for the creation of novel catalyst systems. In this talk, selected stories about utilization of CuM bimetallic nanocatalysts for catalytic and photocatalytic energy-conversion reactions will be introduced.[1] All stories start by the synthesis of Cu nanocubes which serve as the templates for further surface engineering. On the Cu nanocubes, we reduce various kinds of noble metallic ions to form CuM surfaces with precise-controlled thickness less than 2 nm (7-8 atomic layers). In typical, template-based syntheses exhibit the coating shells with a consistent morphology to their mother nanotemplates via epitaxial growth. However, our atom-level surface modulation on the surfaces of Cu nanocubes exhibit unconventional morphological transformation after formation of CuM shells. Moreover, treating Cu-CuM core-shell nanocrystals with acid to remove Cu cores triggers further morphological transformation, leading to final nanocages in a specific shape. Those nanocages are eventually applied to electrocatalysis (oxygen reduction reaction, ORR) and photocatalytic synthetic reaction (4-nitrophenol reduction reaction). It turns out that these nanocages possess at least triply high mass activities than that of commercial catalysts. Apart from surface-coated shells, fabrication of CuM nanoframes on the Cu nanocubes via selective deposition of metallic ions will be also introduced. These nanoframes have 3D-open skeletons with highly exposed surface area and, more importantly, surface defects (i.e. adatoms and terraces).[2] The characteristics make CuM nanoframes excellent catalysts in both electro- and photocatalysis. Below shows the CuPt alloy nanocages and nanoframes synthesized from Cu nanocubes.



**Figure 1.** (a) HAADF-STEM image of hollow CuPt octahedral nanocages, and (b) SEM image of CuPt nanoframe in rhombic dodecahedral shape.