

## Overview of the Program

	June 19 (Wednesday)	June 20 (Thursday)	June 21 (Friday)	June 22 (Saturday)	June 23 (Sunday)
8:30-11:30	-	Opening & Plenary Lecture	Session 4	Session 8	Departure
		Coffee & Photos	Coffee Break	Coffee Break	
		Session 1	Session 5	Session 9	
11:30-13:30	-	Lunch	Lunch	Lunch	
13:30-17:40	Registration	Session 2	Session 6	Session 10	
		Coffee & Poster	Coffee & Poster		
		Session 3	Session 7		
17:40-20:30	Registration & Reception Dinner	Dinner	Banquet & Cultural Exchange Activity	Dinner	

- Plenary Lecture (PL): 40 min
- Oral: 20 min (15min + 5 min)
- Venue: Conference Room of Basic Energy Building (1<sup>st</sup> Floor), DICP, Dalian, China
- Poster session: Lobby of Basic Energy Building, June 20-21

## The 3<sup>rd</sup> Seminar of the NSFC-NRF Major International Joint Research Project

---- Mechanistic Approaches on Efficient Photocatalytic Systems for Solar Fuels Production

Date: June 19-23, 2019

Venue: Basic Energy Building, DICP, Dalian, China

<b>June 19 (Wednesday)</b>	
<b>Time</b>	<b>Program</b>
13:00-20:00	Registration (Bayshore Hotel, 星海假日酒店)
18:00-21:00	Reception Dinner (Bayshore Hotel, 星海假日酒店)
<b>June 20 (Thursday)</b>	
<b>Time</b>	<b>Program</b>
	<b>Chair: Prof. Hongxian Han</b>
<b>08:30-09:00</b>	<b>Opening Ceremony: Prof. Can Li</b>
<b>09:00-09:40</b>	<b>PL-1 Jae Sung Lee, UNIST</b> Toward Practical Solar Hydrogen Production by Photoelectrochemical Water Splitting
<b>09:40-10:10</b>	<b>Coffee Break &amp; Taking Photos</b>
<b>Session 1</b>	<b>Chair: Deng Li, Jeong Hun Kim</b>
10:10-10:30	<b>C1-Zijian Zhang, Tsinghua Univ.</b> From Super Molecule to Supramolecular Photocatalyst: A Self-assembled Porphyrin for Water Splitting and Cancer Therapy
10:30-10:50	<b>K1-Min Seok Koo, POSTECH</b> Visible Light-Induced Photoelectrochemical Generation of Reactive Chlorine Species on WO <sub>3</sub> Electrode with Simultaneous Water Treatment and H <sub>2</sub> Evolution
10:50-11:10	<b>C2 –Yunxuan Zhao, TIPC</b> Ammonia Detection Methods in Photocatalytic and Electrocatalytic Experiments: How to Improve the Reliability of NH <sub>3</sub> Production Rates?
11:10-11:30	<b>K2-Mi Jung, SogangUniv.</b> Effect of rGO on ZnTe/ZnO Nanorods for Photoelectrochemical CO <sub>2</sub> Reduction
<b>11:30-13:30</b>	<b>Lunch</b>
<b>Session 2</b>	<b>Chair: Yunxuan Zhao, Min Hee Lee</b>
13:30-14:10	<b>PL-2 Tierui Zhang, TIPC</b> Nanostructured Layered Double Hydroxide Based Photocatalysts for Efficient Solar Fuels and Value-added Chemicals
14:10-14:30	<b>K3-Edgardo Gabriel Santoro, SogangUniv.</b> Hollow Up-conversion Ag@Y <sub>2</sub> SiO <sub>5</sub> :Pr <sup>3+</sup> Enhanced via SPR for Photochromic Applications.
14:30-14:50	<b>C3-Jijie Wang, DICP</b> A Highly Selective and Stable ZnO-ZrO <sub>2</sub> Solid Solution Catalyst for CO <sub>2</sub> Hydrogenation to Methanol

14:50-15:10	<b>K4-Hyejin Kim, POSTECH</b> Photocatalytic Hydrogen Peroxide Production from Water and Dioxygen only from Organic Polymer
15:10-15:30	<b>C4-Wenjiao Luo, Tsinghua Univ.</b> Three-dimensional Network Structure Assembled by g-C <sub>3</sub> N <sub>4</sub> Nanorods for Improving Visible-light Photocatalytic Performance
15:30-16:00	<b>Coffee Break &amp; Poster Session</b>
<b>Session 3</b>	
<b>Chair: Mi Jung, Yong Liu</b>	
16:00-16:20	<b>C5 –Zhenhua Li, TIPC</b> Co-Based Catalysts Derived from Layered-Double-Hydroxide Nanosheets for the Photothermal Production of Value-added Hydrocarbons
16:20-16:40	<b>C6-Zheng Li, DICP</b> Photogenerated Charge Separation Between Polar and Nonpolar Surfaces of GaN NanorodArrays
16:40-17:00	<b>C7-Jun Yang, Tsinghua Univ.</b> Designed Synthesis of p-Ag <sub>2</sub> S/n-PDI Self-assembly Supramolecular Heterojunction for Enhanced Full-spectrum Photocatalytic Activity
17:00-17:20	<b>K5-Bupmo Kim, POSTECH</b> The Design of Selective Electron Transfer Pathways by Controlling of Tungsten Oxide Defect Engineering
17:20-17:40	<b>C8-Hanjie Zhang, Tsinghua Univ.</b> Poly-perylene Diimide Nanoparticles for Photocatalytic Reductive Dehalogenation
17:40-20:30	<b>Dinner</b>
<b>June 21 (Friday)</b>	
<b>Session 4</b>	
<b>Chair: Hemin Zhang, Zijian Zhang</b>	
08:30-09:10	<b>PL-3 Xu Zong, DICP</b> Charge Transportation Engineering of Organic-Inorganic Hybrid Perovskite Towards Enhanced Solar Fuel Production
09:10-09:30	<b>K6-Amol U. Pawar, SogangUniv.</b> Formation of Formaldehyde and Acetaldehyde with Photoelectrochemical CO <sub>2</sub> Reduction via Effective Composite Cathode Electrode
09:30-09:50	<b>C9-Hefeng Zhang, DICP</b> Decorating Mesoporous Silicon with Amorphous Metal-Phosphorous-derived Nanocatalysts towards Enhanced Photoelectrochemical Water Reduction
09:50-10:10	<b>K7-Jeong Hun Kim, UNIST</b> Intentional Extrinsic Dopant (Ti and Sn) Doped ZnFe <sub>2</sub> O <sub>4</sub> Nanorods Photoanode for Efficient Photoelectrochemical Water Splitting
10:10-10:30	<b>Coffee Break</b>
<b>Session 5</b>	
<b>Chair: Min Seok Koo, Jun Yang</b>	

10:30-10:50	<b>K8-Jin Hyun Kim, UNIST</b> Multiple Light Absorber System for Solar Energy Harvesting and Utilization
10:50-11:10	<b>C10-Deng Li, DICP</b> Crystallographic-Orientation-Dependent Charge Separation of BiVO <sub>4</sub> for Solar Water Oxidation
11:10-11:30	<b>K9-Hemin Zhang, UNIST</b> Ta:Fe <sub>2</sub> O <sub>3</sub> @Fe <sub>2</sub> O <sub>3</sub> Homojunction Nanorods for Photoelectrochemical Water Splitting
11:30-13:30	<b>Lunch</b>
<b>Session 6</b>	
<b>Chair: Hefeng Zhang, Shinbi Lee</b>	
13:30-14:10	<b>PL-4 Young Soo Kang, Sogang Univ.</b> Artificial Photosynthesis with Waste Plastics as Renewable Resources
14:10-14:30	<b>C11-Xianjie Chen, Tsinghua Univ.</b> Three-dimensional Porous g-C <sub>3</sub> N <sub>4</sub> for Highly Efficient Photocatalytic Overall Water Splitting
14:30-14:50	<b>K10-Kwang Young Kim, UNIST</b> Cobalt Ferrite as Efficient Bimetallic Catalyst Precursor for Production of Light Olefins
14:50-15:10	<b>C12-Kunyi Yu, Tsinghua Univ.</b> Heterogeneous Visible Light Catalyzed Aerobic Dehydrogenation of N-Heterocycles
15:10-15:30	<b>K11-Chuhyung Kim, POSTECH</b> Catalytic Oxidation of Aromatic Compounds by Fe <sub>2</sub> O <sub>3</sub> NR/CNF under Dark and Ambient Condition
15:30-16:10	<b>Coffee Break &amp; Poster Session</b>
<b>Session 7</b>	
<b>Chair: Wenjiao Luo, Kwang Young Kim</b>	
16:10-16:50	<b>PL-5 Yongfa Zhu, Tsinghua Univ.</b> Supramolecular Photocatalysts for Pollutant Degradation and Tumor Removal
16:50-17:10	<b>C13-Yong Liu, DICP</b> "Turbocharging" at BTO/Au Ferroelectric Interface
17:10-17:20	<b>K12-Shinbi Lee, POSTECH</b> Robust Assembly of Light Absorber-Catalyst in Nafion Polymer for Photocatalytic CO <sub>2</sub> Reduction
17:20-17: 50	<b>C14-Shan Pang, DICP</b> 2D Simulation of Charge Separation in a Single-Particle Photocatalyst
17:50-20:00	<b>Banquet</b>
20:30-24:00	<b>Cultural Exchange Activity</b>
<b>June 22 (Saturday)</b>	
<b>Session 8</b>	
<b>Chair: Amol U. Pawar, Xuyang Xiong</b>	
09:00-09:40	<b>PL-6 Wonyong Choi, POSTECH</b> Hydrogen Peroxide as a Solar Fuel Produced through Reduction of Dioxygen
09:40-10:00	<b>K13-Minkyung Kim, UNIST</b> Activating MoS <sub>2</sub> Basal Plane with Ni <sub>2</sub> P Nanoparticles for Hydrogen Evolution Reaction in Acidic Media

10:00-10:20	<b>C15-Anum Shahid Malik , DICP</b> Role of Phases and Oxygen Vacancies on Product Selectivity and Overpotential in Water Oxidation on Rutile, Anatase, and Brookite TiO <sub>2</sub>
10:20-10:40	<b>K14- Woo Yeong Noh, UNIST</b> Selective Microwave Annealing Enabled Synthesis of Atomically Dispersed Fe-N/C Catalysts for Efficient Oxygen Reduction Reaction
10:40-11:00	<b>Coffee Break</b>
<b>Session 9</b>	
<b>Chair: Xianjie Chen, Hyejin Kim</b>	
11:00-11:20	<b>K15-Min Hee Lee, UNIST</b> Nanostructured Molybdenum Phosphide/N-Doped Carbon Nanotube-Graphene Composites as Efficient Electrocatalysts for Hydrogen Evolution Reaction
11:20-11:40	<b>C16-Xuyang Xiong, TIPC</b> Selective Photo-reduction of Carbon Dioxide with Zinc-based Layered Double Hydroxides
11:40-12:00	<b>K16-Young Kyeong Kim, UNIST</b> Precipitating Metal Nitrate Deposition of Amorphous Metal Oxyhydroxide Electrodes Containing Ni, Fe and Co for Electrocatalytic Water Oxidation
12:00-14:00	<b>Lunch</b>
<b>Session 10</b>	
<b>Chair:Shan Pang, Woo Yeong Noh</b>	
14:00-14:40	<b>PL-7 Xin Guo, DICP</b> Two-dimensional Perovskite Materials for Improved Stability of Solar Cells
14:40-15:00	<b>C17-Qing Yang, DICP</b> High-performance Non-fullerene Solar Cells With g-C <sub>3</sub> N <sub>4</sub> Doped PEDOT:PSS as Hole Transport Layer
15:00-15:20	<b>C18 - Hong Miao, Tsinghua Univ.</b> Visible-light Photocatalytic Activity of PDI Nanowires Enhanced by Plasmonic Effect of the Gold Nanoparticles
15:20-15:40	<b>K17-Peng Zhang, POSTECH</b> Photocatalytic Bifunctional Nanozyme Mimicking Glucose Oxidase-Peroxidase
15:40-16:00	<b>C19-Yuqiang Sheng, Tsinghua Univ.</b> Enhanced Photodegradation of 3D g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub> Free-separation Photocatalyst via Adsorption/Photocatalysis Synergy
16:00-16:20	<b>C20- Shuai Zhang, TIPC</b> Nanostructured Layered Double Hydroxide Photocatalysts for Efficient N <sub>2</sub> Reduction
16:20-19:00	<b>Dinner</b>
<b>June 23 (Sunday)</b>	
08:00-18:00	Departure

## Poster Presentation

### Lobby of Basic Energy Building

P1	Wang Hong	DICP	Promoting photocatalytic H <sub>2</sub> evolution on organic–inorganic hybrid perovskite nanocrystals by simultaneous dual-charge transportation modulation
P2	Ming Shi	DICP	Crystalline structure evolution of all-inorganic halide perovskites for boosting visible-light-driven photocatalytic hydrogen evolution
P3	Kyoungwoong Kang	UNIST	Enhanced photoelectrochemical performance of metal, non-metal co-doped hematite
P4	Qing'e Huang	DICP	The research on mononuclear catalyst for water oxidation
P5	Wei Nie	DICP	<i>In situ</i> imaging of the electron transfer in electrochemical process at single Au nanoparticle
P6	Dharmesh Parshottambhai Hansora	UNIST	Design and development of multifunctional cell for electrochemical/photoelectrochemical application
P7	Xianwen Zhang	DICP	EPR study of paramagnetic species in SrTiO <sub>3</sub> semiconductor photocatalyst for water splitting
P8	Euncheol Ra	UNIST	Liquid fuel production by CO <sub>2</sub> hydrogenation-Bi-functional catalysts
P9	Mingyao Liu	DICP	Electrochemical behavior of vanadium redox couples on carbon electrode
P10	Eunhyup Kim	UNIST	Direct CO <sub>2</sub> hydrogenation to formic acid using carbon nitride in neutral media
P11	Jiangping Ma	DICP	Highly efficient c-Si based photoanode for photoelectrochemical water oxidation
P12	Jinho Lee	UNIST	Nickel gallium intermetallic compounds derived from layered double hydroxides for electrochemical CO <sub>2</sub> reduction
P13	Wenwen Shi	DICP	Effects of hole-extracting layer on the activity and stability of polymer-based photocathodes toward photoelectrochemical hydrogen production
P14	Yimeng Sun	DICP	Fluorine doping on manganese oxides to achieve enhanced oxygen evolution catalysis
P15	Juhyeong Lee	UNIST	Direct CO <sub>2</sub> hydrogenation to formic acid using carbon nitride in neutral conditions
P16	Changtong Ma	DICP	Surface activation treatment of lower temperature calcined hematite for efficient photoelectrochemical water oxidation

P17	Dandan Tu	DICP	Bandgap engineering of dual acceptor-containing naphthalene
P18	Jeehye Kim	UNIST	Solution based synthesis of copper bismuth oxide and NiO hole transport layer
P19	Ahmed Mahmoud Idris	DICP	Crystal facet engineering of novel Sr <sub>2</sub> CoTaO <sub>6</sub> double perovskite for efficient water oxidation
P20	Xuchao Wang	DICP	Decorating polymer backbone with benzyl alcohol and its dual functions for inverted perovskite solar cells
P21	Love Kumar Dhandole	UNIST	CdIn <sub>2</sub> S <sub>4</sub> /TiO <sub>2</sub> nanorod heterostructured photoanode: an advanced material for photoelectrochemical applications
P22	Jafar Hussain Shah	DICP	Effect of cocatalyst on photocatalytic water oxidation activity of BiFeO <sub>3</sub> : ferroelectric semiconductor photocatalyst
P23	Yue Zhao	DICP	Crystal engineering of bismuth vanadate photocatalysts for efficient water oxidation
P24	Woo Yeong Noh	UNIST	Selective microwave annealing enabled synthesis of atomically dispersed Fe–N/C catalysts for efficient oxygen reduction reaction
P25	Jinuk Lee	UNIST	Synthesis CuW <sub>1-x</sub> Mo <sub>x</sub> O <sub>4</sub> photoanodes for enhanced water splitting performance
P26	Bin Zeng	DICP	Interfacial engineering for modulating photoexcited “hot” carriers in plasmonic photocatalysts
P27	Hyo Eun Kim	UNIST	Photoelectrochemical hydrogen peroxide production via delafossite CuFeO <sub>2</sub> photocathode
P28	Hao Li	DICP	Effect of the interfacial defects on plasmon-induced water oxidation

# Plenary Lecture



## Plenary Lecture 1

### **Toward practical solar hydrogen production by photoelectrochemical water splitting**

Jae Sung Lee

*School of Energy and Chemical Engineering, Ulsan National Institute of Science & Technology (UNIST),  
Ulsan 44919, Korea*

Email: jlee1234@unist.ac.kr

Solar water splitting is a promising approach to store sunlight into renewable, sustainable and green hydrogen energy. There are three representative ways of transforming solar radiation into molecular hydrogen- photocatalytic, photoelectrochemical, and photovoltaic–electrolysis routes. Photoelectrochemical (PEC) cells have received immense interest as a promising technology of renewable solar hydrogen production. Among about 400 semiconductor solids of photocatalytic activity for water splitting, we have selected intrinsically stable metal oxide semiconductors made of earth-abundant elements to fabricate photoelectrodes. But because of their poor charge mobility, we employ multiple modifications strategy to minimize recombination of generated photoelectrons and holes, and extract full potential of the materials.<sup>1</sup> The modification strategies include nanostructuring, doping, heterojunction formation, surface passivation, and co-catalyst loading. Then, we construct a stand-alone solar fuel production system by combining with a solar cell in tandem, which provides bias voltage needed for unassisted solar fuel production utilizing only solar energy.<sup>2-4</sup> Due to the rapid materials development in the field during the past two decades, it is the time now to consider practical applications of the technology. The presentation will be concluded by providing a perspective on the scale-up and dissemination of the solar hydrogen production technology.

#### **References**

1. J.H. Kim, D. Hansora, P. Sharma, J.-W. Jang, J.S. Lee, "Toward practical solar hydrogen production – An artificial leaf-to-farm challenge", *Chem. Soc. Rev.* 48, 1908-1971 (2019)
2. J.H. Kim, J.S. Lee, "Elaborately Modified BiVO<sub>4</sub> Photoanodes for Solar Water Splitting" *Adv. Mater.* 1806938 (2019)
3. J.H. Kim, Y. Jo, J.W. Jang, H.J. Kang, Y.H. Lee, D.S. Kim, Y. Jun, and J.S. Lee, *ACS Nano.* 9, 11820–11829 (2015).
4. J. H. Kim, J.-W. Jang, Y.H. Jo, F.F. Abdi, Y.H. Lee, R. van de Krol, J.S. Lee, *Nat. Commun.* 7, 13380 (2016)

## Nanostructured layered double hydroxide based photocatalysts for efficient solar fuels and value-added chemicals

Tierui Zhang

Key Laboratory of Photochemical Conversion and Optoelectronic Materials/Technical Institute of Physics  
and Chemistry, Beijing, 100190, China

Email: tierui@mail.ipc.ac.cn

Layered double hydroxide (LDH) based nanostructured materials have been considered as very promising photocatalysts for chemical fuels and products. Recently, a series of LDH-based nanostructured photocatalysts have been designed and synthesized in my group for efficient CO, CO<sub>2</sub> and N<sub>2</sub> reduction into high value-added heavy hydrocarbons, light olefins and ammonia, respectively, by introducing oxygen vacancies and heterostructured interfaces to activate reactants and intermediate species.<sup>1-8</sup>

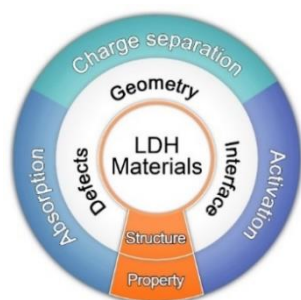


Figure 1. The main research interest in my lab.

### References

1. Yufei Zhao, Tierui Zhang\*, et al., Two-dimensional-related catalytic materials for solar-driven conversion of CO<sub>x</sub> into valuable chemical feedstocks. *Chem. Soc. Rev.*, **2019**, *48*, 1972-2010.
2. Yunxuan Zhao, Tierui Zhang\*, et al., Tuning oxygen vacancies in ultrathin TiO<sub>2</sub> nanosheets to boost photocatalytic nitrogen fixation up to 700 nm. *Adv. Mater.*, **2019**, 180642.
3. Zhenhua Li, Tierui Zhang\*, et al., Co-based catalysts derived from layered double hydroxide nanosheets for the photothermal production of light olefins. *Adv. Mater.*, **2018**, *30*, 1800527.
4. Guangbo Chen, Tierui Zhang\*, et al., Alumina supported CoFe alloy catalysts derived from layered double hydroxide nanosheets for efficient photothermal CO<sub>2</sub> hydrogenation to hydrocarbons. *Adv. Mater.*, **2018**, *30*, 1704663.
5. Yufei Zhao, Xiao-Dong Wen\*, Ding Ma\*, Tierui Zhang\*, et al., Reductive transformation of layered-double-hydroxide nanosheets to Fe-based heterostructures for efficient visible-light photocatalytic hydrogenation of CO. *Adv. Mater.*, **2018**, *30*, 1803127.
6. Yufei Zhao, Tierui Zhang\*, et al., Layered double hydroxide nanosheets as efficient visible-light-driven photocatalysts for dinitrogen fixation, *Adv. Mater.*, 2017, *29*, 1703828.
7. Yufei Zhao, Tierui Zhang\*, et al., Oxide-modified nickel visible-light photocatalyst for hydrocarbon production, *Angew. Chem. Int. Ed.*, **2016**, *55*, 4215-4219.
8. Yufei Zhao, Tierui Zhang\*, et al., Defect-rich ultrathin ZnAl-layered double hydroxide nanosheets for efficient photoreduction of CO<sub>2</sub> to CO with water, *Adv. Mater.*, **2015**, *27*, 7824-7831.

## Plenary Lecture 3

# Charge transportation engineering of Organic-inorganic hybrid perovskites towards enhanced solar fuel production

Xu Zong

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
Zhongshan Road 457, Dalian, 116023, China.

Email: xzong@dicp.ac.cn

Organic-inorganic hybrid perovskites have been extensively investigated for solar-to-electricity transformation due to their excellent optoelectronic properties. However, these materials have been rarely pursued as photocatalysts or photoelectrode for solar-to-fuel conversion. Herein, we presented our recent progress of using Organic-inorganic hybrid perovskites like methylammonium lead iodide (MAPbI<sub>3</sub>) methylammonium lead iodide and methylammonium lead bromide (MAPbBr<sub>3</sub>) for solar fuel production. In photocatalytic system, Pt/TiO<sub>2</sub> nanoparticles were hybridized with MAPbI<sub>3</sub>. The charge transportation efficiency for MAPbI<sub>3</sub> nanoparticles was drastically enhanced and the rate of photocatalytic hydrogen evolution from HI splitting was increased by *ca.* 89 times compared with Pt/MAPbI<sub>3</sub> (Fig.1 left).<sup>1</sup> As for MAPbBr<sub>3</sub>, the simultaneous introduction of Pt/Ta<sub>2</sub>O<sub>5</sub> and PEDOT as the electron and hole transporting motifs, respectively, increased the efficiency of the photocatalytic HBr splitting reaction by 52 times.<sup>2</sup> In photoelectrochemical system, we presented an effective and scalable strategy for the encapsulation of solar cells, which allows the fabrication of a highly efficient and stable sandwich-like photocathode for PEC water reduction reaction (Fig.1 right).<sup>3</sup> The as-prepared photocathode exhibits stable-of-the-art photoelectrochemical activity and stability in water at pH ranging from 0 to 14 and even sea water. These works demonstrate the great potential of using perovskite materials towards efficient and stable solar fuel production through charge transportation engineering.

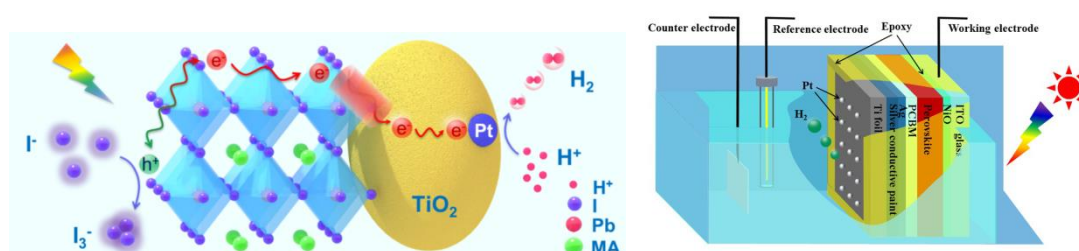


Figure 1. Photocatalytic (left) or photoelectrochemical (right) hydrogen evolution reaction on MAPbI<sub>3</sub>-based photocatalyst or photocathode.

## References

1. Wang X M, Wang H, Zhang H F, Yu W, Wang X L, Zhao Y, Zong X\*, Li C\*. *ACS Energy Lett.*, 2018, 3: 1159–1164.
2. Wang H, Wang X M, Chen R T, Zhang H F, Wang X L, Wang J H, Zhang J, Mu L C, Wu K F, Fan F T, Zong X\*, Li C\*. *ACS Energy Lett.*, 2019, 4: 40-47.
3. Zhang H F, Yang Z, Yu W, Wang H, Ma W G, Zong X\*, Li C\*, *Adv. Energy. Mater.* 2018: 1800795.

## Plenary Lecture 4

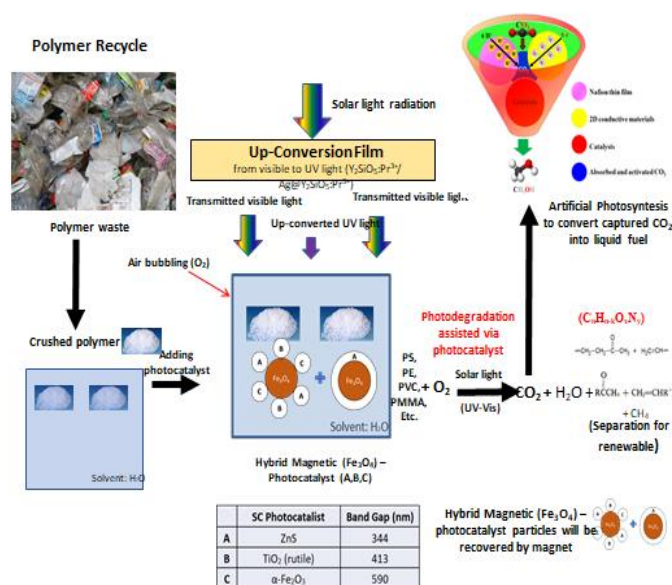
### Artificial photosynthesis with waste plastics as renewable resources

Amol Pawar, Young Soo Kang\*

*Korea Center for Artificial Photosynthesis (KCAP), Seoul 04107, Republic of Korea*

Email: yskang@sogang.ac.kr

The combined technology of artificial photosynthesis with innovative technology for the treatment of waste plastics will be introduced based on the thermodynamics and kinetic aspect. The final ideal products of waste plastics are water and CO<sub>2</sub>. The produced CO<sub>2</sub> could be converted into solar fuels via artificial photosynthesis. So this process makes the ideal process for the waste plastics being used as renewable resources of solar fuels. The point of waste plastic treatment is the up-conversion of solar light to enhance UV light emission and fast photodegradation of micro-particles of waste plastics with hybrid composite photocatalyst/magnetic particles by dispersing into mixed solution of water and organic solvent to have phase transfer photodegradation reaction. The detailed mechanism and insight of the thermodynamics and kinetics will be logically explained.



## References

1. Synthesis and Characterization of Nanometer-Size Fe<sub>3</sub>O<sub>4</sub> and γ-Fe<sub>2</sub>O<sub>3</sub> Particles, Chang Woo Kim, Young Soo Kang\*, Subhash Risbut, John F. Rabolt, *Chem. Mater.* 1996, 89, 2209-2211.
2. Up-converting hollow hybrid composite phosor of Ag@Y<sub>2</sub>SiO<sub>5</sub>:Pr<sup>3+</sup> particles, Santoro Edgardo Gabriel, Young Soo Kang\* (manuscript in preparation)

**Supramolecular photocatalyst  
for pollutant degradation and tumor removal**

Yongfa Zhu

*Department of Chemistry, Tsinghua University, Beijing, China*

Tel: 86-15810290988; Email: zhuyf@tsinghua.edu.cn

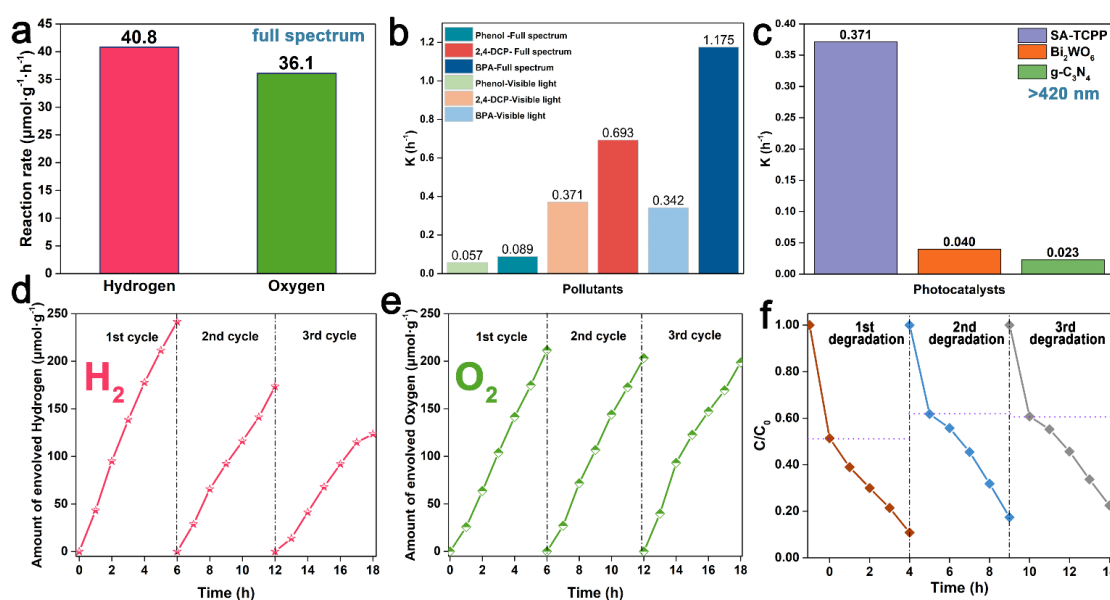
A new class of organic supramolecular photocatalysts with full visible spectrum response has been successfully developed. The texture structure, crystal structure, photoelectric physicochemical properties, organic electron energy band structure, photocatalytic oxidation and anticancer properties can be adjusted via molecular structure and stacking structure. The degradation ability, water splitting ability and anticancer came from the HOMO and LUMO level. The photocatalytic activity came from molecular dipole, ordered stacking and nanostructure.

Self-assembled PDINH supramolecular is an effective visible-light photocatalyst for the photodegradation of pollutants and even split water for oxygen evolution. Compared with monomeric PDINH, self-assembled PDINH supramolecular have band-like electronic energy level structure similar to inorganic semiconductor due to orbital overlaps between PDINH-molecular units. Strong  $\pi$ - $\pi$  stacking between PDINH molecules enables effective long-range electrons delocalization and accordingly promotes photo-generated charge migration and separation, leading to its remarkable photocatalytic activity.

Supramolecular organic nanofibers, self-assembled by a carboxy-substituent PDI molecule via H-type  $\pi$ - $\pi$  stacking and hydrogen bonding, can act as an effective photocatalyst for both organic pollutants degradation and water oxidation under full visible light. The high activity came from the molecular dipole and the nanocrystallization. Higher  $\pi$ - $\pi$  supramolecular packing leads to a smaller bandgap, a deeper valence band position, enhanced light absorption and photo-oxidation capability. The inter-electronic field raised from ordered dipole can effectively promote the migration and separation of photo-generated carriers. H/J-type aggregated PDI supramolecular nanostructures were constructed via length of linear carboxy-substituent side-chains. H-aggregates have higher  $\pi$ -electron conjugation and show more semiconductor characteristics, which results in higher carrier separation and migration efficiency. Whereas, J-aggregates exhibit more molecular properties due to low  $\pi$ -electron conjugation caused by head-to-tail stacking mode. H-aggregated PDI mainly forms superoxide radicals ( $\cdot\text{O}^{2-}$ ) and holes ( $\text{h}^+$ ) through electron-transfer (ET). In contrast, J-aggregated PDI mainly generates singlet oxygen species ( $^1\text{O}_2$ ) via energy-transfer (EnT). Benefit from the stronger oxidization ability of  $\cdot\text{O}^{2-}$  and  $\text{h}^+$ , H-aggregated PDI shows higher photocatalytic activity for degradation and oxygen evolution under visible light. Whereas, J-aggregated PDI exhibits good photocatalytic anti-cancer activity owing to short length of nanofiber.

The full spectrum responsive supramolecular photocatalyst, SA-TCCP has been synthesized via an easy-conducted  $\pi$ - $\pi$  stacking. The SA-TCCP can powerfully split water to hydrogen and oxygen at 40.8 and 36.1  $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  without co-catalyst. The organic pollutants can be efficiently mineralized by the SA-TCCP under visible light irradiation. The degradation performances of SA-TCCP were over 10 times better than the inorganic photocatalysts. The single crystalline structure of  $\pi$ - $\pi$  stacking promoted the transportation and separation of photogenerated carriers. Supramolecular photocatalyst SA-TCCP of bio-safe amount, targeted injection into the solid tumor inside, completely kill the tumor within 10 min under the deep penetration of red light (600-700 nm) irradiation. Photogenerated holes work as the most significant radical in the photocatalytic therapy process, which is abundant on the surface of photocatalyst in cytoplasm. The solid tumors was completely removed via photocatalysts injection and red-light irradiation.

Figure 1. Photocatalytic water splitting and degradation of pollutants. (a) Photocatalytic water splitting



reaction rate of SA-TCCP under full spectrum; (b) Apparent rate constants  $k$  of degradation reactions for different pollutants under visible light and full spectrum; (c) Comparison of apparent rate constants  $k$  of different photocatalysts for 5.00 ppm 2,4-DCP degradation; (d) Cyclic reactions of hydrogen evolution with trolamine as hole scavenger; (e) Cyclic reactions of oxygen evolution with  $\text{AgNO}_3$  as electrons scavenger; (f) Cyclic degradations of 5.00 ppm 2,4-DCP.

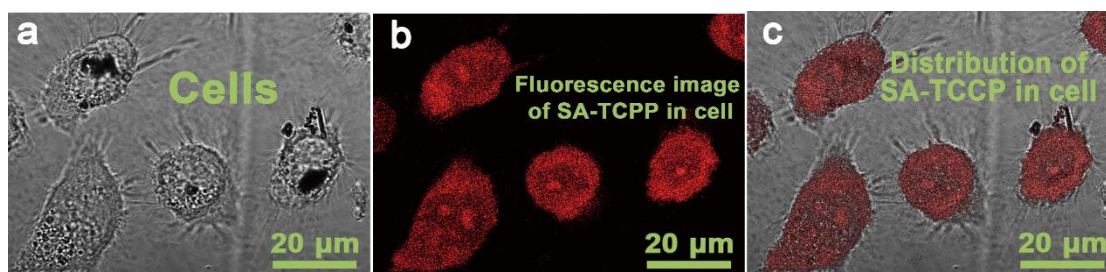
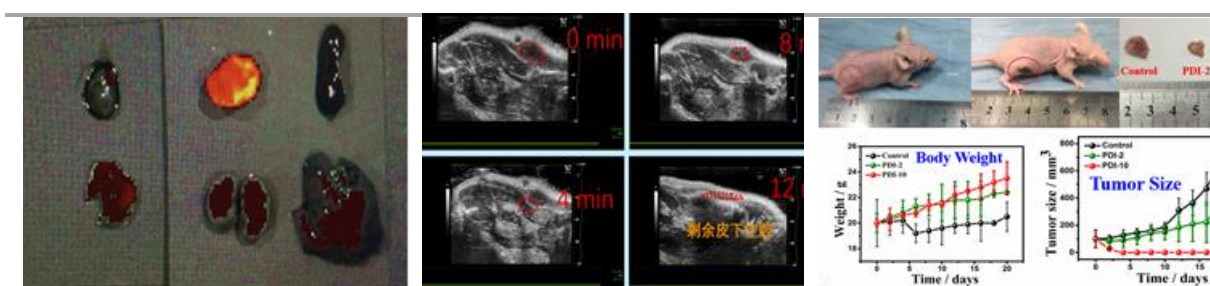


Figure 2. The distribution of SA-TCCP in cancer cells. (a) Bright-field image and (b) Fluorescence image of HeLa cells incubated with SA-TCCP, (c) overlap of (a) and (b).





SA-TCPP self-targeted into tumor Rapid removal of tumor vis Tumor removal on mice by  
 tumor photocatalysis about 12 min photocatalysis

Figure 3. The performances for anti-tumor SA-TCPP supermolecular photocatalysts under visible light of 650 nm

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## Plenary Lecture 6

### **Hydrogen peroxide as a solar fuel produced through reduction of dioxygen**

Wonyong Choi

*Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea.*

Email: wchoi@postech.edu

Photocatalytic and photoelectrochemical conversion of water, carbon dioxide, oxygen to useful chemicals and fuels is a promising solar conversion technology since it needs semiconductor materials and light only to carry out the catalytic reactions. The photocatalytic production of  $\text{H}_2\text{O}_2$  through dioxygen reduction has been receiving great attentions recently since it is an eco-friendly oxidant and fuel that generates water and dioxygen only as the reaction products. However, the low photoconversion efficiency hinders its practical application and expensive noble metals are usually needed as cocatalytic material. Here we report some successful examples of photocatalytic and photoelectrocatalytic systems which efficiently increase the production of  $\text{H}_2\text{O}_2$  through the selective two-electron transfer to dioxygen. Reduced graphene oxide/titania composites (rGO/ $\text{TiO}_2$ ), graphene oxide nanodisks (GONDS) attached to CdS-silica nanocapsules (SNCs) (GOND/CdS-SNC), graphitic carbon nitride photocatalysts modified with multi-component doping were prepared, characterized, and tested for their photoactivities of  $\text{H}_2\text{O}_2$  production. In particular, carbon nitride based photocatalysts are proposed as an ideal photocatalyst for the photosynthesis of  $\text{H}_2\text{O}_2$ . A photoelectrochemical cell in which  $\text{H}_2\text{O}_2$  is produced on both photoanode and cathode was also investigated and introduced. The present photocatalytic and photoelectrochemical systems consisting of earth-abundant elements only under visible light irradiation should make the solar production of  $\text{H}_2\text{O}_2$  more viable.



## **Two-dimensional perovskite materials for improved stability of solar cells**

Xin Guo

*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences;*

*Dalian National Laboratory for Clean Energy, Dalian 116023, P. R. China*

Email: guoxin@dicp.ac.cn

Perovskite solar cells (PSCs) based on traditional three-dimensional (3D) perovskites have achieved power conversion efficiencies (PCE) over 23%, but their low stability upon exposure to humidity, heat and light hinders their further progresses. To surmount this issue, besides efforts from perspectives of interface engineering and encapsulation, seeking alternatives to 3D perovskites is more crucial to intrinsically improve the stability of photoactive materials. Two-dimensional (2D) layered perovskites have emerged as potential alternates to 3D analogues to solve the stability issue of PSCs. However, van der Waals gaps in reported Ruddlesden–Popper (RP) phase 2D perovskites with monoammonium cations provide weak interactions between layers, potentially destabilizing the layered perovskite structure and thus the device.

In this presentation, we eradicate such gaps by incorporating diammonium cations into MAPbI<sub>3</sub>, developing a series of Dion-Jacobson (DJ) phase 2D perovskites which afford a cell efficiency of 13.3% with ultrahigh device stability. Unencapsulated devices retain over 95% efficiency upon exposure to various harsh stresses including ambient air (40-70% relative humidity (RH)) for 4000 hr, damp heat (85 °C and 85% RH) for 168 hr, and continuous light illumination for 3000 hr. The improved device stability over the RP counterpart is attributed to alternating hydrogen bonding interactions between diammonium cations and inorganic slabs, strengthening the 2D layered perovskite structure.

# Oral

Oral 1(China)

## From super molecule to supramolecular photocatalyst: a self-assembled porphyrin for water splitting and cancer therapy

Zijian Zhang, Yongfa Zhu\*

Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China.

Email: zhangzj15@mails.tsinghua.edu.cn, zhuyf@mail.tsinghua.edu.cn

For human beings nowadays, cancer, environment damage and energy crisis have been serious threats to the sustainable development of mankind. The full spectrum (300-700 nm) responsive porphyrin supramolecular photocatalysts with theoretical solar spectrum efficiency of 44.4% have been successfully constructed. For the first time, hydrogen and oxygen evolution ( $40.8$  and  $36.1 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) can be achieved via porphyrin photocatalyst without cocatalysts. And the strong oxidizing performance also presents an efficient photodegradation activity more 10 times than  $\text{g-C}_3\text{N}_4$  for phenol. The high activity of photocatalytic reduction and oxidation comes from the strong inner-built electric field due to molecular dipoles of electron-trapping groups and nano crystal structure of supramolecular photocatalyst. Besides, the self-targeted function was achieved via the difference in phagocytic nano particle size, which contributed that photocatalysts did not enter normal cells and organs, and can only be enriched in cancer and tumor tissues. The supramolecular photocatalyst swallowed by cancer cells produced strong oxidizing holes under the excitation of red light (600-650 nm), and undergoes an oxidation reaction inside the cells, thereby rapidly and completely killing cancer cells and removing tumor tissues. The universal photocatalytic treatment method has significant effects on various cancer cell lines (Hela, MCF-7, and HepG-2). Solid tumors ( $100 \text{ mm}^3$ ) can be completely eliminated by photocatalysis within 10 min, and the survival rate has been significantly prolonged after treatment.

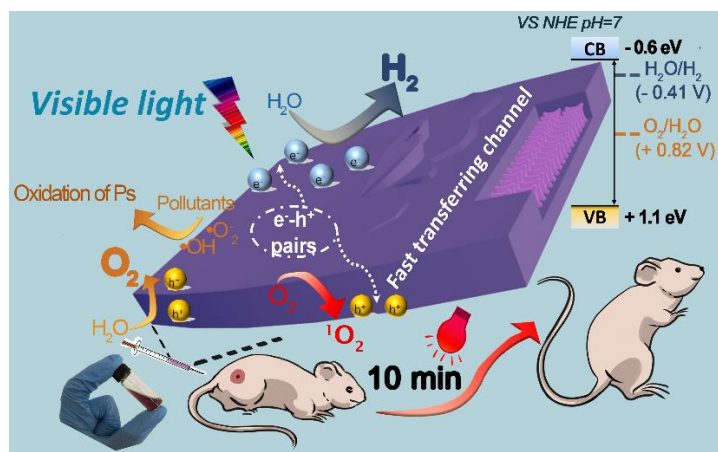


Figure 1. The mechanism of supramolecular SA-TCPP photocatalyst for water splitting and cancer therapy.

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Oral 1 (Korea)

## Visible light-induced photoelectrochemical generation of reactive chlorine species on WO<sub>3</sub> electrode with simultaneous water treatment and H<sub>2</sub> evolution

Min Seok Koo, Seungmok Han and Wonyong Choi\*

Division of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, Korea

Email: wchoi@postech.edu

Reactive chlorine species (RCS) such as HOCl is a strong oxidizing agent and has been widely used for water disinfection.[1] This study investigated a simple photoelectrochemical (PEC) method of RCS production using WO<sub>3</sub> thin film electrode [2] and visible light ( $\lambda > 420$  nm). The PEC production of RCS was optimized with respect to pH, applied potential, and chloride concentration. The degradation of organic substrates coupled with H<sub>2</sub> evolution using WO<sub>3</sub> photoanode was compared among electrochemical (EC), photocatalytic (PC), and PEC conditions (potential bias: +0.5 V vs Ag/AgCl;  $\lambda > 420$  nm). The degradation of 4-chlorophenol, bisphenol A, acetaminophen, carbamazepine, humic acid, fulvic acid, and the inactivation of *E. coli* were remarkably enhanced by RCS generated in PEC condition, whereas the activities of PC and EC conditions were negligible. The activities of the WO<sub>3</sub> photoanode were hindered by diffusion limitation within the nanoparticulate film in the PC condition and the potential bias of +0.5 V (vs Ag/AgCl) did not induce any significant reactions in the EC condition. The H<sub>2</sub> generation efficiency was also the highest at PEC condition compared to PC and EC conditions. In addition, the visible light-irradiated PEC system could prevent the generation of chlorate (ClO<sub>3</sub><sup>-</sup>), and produce H<sub>2</sub> with the simultaneous degradation of organic pollutants regardless of the presence or absence of dioxygen in the solution.

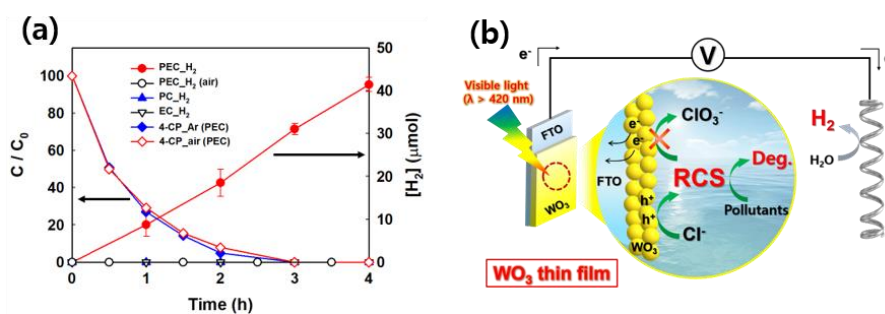


Figure 1. (a) Production of H<sub>2</sub> coupled with 4-CP degradation on WO<sub>3</sub> thin film electrode in PEC, PC, and EC conditions. (b) Illustration of RCS generation for water treatment using WO<sub>3</sub> thin film electrode coupled with molecular hydrogen evolution.

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Oral 2 (China)

## Ammonia detection methods in photocatalytic and electrocatalytic experiments: How to improve the reliability of NH<sub>3</sub> production rates?

Yunxuan Zhao, Tierui Zhang\*

Key Laboratory of Photochemical Conversion and Optoelectronic Materials/Technical Institute of Physics and Chemistry, Beijing, 100190, China

Email: mauling@126.com

The enzyme nitrogenase inspires the development of novel photocatalytic and electrocatalytic systems that can drive nitrogen reduction with water under similar low temperature and low pressure conditions. Whilst photocatalytic and electrocatalytic N<sub>2</sub> fixation are emerging as hot new areas of fundamental and applied research, serious concerns exist regarding the accuracy of current methods used for ammonia detection and quantification. In most studies, the ammonia yields are low and little consideration is given to the effect of interferants on NH<sub>3</sub> quantification. As a result, NH<sub>3</sub> yields reported in many papers may be exaggerated and erroneous. Herein, we systematically explore the advantages and limitations of the various methods commonly used for NH<sub>3</sub> quantification in solution (Nessler's reagent method, indophenol blue method and ion chromatography method), placing particular emphasis on the effect of interferants on each quantification method. On the basis of the data presented, guidelines are suggested for responsible quantification of ammonia in photocatalysis and electrocatalysis.<sup>1-4</sup>

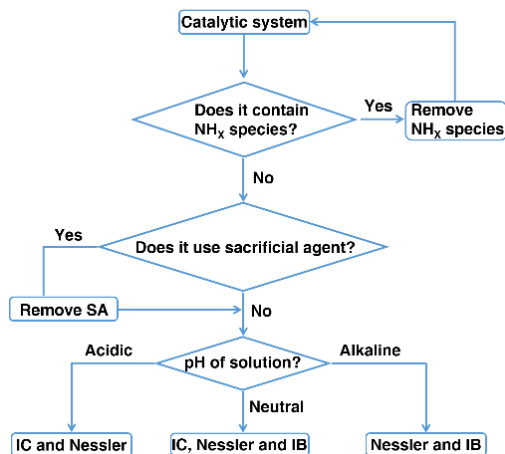


Figure 1. Flow chart showing the criteria that need to be considered when selecting a suitable method for ammonia detection (IC = ion chromatography method, Nessler = Nessler's reagent method and IB = indophenol blue method).

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Oral 2 (Korea)

## Effect of rGO on ZnTe/ZnO nanorods for photoelectrochemical CO<sub>2</sub> reduction

Mi Jung, Soyeon Kim, and Young Soo Kang\*

Korea Center for Artificial Photosynthesis, Department of Chemistry, Sogang University, Seoul 04107,  
Republic of Korea

Email: yskang@sogang.ac.kr

Photoelectrochemical (PEC) CO<sub>2</sub> reduction using a semiconducting photoelectrode suggests an ideal pathway to produce carbon-based fuels from CO<sub>2</sub> conversion using sunlight.<sup>1</sup> Zinc telluride, ZnTe, has attracted attention as a semiconductor photocathode with a direct band gap of 2.26 eV to effectively utilize solar light.<sup>2</sup> Making materials into nanostructures is a way to increase the surface area to volume ratio and the light absorption. Fabrication of graphene-based materials has been extensively studied as a method for improving the CO<sub>2</sub> reduction performance of photocatalysts.<sup>[3]</sup> Here, we reported photocatalytic property of ZnTe/ZnO nanorods and the combined effect of reduced graphene oxides(rGO). ZnTe nanorods were fabricated fluorine doped tin oxide substrate by anion exchange reactions based on ZnO nanorods (see Figure 1). rGO was coated on the ZnO/ZnTe nanorods film. The CO<sub>2</sub> reduction reactions with ZnTe/ZnO and rGO/ZnTe/ZnO photocathodes were performed using BiVO<sub>4</sub> photoanode in PEC system. The as-prepared ZnTe/ZnO shell-core nanorods exhibited p-type conductivity and great photoresponse. We confirm that rGO/ZnTe/ZnO photocathode yielded more major products than those of ZnTe/ZnO photocathode.

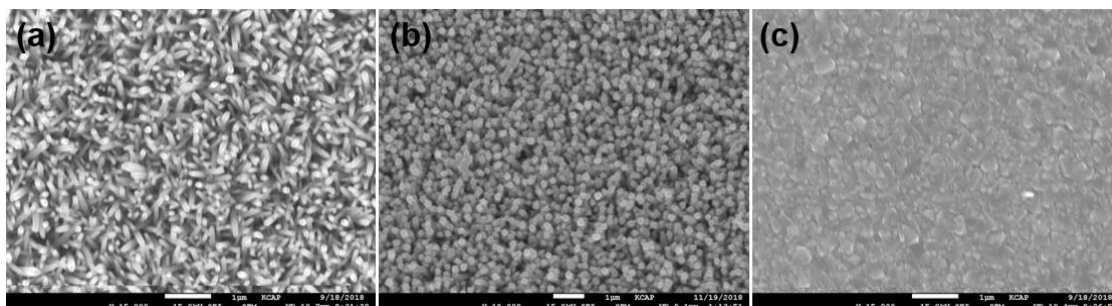


Figure 1. SEM morphology of (a) ZnO nanorods, (b) ZnTe/ZnO nanorods, and (c) rGO/ZnTe/ZnO

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Oral 3 (Korea)

## Hollow up-conversion Ag@Y<sub>2</sub>SiO<sub>5</sub>:Pr<sup>3+</sup> enhanced via SPR for photochromic applications

Edgardo Gabriel Santoro, Young Soo Kang\*

Korea Center for Artificial Photosynthesis and Department of Chemistry, Sogang University, #35, Baekbeom-ro, Mapo-Gu, Seoul, Republic of Korea

Email: yskang@sogang.ac.kr

Y<sub>2</sub>SiO<sub>5</sub>:Pr<sup>3+</sup> (YSO:Pr<sup>3+</sup>) absorbs visible light photons to emit up converted UV light photons via energy transfer up conversion and excited state absorption process.<sup>1</sup> However, the main drawback of YSO:Pr<sup>3+</sup> is a low conversion efficiency. Combining a hollow YSO:Pr<sup>3+</sup> structure with silver nanoparticles (Ag NPs) inside is possible to enhance the conversion efficiency by Surface Plasmon Resonance effect (SPR).<sup>2</sup> We fabricated hollow Ag@YSO:Pr<sup>3+</sup> by covering Ag NPs with carbon shell (hydrothermal carbonization reaction), YO<sub>2</sub>CO<sub>3</sub>:Pr<sup>3+</sup> shell (urea precipitation reaction) and a SiO<sub>2</sub> shell (Stöber reaction). A final calcination at 1000 °C for 3 h formed the final structure via Kirkendall effect.<sup>3</sup> We optimized the hollow structure using different Ag NPs size, hollow diameters and YSO:Pr<sup>3+</sup> shell thickness to maximize the emission of up converted UV light. The best structure had 48.8% of UV light emission enhancement compared with a reference sample of YSO:Pr<sup>3+</sup> without Ag NPs. To analyze the potentiality of using up conversion materials (UCM) and photochromic materials (PCM), we fabricated a layer by layer structure of WO<sub>3</sub> and Ag@YSO:Pr<sup>3+</sup> (See Figure 1) and quantified the coloration rate and kinetic constant.<sup>4</sup>

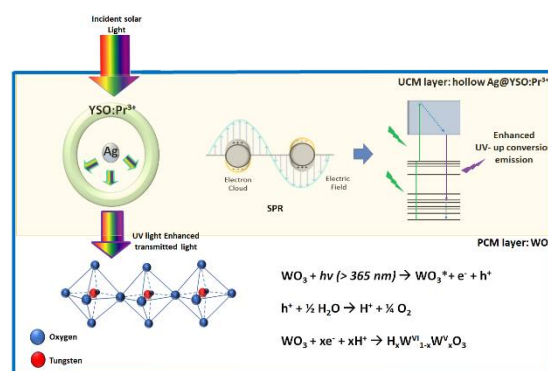


Figure 1. Schematic illustration of the double layer UCM and PCM. Initially Ag@YSO:Pr<sup>3+</sup> converts visible light into UV light and then transmitted to the PCM together with the transmitted UV light from the incident light.

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## A highly selective and stable ZnO-ZrO<sub>2</sub> solid solution catalyst for CO<sub>2</sub> hydrogenation to methanol

Jijie Wang, Chizhou Tang, Zhe Han, Can Li\*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
Dalian 116023, R.P. China

Tel: 86-411-84694447; Email: canli@dicp.ac.cn

A binary metal oxide, ZnO-ZrO<sub>2</sub> solid solution catalyst, which can achieve methanol selectivity up to 86% ~91% with CO<sub>2</sub> single-pass conversion over 10% under the similar industrial conditions. The solid solution structure affords dual active site for H<sub>2</sub> activation by Zn site and CO<sub>2</sub> activation by its neighboring Zr site respectively, and is responsible for the excellent catalytic performance.

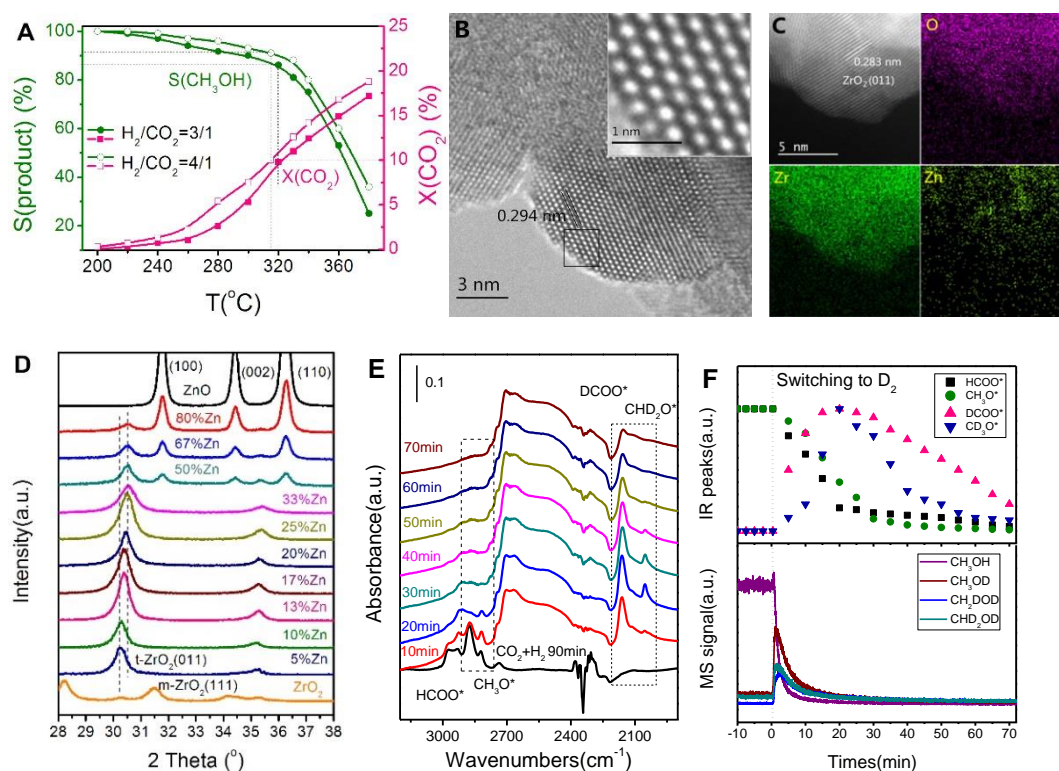


Figure 1. (A) The catalytic performance at the reaction temperatures from 200 to 380 °C with H<sub>2</sub>/CO<sub>2</sub> = 3/1 and 4/1. (B) HRTEM and (C) Aberration-corrected STEM-HAADF images and element distribution of 13%ZnO-ZrO<sub>2</sub>. (D) XRD patterns of ZnO-ZrO<sub>2</sub>. (E) *In-situ* DRIFT spectra of surface species from CO<sub>2</sub> + H<sub>2</sub> and subsequently switched to D<sub>2</sub>. (F) DRIFT-MS of CO<sub>2</sub> + H<sub>2</sub> and subsequently switched to D<sub>2</sub>.

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Oral 4 (Korea)

## Photocatalytic hydrogen peroxide production from water and dioxygen only from organic polymer

Hyejin Kim, Woojung Jeon, Wonyong Choi\*

Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea.

Email: wchoi@postech.edu

Industry synthesis of hydrogen peroxide is an energy and chemical consuming process, restricting sustainable synthesis. The photocatalytic production of  $\text{H}_2\text{O}_2$  can be attractive synthetic method in terms of eco-friendly synthesis only demanding dioxygen and light. However, for photocatalytic  $\text{H}_2\text{O}_2$  production, the alcohol has been consumed for an electron donor and the supply of two protons, which process cost the alcohol usage and extraction of  $\text{H}_2\text{O}_2$  from solution.<sup>1</sup> Here, we apply C, N, O, P-containing organic polymer to  $\text{H}_2\text{O}_2$  production by dioxygen reduction concurrent with water oxidation reaction.<sup>[2]</sup> O or P free-polymers were also synthesized for comparison and energy levels of redox couples are located within the band gap of these CNOP, CNO, CNP, CN polymers. All these polymers were able to produce  $\text{H}_2\text{O}_2$  from water oxidation, however, P-containing polymers prevented the decomposition of  $\text{H}_2\text{O}_2$ . In the case of oxygen contained polymers, long wavelengths can be absorbed. As a result, CNOP shows the best activity for  $\text{H}_2\text{O}_2$  production from dioxygen, water, and light.

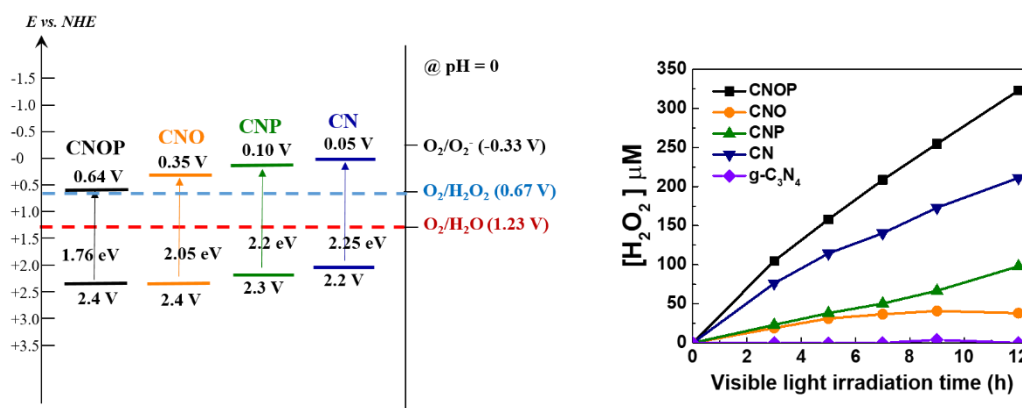


Figure 1. The electronic band structure of CNOP, CNO, CNP and CN (left part). The  $\text{H}_2\text{O}_2$  production from organic polymers (right part).

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Oral 4 (China)

## Three-dimensional network structure assembled by g-C<sub>3</sub>N<sub>4</sub> nanorods for improving visible-light photocatalytic performance

Wenjiao Luo<sup>a</sup>, Xianjie Chen<sup>a</sup>, Zhen Wei<sup>a</sup>, Di Liu<sup>b</sup>, Wenqing Yao<sup>a</sup>, Yongfa Zhu<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China

<sup>b</sup> School of Chemical & Environmental Engineering, China University of Mining & Technology, Beijing, 100083, P. R. China

E-mail : wjluo21@163.com

Bulk g-C<sub>3</sub>N<sub>4</sub> has suffered from its low specific surface area and high recombination of photogenerated electron-hole pairs.[1-2] Herein, three-dimensional network structure g-C<sub>3</sub>N<sub>4</sub> assembled by nanorods (3D g-C<sub>3</sub>N<sub>4</sub> NR) was successfully fabricated via a chemical tailoring route. The as-prepared 3D g-C<sub>3</sub>N<sub>4</sub> NR exhibits larger specific surface areas (6.7 times of bulk g-C<sub>3</sub>N<sub>4</sub>) and faster charge carrier transfer kinetics. Hence, the visible-light photocatalytic activities for degradation of phenol and hydrogen evolution over 3D g-C<sub>3</sub>N<sub>4</sub> NR are evidently enhanced, 4.3 and 5.9 times as high as that of bulk g-C<sub>3</sub>N<sub>4</sub>, respectively. Briefly, this work throws light on structural tuning of carbon nitride polymer photocatalysts for improved solar energy capture and conversion.

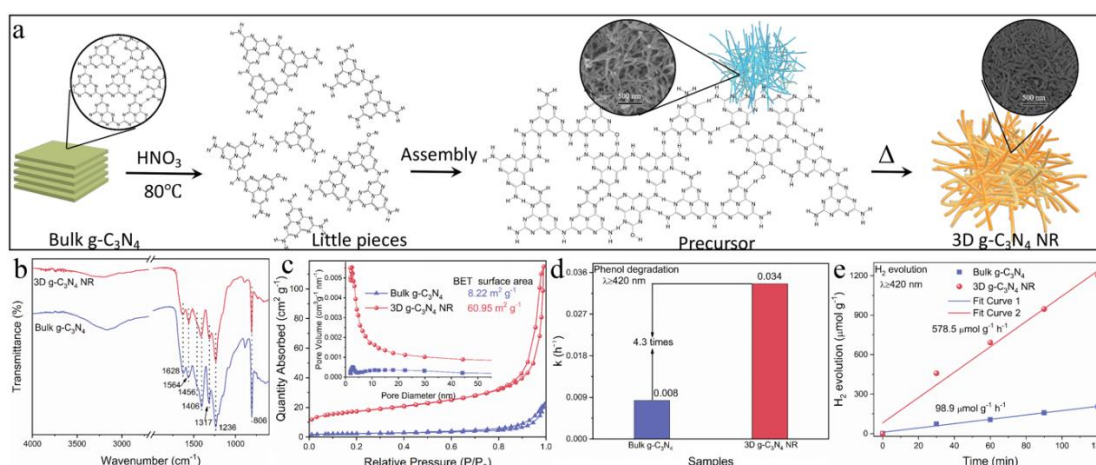


Figure 1. Schematic illustration of the synthetic route for 3D g-C<sub>3</sub>N<sub>4</sub> NR (a), FT-IR spectra (b), nitrogen isothermal adsorption-desorption curves (Pore volume distribution inset) (c), photocatalytic degradation for phenol (d), photocatalytic H<sub>2</sub> evolution (e) of 3D g-C<sub>3</sub>N<sub>4</sub> NR and bulk g-C<sub>3</sub>N<sub>4</sub>.

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Oral 5 (China)

## Co-based catalysts derived from layered-double-hydroxide nanosheets for the photothermal production of value-added hydrocarbons

Zhenhua Li, Tierui Zhang\*

Key Laboratory of Photochemical Conversion and Optoelectronic Materials/Technical Institute of Physics and Chemistry, Beijing, 100190, China

Email: lizhenhua0617@163.com

The Fischer-Tropsch synthesis (FTS) is a pillar of today's coal-to-oil industry based on Co/Fe-based catalysts, especially in China. However, due to the intensive energy consumer and greenhouse gases evolution, the development of green and sustainable FTS processes is much more desirable. Solar-driven Fischer-Tropsch synthesis represents an alternative and potentially low-cost route for the direct production of value-added hydrocarbons from syngas.<sup>[1,2]</sup> Herein, a series of novel Co-based photothermal catalysts are successfully fabricated by H<sub>2</sub> reduction of ZnCoAl-layered double-hydroxide nanosheets.<sup>[3]</sup> Under UV-vis irradiation, the photothermal catalyst prepared at 450 °C demonstrates remarkable CO hydrogenation performance, affording an olefin (C<sub>2-4</sub>) selectivity of 36.0% at a CO conversion of 15.4%. This study demonstrates a novel solar-driven catalyst platform for the production of light olefins via CO hydrogenation.

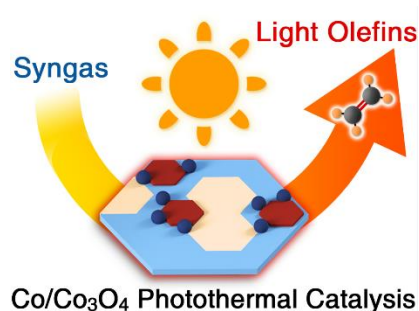


Figure 1. Co-*x* catalysts synthesized by H<sub>2</sub> reduction from ZnCoAl-LDH nanosheets and their photothermal CO hydrogenation under UV-vis irradiation.

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## Photogenerated charge separation between polar and nonpolar surfaces of GaN nanorod arrays

Zheng Li, Rengui Li and Can Li

State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China.

Email: canli@dicp.ac.cn

Artificial photosynthesis has been considered as a promising strategy for solar-to-chemical energy conversion including photocatalytic water splitting for H<sub>2</sub> production and CO<sub>2</sub> reduction for chemicals synthesis. However, most of the artificial photosynthesis systems are limited by low efficiencies primarily due to the poor charge separation property, which is a key process in many optoelectronic applications. Although the spatial separation of photogenerated charges have been demonstrated between different exposed facets of semiconductor crystals (TiO<sub>2</sub>, BiVO<sub>4</sub>, Cu<sub>2</sub>O, and SrTiO<sub>3</sub> etc.), the influence of intrinsic surface properties of semiconductors on charge separation remains unclear and needs to be further understood. Herein, taking gallium nitride (GaN) as a model photocatalyst, we uncovered that the photogenerated electrons and holes can be spatially separated and transferred selectively to the nonpolar and polar surfaces of GaN nanorod arrays. The photogenerated charge separation efficiency of GaN with polar and nonpolar surfaces can exceed 80%, remarkably enhanced from ~8% on the one exposed solely with polar surface. Furthermore, the spatial charge separation enables surface-selective assembling of reduction and oxidation cocatalysts on the nonpolar and polar surfaces via photodeposition method, which remarkably enhances the photocatalytic activity for overall water splitting reaction. This work unravels a spatial charge separation induced by the surface polarity properties of non-centrosymmetric semiconductors, which provides inspirations for the rational design of high efficiency artificial photosynthesis systems for solar energy conversion.

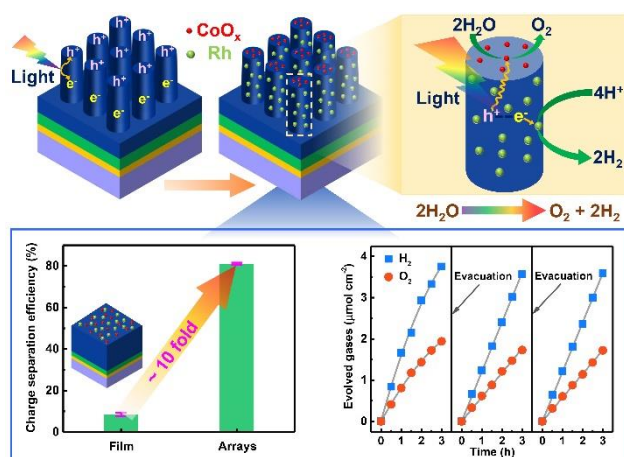


Figure 1. Schematic of charge separation and overall water splitting on GaN nanorod arrays.

Oral 7 (China)

## Designed synthesis of p-Ag<sub>2</sub>S/n-PDI self-assembly supramolecular heterojunction for enhanced full-spectrum photocatalytic activity

Jun Yang, Yongfa Zhu\*

Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China.

Email: zhuyf@tsinghua.edu.cn

It is the ultimate aim to realize the light–chemical energy conversion based on the utilization of the full solar spectrum in photocatalysis. Therefore, it is indisputable that searching for full spectrum-response photocatalysts is crucial. Herein, an efficient full-spectrum responsive p-Ag<sub>2</sub>S/n-PDI (perylene bisimide) heterojunction was successfully constructed. The self-assembly PDI nanostructure was formed via hydrogen bonding and  $\pi$ - $\pi$  stacking. Ag<sub>2</sub>S quantum dots were tightly loaded on the surface of PDI nanofibers via two-step electrostatic process. When the mass ratio of Ag<sub>2</sub>S to PDI was 1:0.6, the p-Ag<sub>2</sub>S/n-PDI heterojunction showed the optimum photocatalytic property. The full-spectrum photocatalytic activity of p-Ag<sub>2</sub>S/n-PDI was respectively 5.13 times and 1.79 times higher than pure PDI for phenol degradation and O<sub>2</sub> evolution. The results showed that Ag<sub>2</sub>S quantum dots promoted the well-organized  $\pi$ - $\pi$  stacking degree of self-assembly PDI, which was helpful for the migration of photo-generated electrons along the quasi-one-dimensional  $\pi$ - $\pi$  stacking of PDI. Simultaneously, Ag<sub>2</sub>S quantum dots enhanced light absorption of Ag<sub>2</sub>S/PDI. More interestingly, p-Ag<sub>2</sub>S/n-PDI heterojunction exhibited excellent photoelectric property, indicating more effective separation of carriers, which was arised from the built-in electric field between Ag<sub>2</sub>S and PDI. Besides, the p-Ag<sub>2</sub>S/n-PDI heterojunction can produce more active species than pure PDI, resulting in much stronger oxidation ability. The work may afford some interesting ideas for designing efficient heterojunction photocatalysts about supramolecular organic nanostructure.

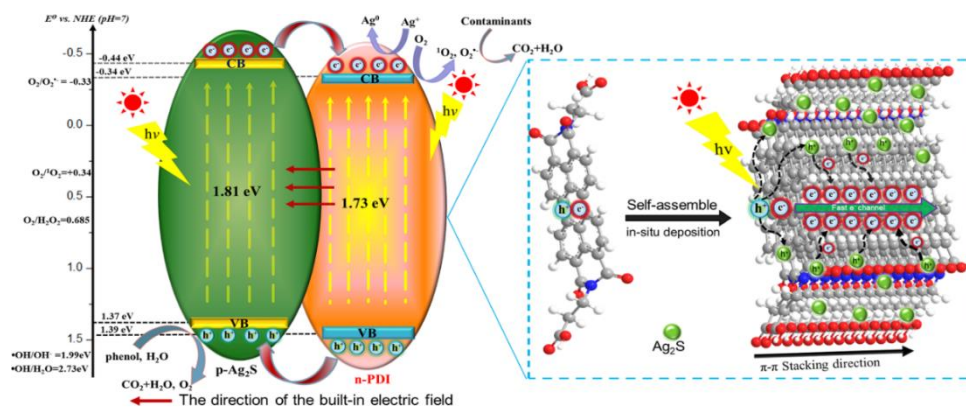


Figure 1. The separation process of photo-generated carriers and the photocatalytic process.

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Oral 5 (Korea)

**The design of selective electron transfer pathways by controlling of tungsten oxide defect engineering**

Bupmo Kim<sup>a</sup>, Wooyul Kim<sup>b\*</sup>, Wonyong Choi<sup>a\*</sup>

<sup>a</sup> *Department of Chemical Engineering/ Division of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, Korea (Email: wchoi@postech.edu)*

<sup>b</sup> *Department of Chemical and Biological Engineering, College of Engineering, Sookmyung Women's University, Seoul, 140-742, Korea*

Email: bupmokim@postech.ac.kr

Tungsten oxide with oxygen deficiency has been extensively studied due to its superior photoactivity. Oxide defect engineering may facilitate the photoactivation of dioxygen activation by changing the electron charge in atomic network, it can help to bind with oxygen species (eg. O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, OH<sup>-</sup>, OOH<sup>-</sup>). The involvement of oxygen vacancies in the photocatalytic process is widely accepted but the nature of the reaction mechanism is complex and not clearly understood because it is difficult to directly monitor oxygen vacancies which are not stable. Herein, we carefully tuned the morphology and the oxygen vacancy of tungsten oxide from W to WO<sub>3</sub> using high temperature anodization method. The non-aqueous anodization process containing potassium could improve thermal and (photo) electrochemical stability of oxygen vacancies in tungsten oxides. Meso-sponge and rod structures with about 10 μm depth were formed by subsequent calcination treatment. The penetration behavior of potassium and oxygen atom has been observed at the surface and bulk atomic network on the tungsten oxides using SIMS depth profiling. All oxygen deficient tungsten oxides species are characterized through W L3-edge XANES/EXAFS, O K-edge XAS, and XPS spectroscopy measurements. We investigated the whole range of (photo) electrochemical properties and applications (e.g., water-oxidation/reduction process, oxygen reduction process) of tungsten oxides. The enhanced photo-oxidation current and oxygen evolution efficiency relative to air-treated tungsten oxides under visible light was attribute to the oxygen defect site and surface morphology control. H<sub>2</sub>O<sub>2</sub> production through the electro-catalytic oxygen reduction was observed in Ar- and H<sub>2</sub>-treated tungsten oxides. In particular, both of OER/ORR selectivity and stability were enhanced by controlling of tungsten oxide defect engineering.

Oral 8 (China)

## **Poly-erylene diimide nanoparticles for photocatalytic reductive dehalogenation**

Hanjie Zhang, Xianjie Chen, Kunyi Yu, Zijian Zhang, Yongfa Zhu\*

*Department of Chemistry, Tsinghua University, Beijing 100084*

Email: zhuyf@mail.tsinghua.edu.cn

The development of visible light catalytic materials for efficient organic conversion process is of great significance. The consecutive photoelectron transfer (ConPET) mechanism of perylene diimide (PDI) overcame the thermodynamic constraints of its own potential and can conduct photocatalytic reduction under certain conditions. In this paper, we prepared polyimide nanoparticles (PINPs) which were insoluble in organic solvents, with introducing 3 different linkers to eventually obtain particles with an average diameter of 100 nm or less, good crystallinity as well. UV-visible (350-740 nm) absorbance showed good light harvesting. PINPs could be subjected to visible-light catalytic reductive dehalogenation reaction (especially dechlorination) under mild conditions without any cocatalyst, avoiding the use of transition metal or super alkali, and can also be used for coupling such as C-B bond construction. The mechanism of ConPET allowed the reaction to be unrestricted by the material's own potential, and the catalyst could be recycled for next cycle. This material enriched the types of two-dimensional polymer photocatalytic materials and was expected to be further applied in other organic photoredox reactions.

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Oral 6 (Korea)

## Formation of formaldehyde and acetaldehyde with photoelectrochemical CO<sub>2</sub> reduction via effective composite cathode electrode

Amol U. Pawar, Young Soo Kang\*

Korea Center for Artificial Photosynthesis and Department of Chemistry, Sogang University, Seoul, 121-742, Republic of Korea

E-mail: yskang@sogang.ac.kr

The most important topic in recent years is an artificial photosynthesis. Because, it shows the best prominent way to produce efficient, clean and renewable energy. Since last several years many photocatalytic materials have been introduced in artificial photosynthesis [1-3]. Generally, artificial photosynthesis splits into two parts; one is water oxidation, and another is CO<sub>2</sub> reduction. Water oxidation can be carried out with light illumination and CO<sub>2</sub> reduction can be done in a dark condition (without light), so photocatalytic material will be used as a photoanode and cathode electrode will be useful for CO<sub>2</sub> capture, activation as well as multi electron process part. In current work, Ca/Fe doped TiO<sub>2</sub> as a photoanode has been prepared by simple co-precipitation method with high temperature calcination. Cathode electrodes have been prepared by various combinations of rGO(reduced graphene oxide)/PVP(poly(4-vinyl)pyridine)/Nafion on Cu foil. The major product of formaldehyde (~475 mM) and acetaldehyde (~480 mM) were observed in case of Cu/rGO and Cu/rGO/PVP/Nafion cathode electrode respectively, with applied bias potential 0.68 V vs RHE. In this work, detail mechanism for CO<sub>2</sub> reduction has been studied with careful attention of CO<sub>2</sub> capture, activation and multi electron shuttling.

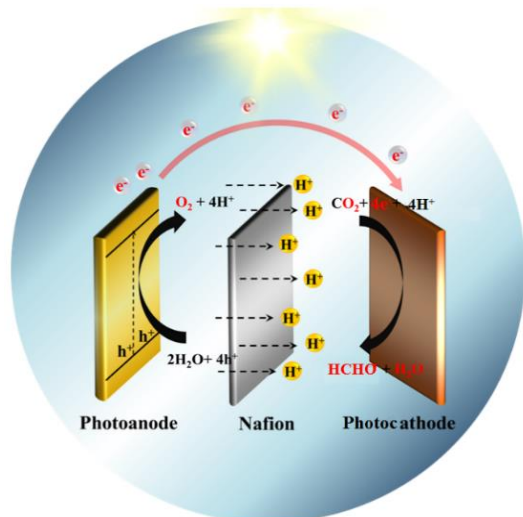


Figure 1. General schematic representation of photoelectrochemical CO<sub>2</sub> reduction to formaldehyde.

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Oral 9 (China)

**Decorating mesoporous silicon with amorphous metal-phosphorous-derived nanocatalysts towards enhanced photoelectrochemical water reduction**

Hefeng Zhang, Xu Zong\* and Can Li\*

*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences;  
Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian, 116023, China*

Email: canli@dicp.ac.cn; xzong@dicp.ac.cn

Developing earth-abundant catalysts as alternatives to noble metals and facile approaches that can integrate catalysts to photoelectrodes for the hydrogen evolution reaction (HER) are critical for the successful application of solar-driven water splitting devices. Herein, we presented a facile and universal synthetic route that can incorporate a series of amorphous metal-phosphorous-derived (denoted as M-P) HER catalysts with p-Si under ambient conditions. An onset potential of +0.3 V vs. reversible hydrogen electrode (RHE) and a photocurrent density of ca. 20 mA cm<sup>-2</sup> at 0 V vs. RHE were obtained under simulated AM 1.5G solar illumination (100 mW cm<sup>-2</sup>), and are among the best values ever reported for Si photocathodes decorated with noble-metal-free catalysts. This excellent performance is ascribed to the drastically reduced charge transfer resistance across the p-Si and electrolyte due to the combination of a high quality semiconductor/catalyst interface and highly active cocatalysts with an amorphous nature. Moreover, the M-Ps/p-Si photocathodes demonstrated excellent stability due to the protection afforded by the M-Ps catalysts that were intimately adhered to p-Si.

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Oral 7 (Korea)

## Intentional extrinsic dopant (Ti and Sn) doped ZnFe<sub>2</sub>O<sub>4</sub> nanorods photoanode for efficient photoelectrochemical water splitting

*Jeong Hun Kim, Ju Hun Kim, Jin Hyun Kim, Young Kyeong Kim, and Jae Sung Lee\**

*Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea*

Email: linuxhoon@unist.ac.kr

Zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>) is a promising candidate for the material for photoanode composing photoelectrochemical overall water splitting cell. However, its poor electronic property deters achieving high performance. To improve electronic property, Ti and Sn were incorporated into Fe sites as dopant, in various synthesis conditions (550 °C , 800 °C of conventional thermal annealing (CTA) and hybrid microwave annealing (HMA)). Doping of those extrinsic metals was conducted by intentional addition of Ti<sup>4+</sup> or Sn<sup>4+</sup> cations in Zn<sup>2+</sup> precursor for fabrication of ZnFe<sub>2</sub>O<sub>4</sub> (ZnO + FeOOH) and successful introduction of dopants to Fe<sup>3+</sup> sites was confirmed by various analytic methods (the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HR-TEM) and depth profiling). The improvement was induced by increment of donor density for metal doped ZnFe<sub>2</sub>O<sub>4</sub> which was confirmed by photoelectrochemical cell analysis (Mott-Schottky plot and photoelectrochemical impedance spectra (PEIS), respectively). Effectiveness of dopants had temperature dependence – low temperature (550 °C) showed better enhancement than the high one (800 °C). Finally, we conducted full modification of ZnFe<sub>2</sub>O<sub>4</sub> by NiFeO<sub>x</sub> OEC loading and achieved ~0.31 mA/cm<sup>2</sup> @ 1.23 V<sub>RHE</sub>.

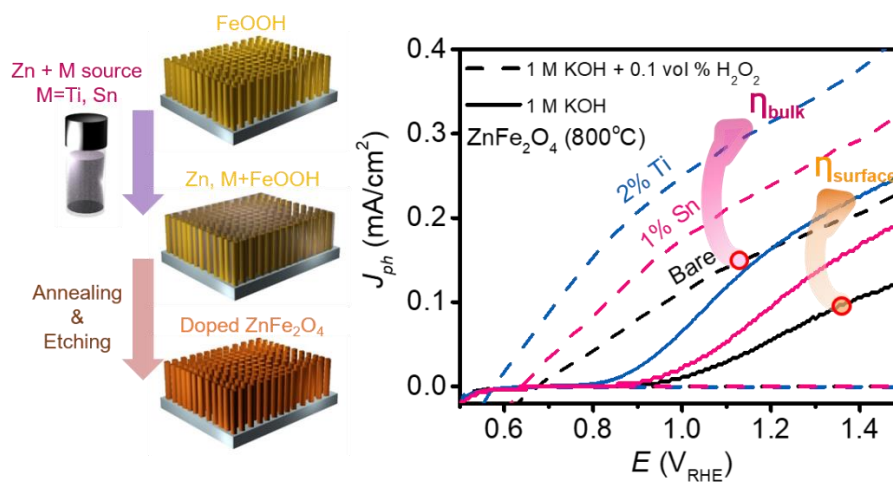


Figure 1. Scheme of the experimental procedure and J-V curve according to dopants effect.

Oral 8 (Korea)

## Multiple light absorber system for solar energy harvesting and utilization

Jin Hyun Kim, Jae Sung Lee\*

Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea

Email: kiji6783@unist.ac.kr

Artificial photosynthesis using photoelectrochemical cell resembles largely to already existing photosynthesis of plant matter – 1) photon utilization to produce exciton, 2) multiple charge transfer and proton (plus reactant) transfer, 3) energy storage via chemical form<sup>1</sup>. The most important aspect of this technology is to increase conversion of solar energy – from total value of ~100 mW/cm<sup>2</sup> by using relatively economically competitive combination of materials. Especially part for photon harvesting, light absorber takes the largest proportion of efficiency and price realizing the whole system – thus it is the most important part to develop. Natural photosynthesis already presented the important aspect of light absorber that usage of two instead one gives significantly increased proton harvesting as well as higher potential, which is called Z scheme system of PSI/PSII for differentiating active site for oxidation and reduction reaction. Herein, we present development of metal oxide based light absorber based photoelectrode as well as usage of multiple light absorbers to construct so called “tandem” PEC cell, to maximize solar to chemical energy production. Stacking two different light absorbers could enable overall water splitting without bias and increased light harvesting – systems described as 1) photoanode– photocathode, 2) photoanode– photovoltaic cell and 3) double photoanode tandem cell could be realized.

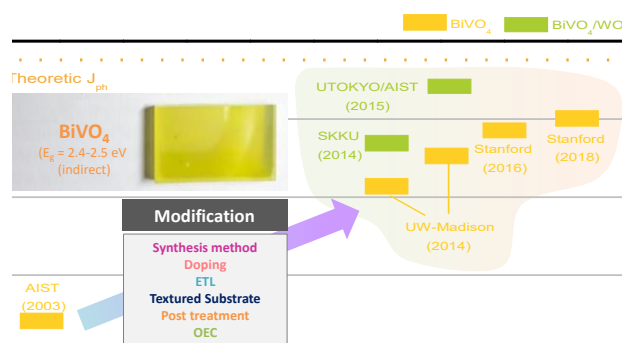


Figure 1. Heterodualphotoanode system - BiVO<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> tandem photoelectrode for PEC cell<sup>2</sup>.

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Oral 10 (China)

## Crystallographic-orientation-dependent charge separation of BiVO<sub>4</sub> for solar water oxidation

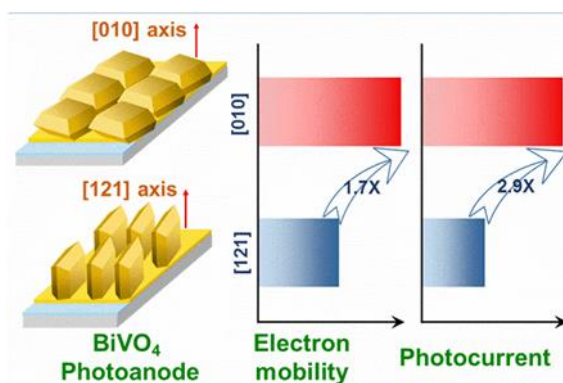
Deng Li,<sup>†‡</sup> Jingying Shi<sup>\*†</sup> and Can Li<sup>\*†</sup>

<sup>†</sup>State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian, 116023, China

<sup>‡</sup>University of Chinese Academy of Sciences, Beijing, 100049, China

Email: jingyingshi@dicp.ac.cn canli@dicp.ac.cn

Charge separation plays a crucial role in determining the solar-to-hydrogen conversion efficiency for photoelectrochemical water splitting. Of the factors that affect charge separation, the anisotropic charge transport property of semiconductors shows great potential in promoting charge separation, but it has received little attention. Herein, we report BiVO<sub>4</sub> photoanodes with predominant [010] and [121] orientations and demonstrate a crystallographic-orientation-dependent charge separation of BiVO<sub>4</sub> for solar water oxidation. We found that a [010]-orientated BiVO<sub>4</sub> photoanode generated a photocurrent 2.9 times that of the [121]-orientated one, owing to the significantly improved charge separation. An in-depth investigation of the surface band bending by open-circuit potential and film conductivity by contacting atomic force microscopy reveals that the higher electron mobility along the [010] direction than that of [121] accounts for the improvement in charge separation. This work offers a fundamental insight into charge separation in anisotropic photoanodes for rational design of efficient photoanodes for solar energy conversion.



Oral 9 (Korea)

## Ta:Fe<sub>2</sub>O<sub>3</sub>@Fe<sub>2</sub>O<sub>3</sub> homojunction nanorods for photoelectrochemical water splitting

Hemin Zhang, Jae Sung Lee\*

Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea

Email: heminzhang18@gmail.com

Photoelectrochemical water splitting (PEC) into H<sub>2</sub> and O<sub>2</sub> is a most promising technology for production of renewable H<sub>2</sub> (called as *hydrogen economy*), which requires high efficiency, chemical robustness, and scalability of the photoelectrodes. Hematite is considered an ideal candidate photoanode material for PEC water splitting because of earth abundance, good stability, an ideal bandgap of 2.1 eV for ample visible light absorption, and a suitable band position to drive water oxidation.<sup>[1]</sup> However, it has critical drawbacks including a short hole diffusion length, poor conductivity, and a large overpotential for water oxidation, which should be overcome to obtain a high solar-to-hydrogen conversion efficiency. Several strategies have been developed to improve the PEC performance of hematite by addressing these shortcomings: making a nanostructure, introducing M<sup>n+</sup> (n>3) dopants, fabricating a type II heterojunction, and loading a co-catalyst.<sup>[2-3]</sup>

Here, we report a homojunction hematite nanorods by second hydrothermal growth and hybrid microwave annealing (HMA) (see Figure 1), which can improve effectively the PEC performance on both photocurrent density and onset potential. As a result, the finally optimized homojunction photoanode (including dopant amount, layer thickness and cocatalyst) improves current density by 66.8% from 1.93 to 3.22 mA cm<sup>-2</sup> at 1.23 V<sub>RHE</sub>. More importantly, the onset potential shifts negatively ~270 mV from 0.82 to 0.55 V<sub>RHE</sub>. As a proof of concept, the study might be extended to other metal oxide semiconductors to boost their PEC water splitting activities.

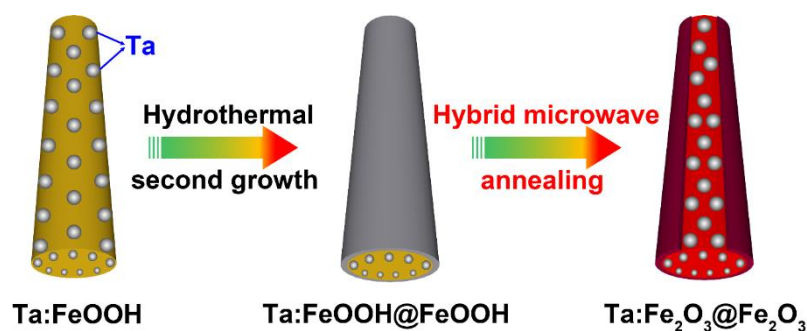


Figure 1. Synthesis of Ta:Fe<sub>2</sub>O<sub>3</sub>@Fe<sub>2</sub>O<sub>3</sub> homojunction nanorods

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## Three-dimensional porous g-C<sub>3</sub>N<sub>4</sub> for highly efficient photocatalytic overall water splitting

Xianjie Chen, Yongfa Zhu\*

*Department of Chemistry, Tsinghua University, Beijing, 100084, PR China*

Email: zhuyf@tsinghua.edu.cn

Photocatalytic overall water splitting into H<sub>2</sub> and O<sub>2</sub> without using sacrificial agents is considered as one of the most ideal ways to convert solar energy into renewable H<sub>2</sub> energy.<sup>1-3</sup> Herein, this work constructs a three-dimensional porous graphitic carbon nitride assembled by highly crystalline and ultrathin nanosheets (3D g-C<sub>3</sub>N<sub>4</sub> NS). 3D g-C<sub>3</sub>N<sub>4</sub> NS could directly split pure water into H<sub>2</sub> and O<sub>2</sub> with high evolution rate up to 101.4 and 49.1 μmol g<sup>-1</sup> h<sup>-1</sup> under visible light, respectively, approximately 11.8 and 5.1 times higher than bulk g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> NS. Besides, it achieves a notable apparent quantum yield of 1.4% at 420 nm, significantly superior to previously reported Pt/g-C<sub>3</sub>N<sub>4</sub>.<sup>4</sup> The efficient activity of 3D g-C<sub>3</sub>N<sub>4</sub> NS is mainly attributed to its 3D interconnected open-framework, assembled by highly crystalline ultrathin nanosheet unit, provides a pathway for faster charge carrier transport. Moreover, benefitting from its 3D structure for preventing agglomeration of nanosheets, 3D g-C<sub>3</sub>N<sub>4</sub> NS is stable for more than 100 h of overall water splitting reaction. Briefly, this work throws light on designing polymer photocatalysts with 3D porous structure assemblies of low-dimensional nanomaterials for improved solar energy capture and conversion.

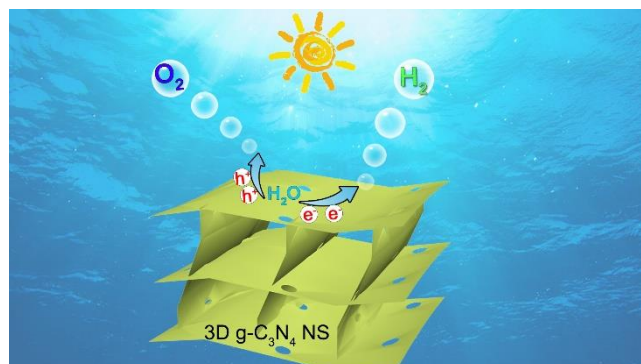


Figure 1. Schematic illustration of the photocatalytic overall water splitting over 3D g-C<sub>3</sub>N<sub>4</sub> NS

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Oral 10 (Korea)

## Cobalt ferrite as efficient bimetallic catalyst precursor for production of light olefins

Kwang Young Kim, Hojeong Lee, Kwangjin An\*, Jae Sung Lee\*

Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea

Email: glorykim@unist.ac.kr

An unrelenting growth of anthropogenic carbon dioxide ( $\text{CO}_2$ ) emission into the atmosphere seriously threatens the world's sustainability with the global warming. recently, carbon capture and utilization (CCU) has started to attract attention worldwide because it can turn waste  $\text{CO}_2$  emissions into value-added products such as chemicals, fuels, plastics, and alternative building materials, while at the same time contributing to climate change mitigation. Among the various technology, catalytic hydrogenation of  $\text{CO}_2$  to light olefins has attracted attention to reduce the amount of  $\text{CO}_2$  and selectively produce light olefins.  $\text{CO}_2$ -FT route is one of the routes of catalytic hydrogenation of  $\text{CO}_2$  which involves two successive reactions, RWGS and FTS. Fe-based catalysts have traditionally been the most widely used as a  $\text{CO}_2$  hydrogenation catalyst, because of their high activity in RWGS and FTS reactions. Adding of a secondary metal (Co, Cu, Mn) or alkali metal to a single iron-based catalyst is crucial to improve  $\text{CO}_2$  conversion and light olefin selectivity. Here we report that the homogeneously distributed cobalt and iron bimetallic catalyst by using  $\text{CoFe}_2\text{O}_4$  nanoparticle precursor. Sodium promoted and unpromoted nanoparticles ( $\text{Fe}_3\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ ) with narrow particle size distribution are synthesized by oleate mediated thermal decomposition method. Synthesized nanoparticle supported on the carbon nanotube and tested at 613K, 10 bar. The catalytic activity of unpromoted  $\text{CoFe}_2\text{O}_4$  shows much high light olefin selectivity compare to other nanoparticles ( $\text{Fe}_3\text{O}_4$ , Co and Co- $\text{Fe}_3\text{O}_4$ ) sample. In the Na-promoted sample, the formation of Hagg iron carbide ( $\text{Fe}_5\text{C}_2$ ) is promoted and the olefin selectivity is further increased. In the case of Na- $\text{CoFe}_2\text{O}_4$ , the synergistic effect of homogeneously distributed Co with the generated Hagg iron carbide ( $\text{Fe}_5\text{C}_2$ ) leads to a high carbon dioxide conversion (~35%) and light olefin selectivity (~40%).

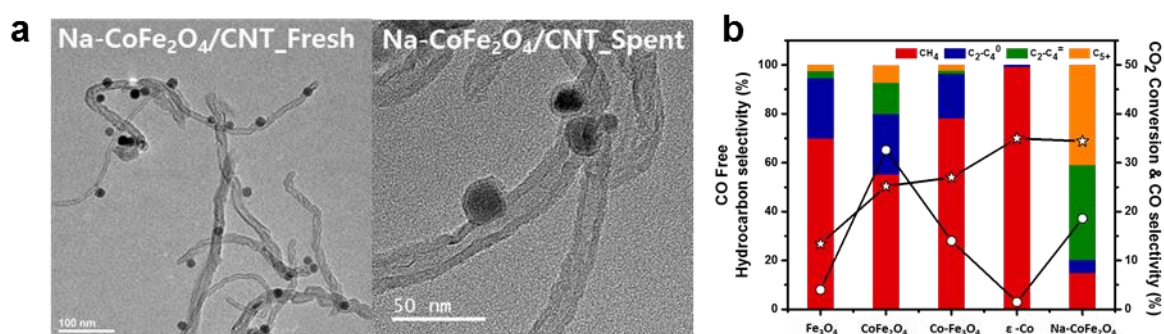


Figure 1. (a) TEM images of fresh, spent catalyst and (b) reaction data of catalytic hydrogenation of  $\text{CO}_2$  to light olefins

Oral 12 (China)

## Heterogeneous visible light catalyzed aerobic dehydrogenation of N-heterocycles

Kun-yi Yu, Han-jie Zhang, Cheng-liang Su\*, Yong-fa Zhu\*  
Department of Chemistry, Tsinghua University, Beijing 100084  
Email: yuky14@mails.tsinghua.edu.cn

Aromatic N-heterocycle motifs are broadly distributed in bioactive molecules, drugs and artificially synthetic materials. Given the importance, the development of efficient strategies for aromatic N-heterocycle motifs is a central research area<sup>1</sup>. Compared with traditional thermal catalysis, photocatalysis is well-accepted for its mild reaction conditions and good substrate compatibility. Homogeneous photocatalytic aerobic dehydrogenation<sup>2</sup> can be conducted at room temperature, with functional group compatibility improved. However, homogeneous catalysts are hardly recyclable and separable, which is unfavorable to industrial application<sup>3</sup>. By using the heterogeneous photocatalyst covalently anchored PDI on SiO<sub>2</sub>, and household LED as the light source, catalytic dehydrogenation of tetrahydroquinoline (THQ) and its derivatives can be achieved in air at RT. Our method features in metal-free, simple procedure, high conversion and selectivity.

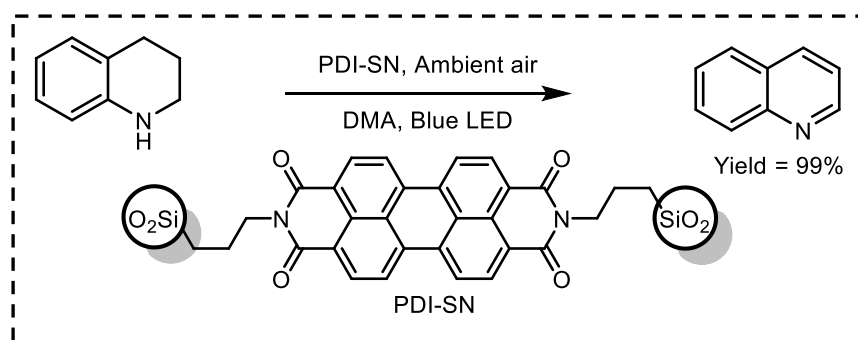


Figure 1. Heterogeneous visible light catalyzed aerobic dehydrogenation of THQs

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Oral 11 (Korea)

## Catalytic oxidation of aromatic compounds by Fe<sub>2</sub>O<sub>3</sub> NR/CNF under dark and ambient condition

Yiseul Park<sup>1,†</sup>, Chuhyung Kim<sup>2,†</sup>, Muliane Ulfi<sup>2</sup>, Soonhyun Kim<sup>3,\*</sup>, Wonyong Choi<sup>2,\*</sup>

<sup>1</sup>Department of Chemical Engineering, Pukyong National University, Busan, 48513, Republic of Korea.

<sup>2</sup>Department of Chemical Engineering & Division of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 37673, Republic of Korea

<sup>3</sup>Smart Textile Convergence Research Group, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, 42988, Republic of Korea.

Email: kimchem@postech.ac.kr, muliane@postech.ac.kr

This study is the first intense of catalytic oxidation of aromatic compounds by Fe<sub>2</sub>O<sub>3</sub> nanorods loaded on carbon nanofiber (CNF) sheets spontaneously under dark and ambient condition without the addition of chemical reagents or external energy. In this study, the addition of 4-chlorophenol (4-CP) immediately initiate catalytic oxidation on Fe<sub>2</sub>O<sub>3</sub>/CNF and further confirmed several intermediates and CO<sub>2</sub> generation after the reaction completed. The multi-activity assessment indicated that the selective catalytic oxidation was initiated by only aromatic compounds, not by aliphatic compounds. Through several characterizations and analyses, the formation of ROS was confirmed by (1) quenching effect by radical quenchers, (2) terephthalic acid hydroxylation as ROS indicator, and (3) EPR technique. Moreover, the spontaneous current generation revealed that the electron transfer from 4-CP to Fe<sub>2</sub>O<sub>3</sub>/CNF for further generation of ROS.

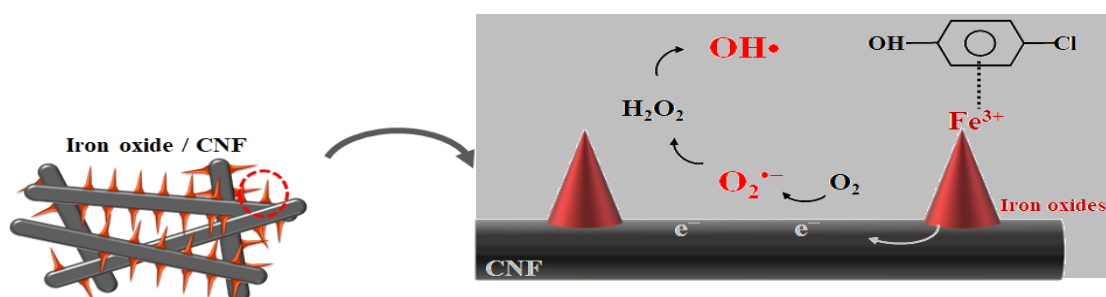


Figure 1. Proposed catalytic oxidation of 4-CP by Fe<sub>2</sub>O<sub>3</sub>/CNF under dark and ambient condition.

Oral 13 (China)

## “Turbocharging” at BTO/Au ferroelectric interface

Yong Liu, Fengtao Fan\*, Can Li\*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian 116023, China.

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, China.

Email: canli@dicp.ac.cn, ftfan@dicp.ac.cn

Insulating ferroelectric materials have switchable internal ferroelectric electric field that can be switched by external bias, which attracted much attentions in photovoltage and photocatalysis. Only can ferroelectricity exit in low charge concentration as ferroelectric spontaneous polarization would be screened by internal mobile charges. The low charge concentration makes the application of ferroelectrics elusive. Here, we directly observe anomalous photogenerated charges concentration at ferroelectric/metal interface under illumination due to the Debye screen of ferroelectric spontaneous polarization and ballistic transport. Differing from photovoltaic I-V measurement, surface potential measurement disentangles the interface charges concentration character from the bulk. Thus, we confirm that the charges concentration is independent of either Schottky barrier or polarized light direction. The photogenerated charges are concentrated within a hemisphere of radius  $L$  around metal, which is thermalization length and dependent on oxygen vacancies concentration. Transparent single layer metallic graphene also works the same as common metal. This provide new approach for photovoltaic device, photoelectrocatalysis and photocatalysis. In summary, the photogenerated charges concentration at the nanoscale provides an exciting new route for obtaining high-efficiency solar energy conversion.

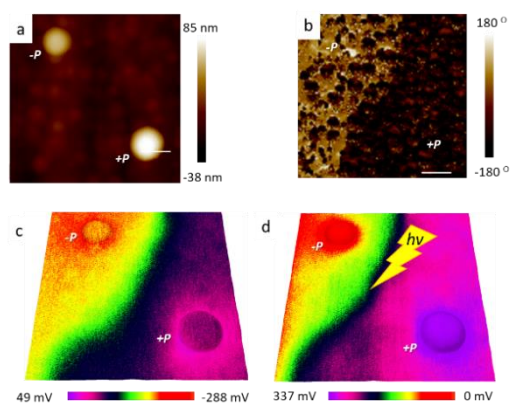


Figure 1. (Optional). AFM, PFM and KPFM of BTO/Au at +P and -P domain. Under illumination, band bending around Au particles are enhanced at either +P or -P.

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Oral 12 (Korea)

**Robust assembly of light absorber-catalyst in nafion polymer  
for photocatalytic CO<sub>2</sub> reduction**

Shinbi Lee<sup>1</sup>, Yoojin Lee<sup>1</sup>, Sujeong Kim<sup>1</sup>, Cheolwoo Park<sup>2</sup>, Gun-hee Moon<sup>1</sup>,  
Wooyul Kim<sup>2\*</sup>, Wonyong Choi<sup>1\*</sup>

<sup>1</sup>*Department of Chemical Engineering/ Division of Environmental Science and Engineering, Pohang  
University of Science and Technology (POSTECH), Pohang, 37673, Korea.*

<sup>2</sup>*Department of Chemical and Biological Engineering, College of Engineering, Sookmyung Women's  
University, Seoul, 140-742, Korea*

Photosynthetic conversion of carbon dioxide produces solar fuels with reducing the atmospheric concentration of the major greenhouse gas. Homogeneous metal-organic complexes have been commonly employed as a CO<sub>2</sub> conversion photocatalyst which suffers from poor durability. To solve such problems, we developed [Ru-(bpy)<sub>3</sub>]<sup>2+</sup> (RuL) and fac-Re(bpy)(CO)<sub>3</sub>Cl (**Re(I)**) assemblies for converting CO<sub>2</sub> to high energy product (CO) with the aid of Nafion film. The Nafion film worked as a platform for anchoring RuL to make a robust heterogenized system. Introducing a Nafion layer on Ru-complex/Re-complex system enhances the photocatalytic conversion efficiency (up to 1.5 times) and the photostability compared with those in **Re(I)**-RuL homogeneous system. The turn over number (TON) of produced CO using Nafion-assisted Ru-complex/Re-complex system was not decreased during repeated experiments and maintained its high catalytic performances even after 10 cycles. As a result, TON of produced CO for 10 hours was 242, which represents a durable and efficient system photocatalytic system that can convert CO<sub>2</sub> into CO. Two roles of the Nafion in this system are proposed as follows: it provides binding sites for cationic light absorber, and it accelerates the charge transfer from light absorber to catalyst. The details including the coupling of the light absorber with the catalyst, and charge transfer kinetics between Ru-(bpy)<sub>3</sub><sup>2+</sup> and fac-Re(bpy)(CO)<sub>3</sub>Cl will be presented.

Oral 14 (China)

## 2D simulation of charge separation in a single-particle photocatalyst

Shan Pang, Fengtao Fan\*, Can Li\*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian 116023, China.,

Email: [ftfan@dicp.ac.cn](mailto:ftfan@dicp.ac.cn), [canli@dicp.ac.cn](mailto:canli@dicp.ac.cn)

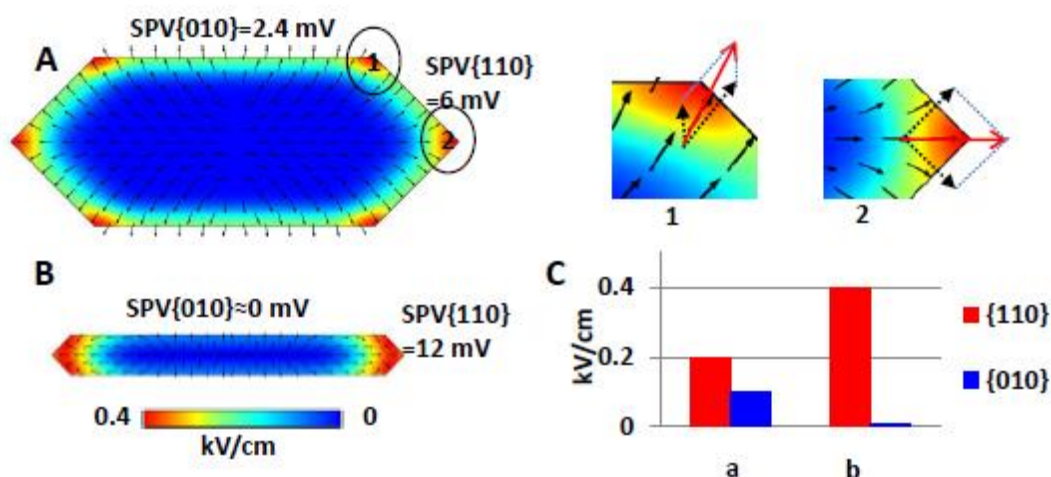


Figure 1. (A and B) The 2D Built-in electric field (BEF) simulations in  $\text{BiVO}_4$  crystals with different morphologies, and (C) The relative intensity of BEF between  $\{110\}$  facets and  $\{010\}$  facets. The surface photovoltage (SPV) intensities were obtained from our previous experimental results, and addition of BEF vectors at the corners in two neighboring facets are shown in the inset 1 and 2.

Design and morphological control of single crystals is one of the challenging issues in chemistry and materials science to optimize the performance of various crystalline catalysts from noble metals to semiconductors. In recent years, the related research in this field attracts much attention in heterogeneous photocatalysis. It is found that engineering the single crystal photocatalyst with certain morphology and preferentially exposed facet would be an useful method to improve the photocatalytic reactivity. Single semiconductor crystals, such as  $\text{TiO}_2$ ,  $\text{BiVO}_4$ ,  $\text{Cu}_2\text{O}$ ,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Ag}_3\text{PO}_4$ , and  $\text{BiOCl}$ , have shown strong facet-dependent photocatalytic performances. We developed a method to give the 2D distribution of built-in electric field (BEF) in photocatalyst particle. The influence of structure morphology, size and doping concentration on the key step of photocatalyst, the charge separation can be clearly visualized.

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Oral 13 (Korea)

## Activating MoS<sub>2</sub> basal plane with Ni<sub>2</sub>P nanoparticles for hydrogen evolution reaction in acidic media

Minkyung Kim, MohsinAli Raza Anjum, Jae Sung Lee\*

Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea

Email: mkk0411@unist.ac.kr

The hydrogen production via electrochemical water splitting is a sustainable way to address both energy and environmental issues of the world. An efficient, durable and cheaper electrocatalyst is desired for effectively catalyzing hydrogen evolution reaction (HER) in real applications. The noble metals (Pt, Ru) based are most efficient catalysts in acidic electrolyte due to their low metal-hydrogen (M-H) bond strength desired for fast HER kinetics. Two dimensional MoS<sub>2</sub> is considered as an alternative Pt that displays a modest hydrogen evolution reaction (HER) activity in acidic media because the active sites are limited to a small number of edge sites with broader basal planes remaining mostly inert. Here we report that the basal planes could be activated by growing Ni<sub>2</sub>P nanoparticles on it. Thus, a Ni<sub>2</sub>P/MoS<sub>2</sub> heterostructure is constructed via in-situ phosphidation of an ingeniously synthesized NiMoS<sub>4</sub> salt to form a widely cross-doped and chemically connected heterostructure. The conductivity and stability of the Ni<sub>2</sub>P/MoS<sub>2</sub> are further enhanced by hybridization with conductive N-doped carbon support. As a result, the Ni<sub>2</sub>P/MoS<sub>2</sub>/N:RGO or N:CNT displays Pt-like HER performance in acidic media, outperforming the incumbent best HER electrocatalyst, Pt/C, in more meaningful high current density region (>200 mA/cm<sup>2</sup>) making them a promising candidate for practical water electrolysis applications. Non-precious metal catalysts showing Pt-like HER performance in acidic media are rare, our hybrid catalyst is a promising candidate for practical hydrogen production via water electrolysis.

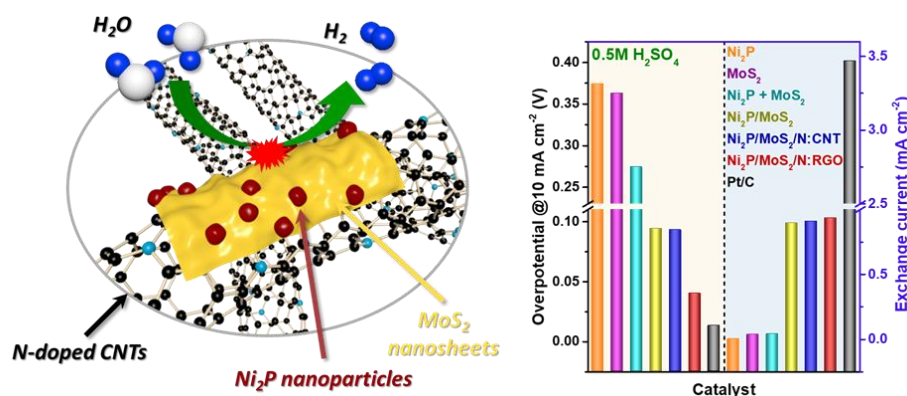


Figure 1. Ni<sub>2</sub>P anchored on MoS<sub>2</sub> supported by N-doped CNT and its HER performance in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte

Oral 15 (China)

## Role of phases and oxygen vacancies on product selectivity and overpotential in water oxidation on rutile, anatase, and brookite TiO<sub>2</sub>

Anum Shahid Malik<sup>a</sup>, Taifeng Liu<sup>b</sup>, Michel Dupuis<sup>a,c</sup>, Rengui Li<sup>a</sup>, and Can Li<sup>a\*</sup>

<sup>a</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian 116023.

<sup>b</sup> National & Local Joint Engineering Research Center for Applied Technology of Hybrid Nanomaterials, Henan University, Kaifeng, 475004.

<sup>c</sup> Department of Chemical and Biological Engineering, University at Buffalo, State University of New York, Buffalo, NY 14260, USA.

The surface reactions of photocatalyzed or photoelectrocatalyzed water oxidation on rutile, anatase, and brookite TiO<sub>2</sub> are quite different. However, the reasons for this observation are not fully understood. In this work, we carried out a comparative density functional theory (DFT) investigation of the mechanisms and energetics of water oxidation on clean rutile TiO<sub>2</sub> (110), anatase TiO<sub>2</sub> (101), and brookite TiO<sub>2</sub> (210) surfaces, as well as on reduced slabs containing oxygen vacancies (Ov's).

Our results show that water oxidation on clean surfaces of three phases proceeds as a two-electron process toward H<sub>2</sub>O<sub>2</sub> formation via surface peroxo O\* intermediates. On all O<sub>v</sub>-reduced surfaces, water oxidation proceeds as a four-electron process toward O<sub>2</sub> evolution via dangling O\* intermediate species. The differences in mechanisms and product evolution can be rationalized from the stabilizing interactions of the 'vacancy' excess electrons with the surface and the adsorbed intermediates. We identified that the clean surfaces transfer a partial electron density charge to the electronegative adsorbates, making their absorption stronger. The vacancy electrons interact further with both the adsorbates and the electron-deficient surfaces to induce increased stabilization of the intermediates. Surface peroxo intermediates are not susceptible to charge transfers, while dangling intermediates are.

The binding energies of the intermediates correlate directly with the electrochemical overpotential through the traditional proton coupled electron transfer analyses, in accord with Sabatier's principle of reactivity. For adsorbates that bind too weakly, the reaction will not occur, and for adsorbates that bind too strongly, desorption and/or reactivity will require too much energy and will be too slow, making the catalyst inefficient. The findings are consistent with experimental observations that rutile has better water oxidation activity than anatase and brookite in both circumstances of clean slabs and reduced slabs.

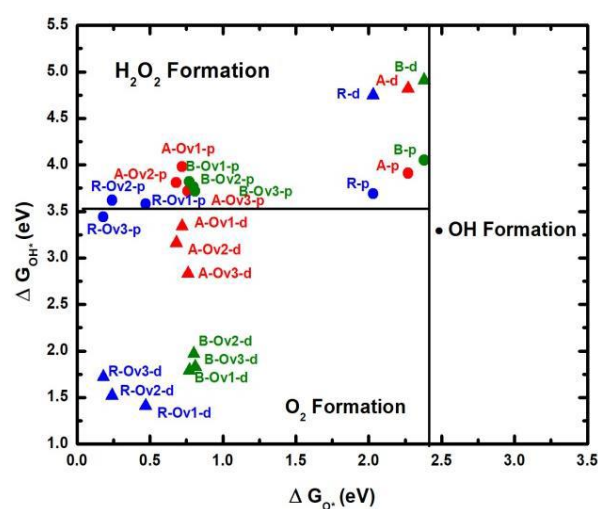


Figure 1. Phase diagram of 1-electron, 2-electron, and 4-electron processes for clean and reduced surfaces of TiO<sub>2</sub> rutile, anatase, and brookite.

Oral 14 (Korea)

## Selective microwave annealing enabled synthesis of atomically dispersed Fe–N/C catalysts for efficient oxygen reduction reaction

Woo Yeong Noh<sup>1</sup>, Kwang Young Kim<sup>1</sup>, Jin Hyun Kim<sup>1</sup>, Sun Hee Choi<sup>2</sup>, Hu Young Jeong<sup>1</sup>, Pankaj Sharma<sup>1</sup>, Ji-Wook Jang<sup>1,\*</sup>, Sang Hoon Joo<sup>1,\*</sup>, Jae Sung Lee<sup>1,\*</sup>

<sup>1</sup>Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

<sup>2</sup>Pohang Accelerator Laboratory (PAL), 80 Jigok-ro 127 beon-gil, Pohang 37673, Republic of Korea

Carbon is one of the most widely used catalyst supports due to its high surface area, good conductivity, relative chemical inertness, and low cost. However, the conventional high-temperature annealing method for carbon supported catalysts causes serious catalyst agglomeration. Herein, we report a simple, ultrafast, and selective microwave annealing method using a carbon support as an excellent microwave absorber for effective single-iron-atomic site catalyst immobilization. This catalyst showed superior oxygen reduction reaction performance, with a half-wave potential of 0.92 V vs. reversible hydrogen electrode and superior durability, compared to thermally annealed and platinum (Pt)/C catalysts in alkaline media. Furthermore, the microwave-annealed catalyst exhibited a power density of 4.63 mW cm<sup>-2</sup> in an aqueous sodium-air battery, which is higher than and comparable to those of thermally annealed catalysts (3.15 mW cm<sup>-2</sup>) and Pt/C catalysts (4.71 mW cm<sup>-2</sup>), respectively.

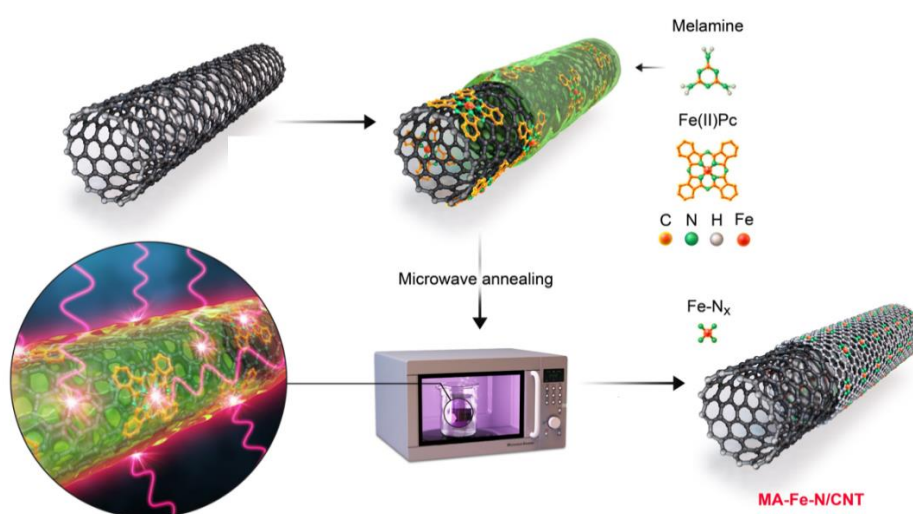


Figure 1. Illustration of the preparation of carbon-hosted, N-coordinated Fe (Fe–N<sub>4</sub>) on a CNT via microwave annealing (MA-Fe-N/CNT catalyst).



Oral 15 (Korea)

## Nanostructured molybdenum phosphide/N-doped carbon nanotube-graphene composites as efficient electrocatalysts for hydrogen evolution reaction

Min Hee Lee,<sup>a</sup> Duck Hyun Youn,<sup>b\*</sup> and Jae Sung Lee<sup>a\*</sup>

<sup>a</sup> School of Energy & Chemical Engineering, Ulsan National University of Science & Technology (UNIST)

<sup>b</sup> Department of Chemical Engineering, Kangwon National University

Email: photon@unist.ac.kr

Uniformly dispersed 10 nm MoP nanoparticles on N-doped carbon nanotube and graphene support (MoP/NCNT-NGR) were synthesized via a simple temperature programmed reduction (TPR) method, and their electrocatalytic performances for hydrogen evolution reaction (HER) were evaluated. The NCNT-NGR support was composed of well intercalated carbon nanotubes (CNT) between graphene (GR) layers, resulting in reduced CNT bundling and graphene re-stacking and hence providing large surface area. The prepared MoP/CNT-GR composite exhibited higher HER activity than control catalysts (MoP/NCNT, MoP/NGR, and bare MoP) with a small benchmark overpotential of 100 mV to drive 10 mA/cm<sup>2</sup> and an improved Tafel slope of 44 mV/dec. It also exhibited excellent stability for 1000 potential cycle and 10 h chronoamperometry tests. Such high HER performance arises from synergies between highly active MoP nanoparticles, large surface area, and highly conductive NCNT-NGR support.

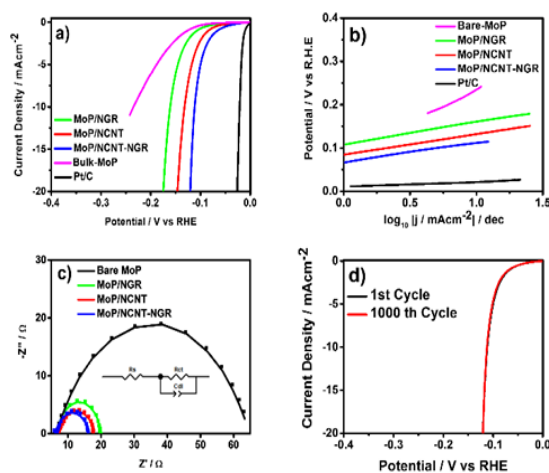


Figure 1. Electrochemical measurements for as-synthesized catalysts: (a) polarization curves, (b) Tafel plot, (c) Nyquist plot (d) MoP/NCNT-NGR polarization curve before and after 1,000 CV stability test cycles.

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## Selective photo-reduction of carbon dioxide with Zinc-based layered double hydroxides

Xuyang Xiong, Tierui Zhang\*

Key Laboratory of Photochemical Conversion and Optoelectronic Materials/Technical Institute of Physics and Chemistry, Beijing 100190, China

Email: Xiong0603@163.com

Photocatalytic reduction of CO<sub>2</sub> to fuels has received extensive research interests for decades as it represents a sustainable low-temperature route for energy storage and conversion.<sup>[1]</sup> Considering the general adsorption model of CO<sub>2</sub> determined its final reduction products, we proposed a Zn-based layered double hydroxide (ZnM-LDH) as an ideal model to investigate the effect of metal cations on the adsorption and selectivity on CO<sub>2</sub> photoreduction.<sup>[2,3]</sup> The ratio of Zn/M was kept as 2, so that the Zn-O-H framework was the fundamental configuration in these ZnM-LDHs. Subsequently, with separately altering M metals as Ti, Fe, Co, Ga, Al, the dominate reduction products for ZnTi, ZnFe/ZnCo, ZnGa/ZnAl were CH<sub>4</sub>, H<sub>2</sub>, CO, respectively (see Figure 1). Since the roles of these metal cations were carefully explored, our work was thus opening new possibilities for developing novel photocatalysts with higher CO<sub>2</sub> selectivities.

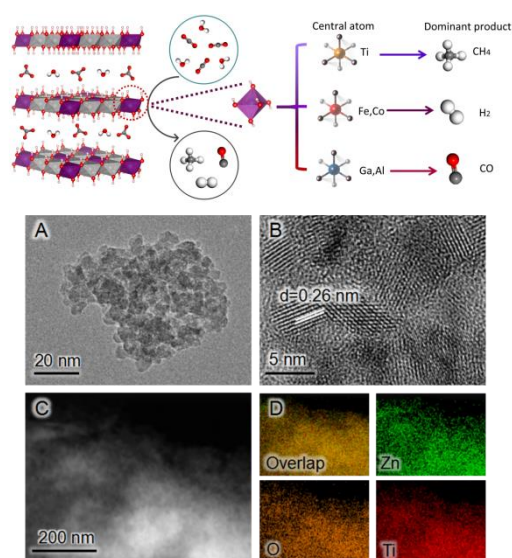


Figure 1. Schematic diagram of CO<sub>2</sub> reduction (upper) and general structure of ZnM-LDHs (A-D).

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Oral 16 (Korea)

## Precipitating metal nitrate deposition of amorphous metal oxyhydroxide electrodes containing Ni, Fe and Co for electrocatalytic water oxidation

Young Kyeong Kim<sup>a†</sup>, Jin Hyun Kim<sup>a†</sup>, Yim Hyun Jo<sup>b</sup> and Jae Sung Lee<sup>a\*</sup>

<sup>a</sup>Ulsan National Institute of Science & Technology (UNIST), Ulsan, 44919 Republic of Korea

<sup>b</sup>Advanced Center for Energy, Korea Institute of Energy Research (KIER),

We report a facile, one-step precipitating metal nitrate deposition (PMND) method to prepare amorphous metal oxyhydroxide films containing Fe, Co, and Ni as efficient electrocatalysts for water oxidation. The unique synthesis technique is versatile allowing easy control of the metal composition over a wide range on various substrates. A series of unary and binary metal oxyhydroxides of 30 compositions are synthesized by PMND on fluorine-doped tin oxide (FTO) substrate as water oxidation electrocatalysts. The activity of the metal oxyhydroxide films is represented by a volcano plot as a function of a single experimental descriptor, *i.e.* the percentage of hydroxide on the surface. The optimum compositions for binary metal oxyhydroxide (NiFe, NiCo and CoFe) are determined on conductive substrates of FTO, nickel foam (NF), nickel mesh (NM) and carbon felt (CF), and the best NiFe (2:8) electrocatalyst on NF exhibits a water oxidation current density of 100 mA/cm<sup>2</sup> with only 280 mV of overvoltage, which outperforms conventional noble metal catalysts like IrO<sub>x</sub> and RuO<sub>x</sub>. Finally, we demonstrate a tandem PV-electrolysis system by using a c-Si PV module with a power conversion efficiency of 13.71 % and an electrochemical cell composed of NiFe (2:8)/NF anode and a bare NF cathode, which records a solar-to-hydrogen conversion efficiency of 9.84 % which represents a conversion efficiency of 71.8 % for our electrolysis system.

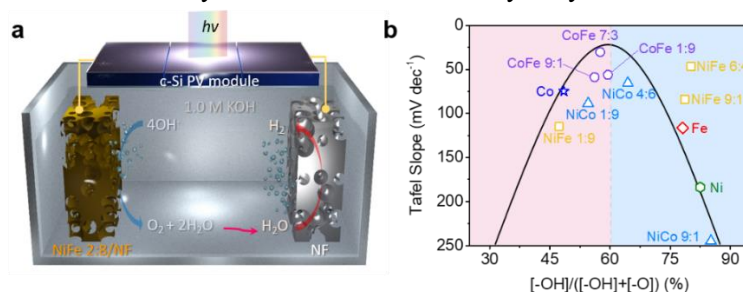


Figure 1. (a) Schematic diagram of the PV-EC system combining c-Si PV module with NiFe (2:8)/NF (anode) and bare NF (cathode) in 1.0 M KOH. (b) Volcano plot suggesting activity trends toward oxygen evolution reaction for single and binary mixed metal oxyhydroxide on FTO.

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Oral 17 (China)

## High-performance non-fullerene solar cells with g-C<sub>3</sub>N<sub>4</sub> doped PEDOT:PSS as hole transport layer

Qing Yang,<sup>a,b</sup> Ping Fu,<sup>a</sup> Shuwen Yu,<sup>a</sup> Wei Yu,<sup>a</sup> Zhaochi Feng,<sup>a</sup> Xin Guo<sup>a,\*</sup> and Can Li<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian 116023, China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China

Email: guoxin@dicp.ac.cn; canli@dicp.ac.cn

PEDOT:PSS is widely used as hole transport layer (HTL) in organic solar cells (OSCs), but suffers from low conductivity because the conductive PEDOT is surrounded by the hydrophilic yet insulating PSS forming a coiled structure in aqueous solution. In order to improve the conductivity of the PEDOT:PSS film, the conductive g-C<sub>3</sub>N<sub>4</sub> herein is added into the PEDOT:PSS to reduce the Coulomb interaction between PEDOT and PSS chains, enabling exposure of more conductive PEDOT on the surface of the PEDOT:PSS coil. The destruction of the PEDOT:PSS coiled structure is realized by the attraction between the negatively charged insulating PSS and the protonated g-C<sub>3</sub>N<sub>4</sub> after being added into the PEDOT:PSS. By employing the g-C<sub>3</sub>N<sub>4</sub> doped PEDOT:PSS film as HTL in OSCs, a higher PCE of 13.16% than that of the traditional PEDOT:PSS-based device is obtained. This work suggests that the g-C<sub>3</sub>N<sub>4</sub> is a suitable dopant to increase the conductivity of the PEDOT:PSS, making the g-C<sub>3</sub>N<sub>4</sub> doped PEDOT:PSS promising as HTL for OSCs.

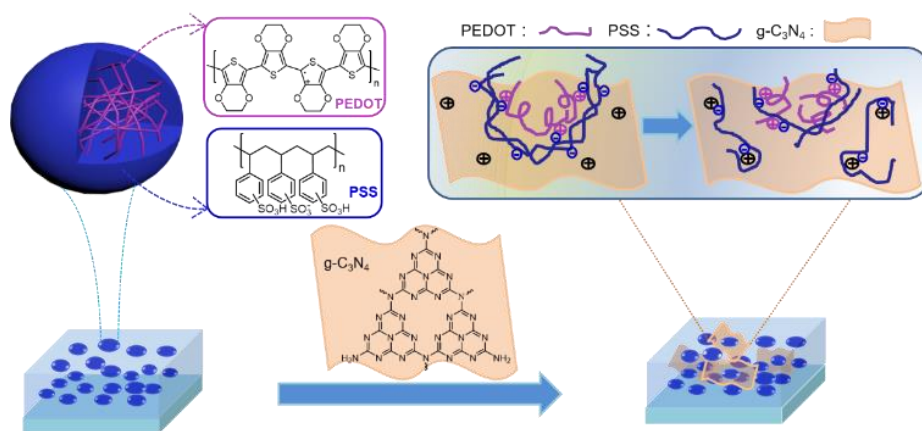


Figure 1. A schematic illustration of the compositional changes in the PEDOT:PSS core-shell structure before and after g-C<sub>3</sub>N<sub>4</sub> doping for improved conductivity.

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Oral 18 (China)

## Visible-light photocatalytic activity of PDI nanowires enhanced by plasmonic effect of the gold nanoparticles

Hong Miao, Yongfa Zhu\*

Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China

E-mail: zhuyf@mail.tsinghua.edu.cn

Perylene diimide (PDI) molecules catalysts had shown much great advantages such as optical properties and chemical electronic tunability, rich elements of resources and structural diversity. These organic materials are considered as a promising route to mitigate water pollution or other environmental problems.<sup>1</sup> Otherwise, surface plasmon resonance (SPR) effect of the gold nanoparticle (AuNPs) could promote the absorption of visible light effectively.<sup>2,3</sup> Herein, SPR-supported visible-light-responsive photocatalyst of PDI/AuNPs were prepared through the electrostatic adsorption. The results show that the PDI/AuNPs composite appeared higher visible light degradation rate ( $k$ ) towards the phenol, which is 1.7 times than the PDI nanowires. The highly photocatalytic activity of the PDI/AuNPs could own to the surface plasmon resonance (SPR) of AuNPs. Specifically, SPR effect of the AuNPs and the RET process between AuNPs and PDI could be beneficial for utilizing the visible light. Meanwhile, the ability of electrons and holes separation are greatly improved by the lower Fermi level of Au, which is favorable for the efficient transfer of the photo-excited electron-hole pairs.<sup>4</sup> Overall, the system of the PDI/AuNPs composite is responsible for the highly efficient photocatalytic degradation of pollutants.

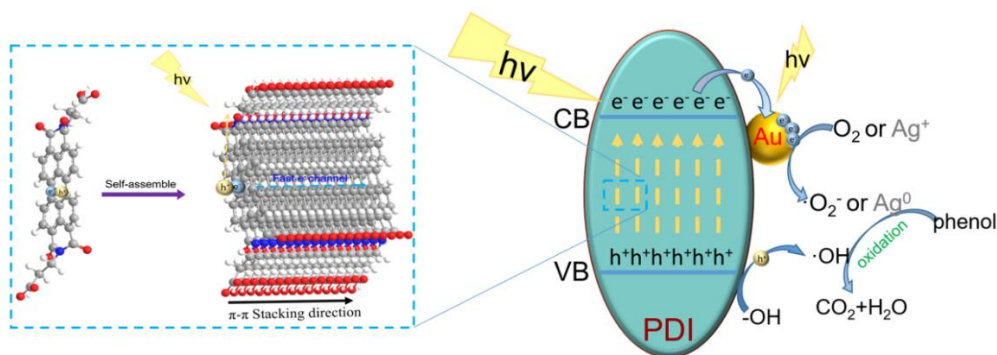


Figure 1. Schematic description of the mechanism for the photocatalytic oxidation of pollutants (e.g. phenol) on PDI/AuNP<sub>s</sub> photocatalyst.

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Oral 17 (Korea)

## Photocatalytic bifunctional nanozyme mimicking glucose oxidase-peroxidase

Peng Zhang, Dong-Pyo Kim, Wonyong Choi\*

Division of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 37673, Republic of Korea

Email: wchoi@postech.edu

Nanomaterials-based biomimetic catalysts with multiple functions are necessary to address challenges in artificial enzymes mimicking physiological processes.<sup>[1]</sup> We prepared a modified carbon nitride ( $C_3N_4$ ) with alkali-incorporation through one-pot thermal polycondensation as a new bifunctional nanozyme.<sup>[2]</sup> The introduced chemical functionalities (i.e., KCl-bridged adjacent layers and hydroxyl group grafting) promote the two-electron reduction of dioxygen via the rapid formation of 1,4-endoperoxide species in the polymeric structure, which was in line with the theoretical simulation. The resultant metal-free photocatalyst (nanozyme) generated hydrogen peroxide ( $H_2O_2$ ) with an apparent quantum yield of 100% (at 420 nm) and a good catalytic stability. The nanozyme of modified  $C_3N_4$  exhibited the bifunctional biomimetic roles (see in the figure below): (1) it plays the role of photoenzyme to mimic GOx that oxidizes glucose with the concurrent production of  $H_2O_2$  under visible light; (2) it mimics HRP that oxidizes the chromogenic substrate (TMB) to induce blue coloration in the dark. The bio-mimicking catalytic process could be facilitated within a few seconds in a continuous flow microfluidic reactor that serves as a smart and miniature device for the real-time colorimetric detection of glucose.

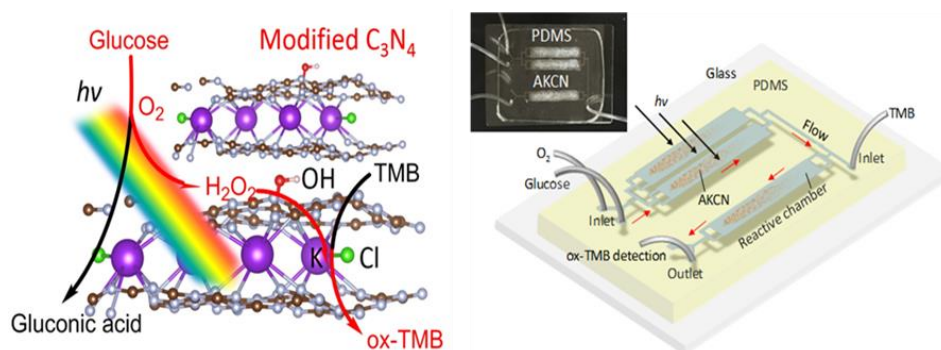


Figure 1. Glucose detection model in cascade reaction through the in-situ  $H_2O_2$  generation from the synthetic bifunctional nanozyme (left). Scheme of the cascade reaction in a microfluidic device with the actual device image inset (right)

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## Enhanced photodegradation of 3D g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> free-separation photocatalyst via adsorption/photocatalysis synergy

Yuqiang Sheng, Yongfa Zhu\*

Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China

Email: zhuyf@mail.tsinghua.edu.cn

The three dimensions (3D) g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> heterojunction photocatalyst has been synthesized and exhibits efficient pollutants degradation performances. The degradation efficiency of methylene blue (MB) and phenol is 4.0 and 4.5 times as high as bulk g-C<sub>3</sub>N<sub>4</sub> in the static system. In the dynamic system, the pollutants can be continuously degraded without separation, and it is very stable for 90 hours with a removal rate of 16.0%. The enhanced activity is mainly attributed to the 3D structure and heterojunction of g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>. The 3D structure can effectively improve the adsorption-enrichment capability and supply multidimensional mass and electron transfer channels. Meanwhile, the heterojunction can promote the separation and migration of the photo-generated carriers. Therefore, the 3D g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> heterojunction photocatalyst with separation free can facilitate the potential application in the treatment of water pollution.

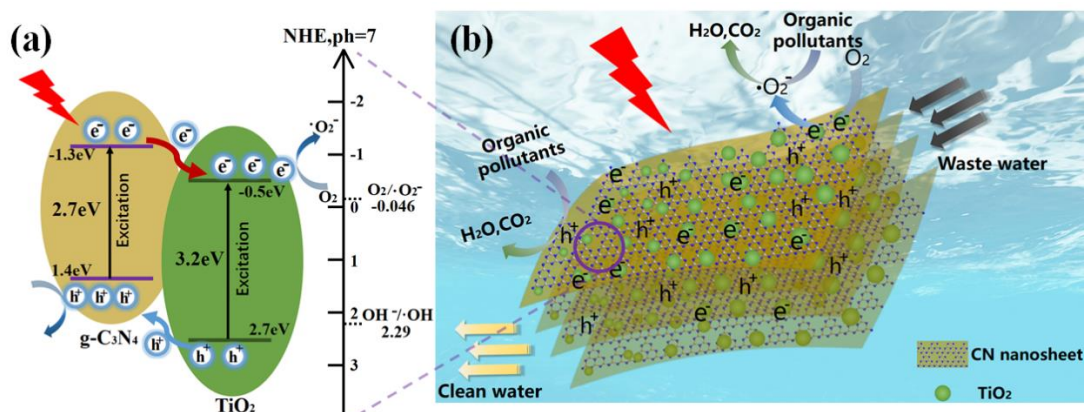


Figure 1. Schematic illustration of photo-induced carrier separation by g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>; (b) Schematic illustration of the possible degradation mechanism.

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Oral 20 (China)

## Nanostructured layered double hydroxide photocatalysts for efficient N<sub>2</sub> reduction

Shuai Zhang, Tierui Zhang\*

Key Laboratory of Photochemical Conversion and Optoelectronic Materials / Technical Institute of  
Physics and Chemistry, Beijing, 100190, China

Email: zhangshuai174@mails.ucas.ac.cn

Ammonia is one of the most essential chemicals because of its functions as building blocks for production of various valued chemicals and a new potential energy carrier. Compared to tradition Haber-Bosch process for ammonia synthesis with massive energy consumption and pollutant emissions, photocatalytic N<sub>2</sub> reduction has attracted considerable attention as a sustainable approach to produce ammonia under mild condition. At present, two dimensional (2D) nanosheets have been extensively applied in photocatalytic ammonia synthesis owing to their special advantages, such as abundant surface defects, large surface area. As one of the promising 2D nanosheets materials, layered double hydroxide (LDH) nanosheets have been strategically designed and synthesized to efficiently convert N<sub>2</sub> into NH<sub>3</sub>. By introducing oxygen vacancies and tuning metal compositions, efficient adsorption and activation of N<sub>2</sub> molecules on the surface of LDH nanosheets can be realized, thereby leading to light-driven ammonia synthesis.<sup>1-2</sup>

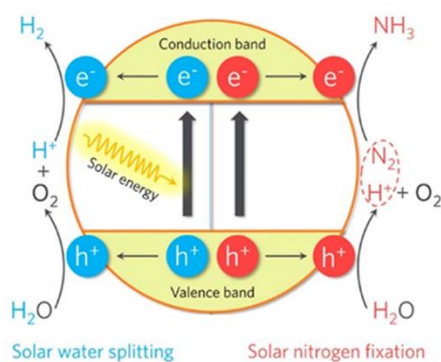


Figure 1. Schematically showing the overall reaction of N<sub>2</sub> reduction to NH<sub>3</sub>.

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2. Shuai Zhang, Yunxuan Zhao, Run Shi, Geoffrey I.N. Waterhouse, Tierui Zhang\*, *Photocatalytic Ammonia Synthesis--Recent Progress and Future* (In preparation).

# Poster Presentation



Poster 1 (China)

## Promoting photocatalytic H<sub>2</sub> evolution on organic–inorganic hybrid perovskite nanocrystals by simultaneous dual-charge transportation modulation

Hong Wang, Xiaomei Wang, Ruotian Chen, Hefeng Zhang, Xu Zong\* and Can Li\*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, The Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Zhongshan Road 457, Dalian 116023, China

Email: xzong@dicp.ac.cn, canli@dicp.ac.cn

Organic–inorganic hybrid perovskites have demonstrated great potential in solar cell fabrication due to excellent optoelectronic properties. However, their success in solar cells has been hardly translated to producing solar fuels because of instability issues and serious charge recombination at the nanoscale domain. Herein, we show for the first time that organic–inorganic hybrid perovskite methylammonium lead bromide (MAPbBr<sub>3</sub>) nanocrystals can be stabilized in aqueous HBr solution and achieve photocatalytic H<sub>2</sub> production reaction under visible light. More impressively, by hybridizing MAPbBr<sub>3</sub> with Pt/Ta<sub>2</sub>O<sub>5</sub> and poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) nanoparticles as electron- and hole-transporting motifs, respectively, drastically enhanced charge transportation on MAPbBr<sub>3</sub> and improved catalysis were achieved. As a consequence, the rate of photocatalytic hydrogen evolution on pristine MAPbBr<sub>3</sub> was increased by ca. 52 times by introducing dual nanoscale charge-transporting highways, achieving an apparent quantum efficiency of ca. 16.4% for H<sub>2</sub> evolution at 420 nm.

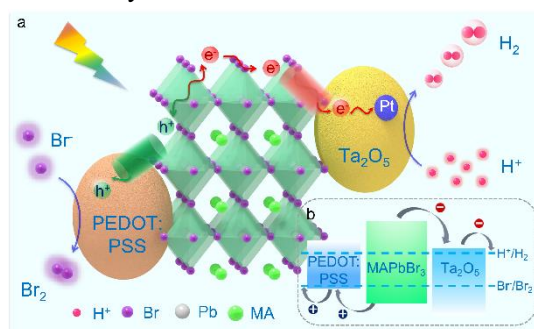


Figure 1. (a) Schematic Illustration of the Reaction Mechanism for MAPbBr<sub>3</sub> with Pt/Ta<sub>2</sub>O<sub>5</sub> and PEDOT:PSS as the Electron- and Hole-Transporting Motifs, Respectively; (b) Schematic Energy Level Diagrams of MAPbBr<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, and PEDOT:PSS for HBr Splitting Reaction

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Poster 2 (China)

## Crystalline structure evolution of all-inorganic halide perovskites for boosting visible-light-driven photocatalytic hydrogen evolution

Ming Shi<sup>1</sup>, Guanna Li<sup>2</sup>, Wenming Tian<sup>1</sup>, Rengui Li<sup>1\*</sup>, Can Li<sup>1\*</sup>

<sup>1</sup>State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian, 116023, China.

<sup>2</sup>Schuit Institute of Catalysis, Inorganic Materials Chemistry Group, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, Eindhoven 5600 MB, The Netherlands.

Email: rgli@dicp.ac.cn; canli@dicp.ac.cn

The specific optoelectronic properties of semiconductors, which are naturally determined by chemical structures, are critical to their applications in optical and electronic fields. Herein, take two all-inorganic metal halide perovskites,  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  and  $\text{Cs}_2\text{AgBiBr}_6$  as examples, we explored the origin of the optoelectronic properties for contributing different photocatalytic performances of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  and  $\text{Cs}_2\text{AgBiBr}_6$  by investigating their backbone structures and combination with time-resolved photoluminescence measurements and density functional theory (DFT) calculations. It is expected that these findings will be instructive for the design of halide perovskites with desired optoelectronic properties by electronic band structure engineering starting off with crystalline structures.

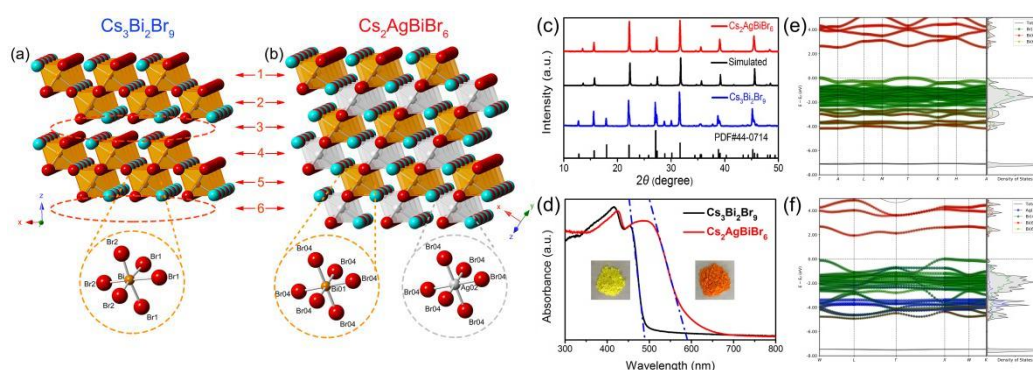


Figure 1. Crystal structure, fundamental characterization and calculated band structure of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  and  $\text{Cs}_2\text{AgBiBr}_6$ .

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## Enhanced photoelectrochemical performance of metal, non-metal co-doped hematite

Kyoungwoong Kang, Jae Jung Lee\*

*Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea*

Fax: 82 54 279 1599; Email: jlee1234@unist.ac.kr (J. S. Lee)

### Abstract

In photoelectrochemical water oxidation using metal oxide materials, there are candidate like  $\text{TiO}_2$ ,  $\text{WO}_3$ ,  $\text{BiVO}_4$ ,  $\text{Fe}_2\text{O}_3$ . Among these materials, hematite ( $\text{Fe}_2\text{O}_3$ ) has advantages in commercialization aspect because of its ideal bandgap and proper band position which is connected to high theoretical photo current value ( $\sim 12\text{mA}/\text{cm}^2$ ). Besides, Fe is earth abundant element and hematite is relatively stable in aqueous condition. However,  $\text{Fe}_2\text{O}_3$  has several drawbacks. The most critical one is poor conductivity of hematite. Diffusion length of hole is very short (2-4nm). That is why most of generated holes can't reach to surface. Not only poor conductivity but also poor oxygen evolution reaction kinetics at the surface is serious problem due to stable state of  $\text{F}=\text{O}$  bond<sup>1</sup>. Holes which reached to surface can't oxidize water directly then recombine<sup>2</sup>. To overcome these drawbacks, doping, heterojunction, co-catalyst, passivation layer, morphology control is recommended.

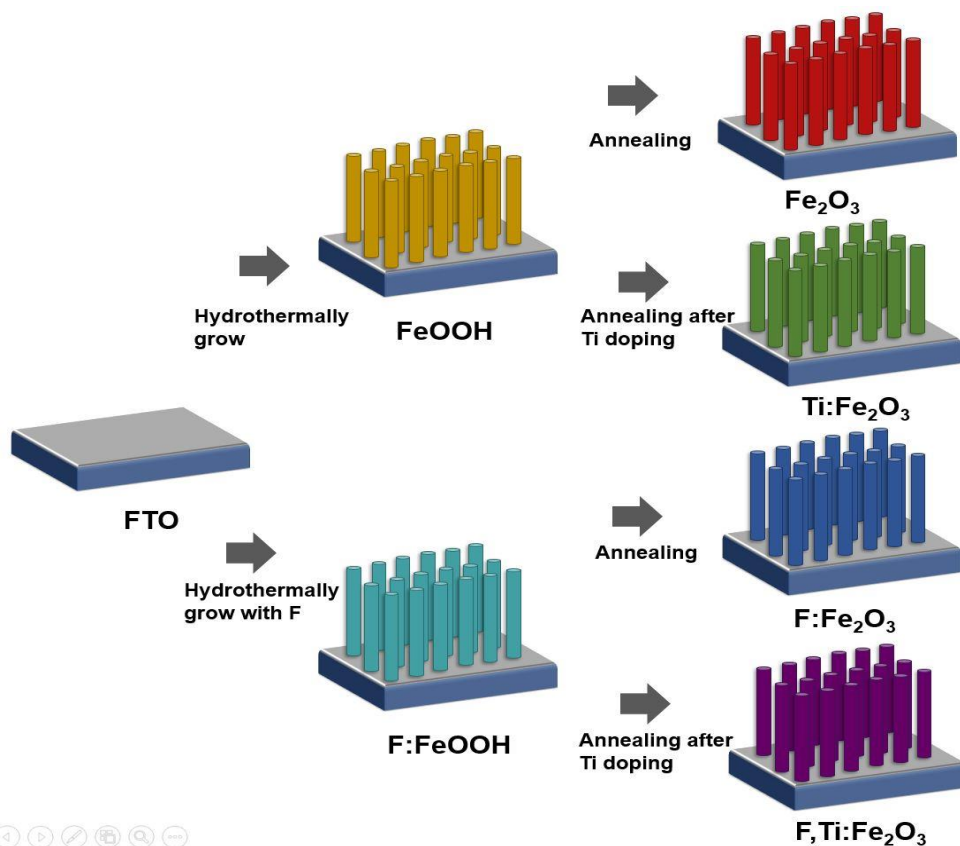


Figure 1. Schematic diagram of F,Ti doped hematite synthesis process

In doping process, there are many papers dealing with doping such as Ti, Sn, Zr, and Pt<sup>3,4</sup>. Although most of works reported about metal dopant which replace Fe site, there are some reported papers which applied non metal dopant such as S, P, F<sup>5,6,7</sup>. In this project, we applied metal, non-metal co doping method using Titanium and Fluorine. We confirmed successfully doped hematite and will introduce different

effect of metal, non-metal dopant using XPS, SIMS, mott-schottky and EIS analysis.

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## The research on mononuclear catalyst for water oxidation

Qing'e Huang<sup>a, b</sup>, Can Li<sup>a, b\*</sup>

<sup>a</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics (DICP), Chinese Academy of Science, Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian, 116023, China.

<sup>b</sup> Department of Chemical Physics University of Science and Technology of China, Hefei 230026, China.

Email: qehuang@dicp.ac.cn

Oxygen evolution reaction (OER) is the bottleneck of hydrogen production by water splitting. Despite tremendous efforts, developing cheap, efficient and durable catalysts for water oxidation still remains as a great challenge. Herein, we develop a new method to get mononuclear catalyst by introduce anchored site and metal step by step. And the cobalt mononuclear anchored on the nitrogen doped graphene (denoted as "Co@N-G") obtained by this way show high OER performance in 1M KOH with 359mV overpotentials for 10 mA/cm<sup>2</sup>. Experimental results show that the anchored site N and metal Co are indispensable parts for that good OER activity.

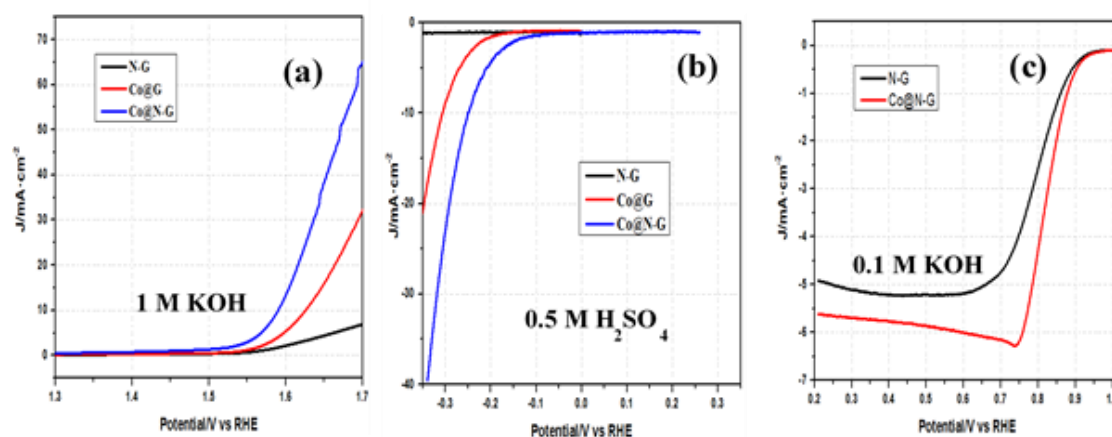


Figure 1. Electrochemical activities of mononuclear Co catalysts with G and N-G as supports.

(a) OER polarization curves of N-G, Co@G, Co@N-G performed in 1 M KOH electrolyte. (b) HER polarization curves of N-G, Co@G, Co@N-G performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. (c) ORR polarization curves of N-G and Co@N-G performed in 0.1 M KOH electrolyte.

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## ***In situ* imaging of the electron transfer in electrochemical process at single Au nanoparticle**

Wei Nie<sup>1,2</sup>, Yuying Gao<sup>1,2</sup>, Shengyang Wang<sup>1,2</sup>, Fengtao Fan<sup>1,2,3</sup>, Can Li<sup>\*,1,2,3</sup>

1. State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
Dalian National Laboratory for Clean Energy, Dalian 116023, China

2. Graduate University of Chinese Academy of Sciences, Beijing 100049, China

3. Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), China

Email: canli@dicp.ac.cn

Understanding the electron transfer process and chemical reaction kinetics on metal nanoparticles in electrolyte solution is of great importance in a wide range of chemical transformations, including energy conversion and utilization. However, due to the structural diversity and the heterogeneous electrochemical interfaces, it is necessary to determine that where the electron transfer occurs and why it happens at such sites to construct structure-activity relationship, yet it still remains challenging, especially under realistic reaction conditions with nanoscale spatial and temporal resolution. Herein, we report the heterogeneous distribution of electrochemical activity on single Au nanoparticle with *in situ* AFM-SECM technique operating in local feedback imaging mode. Highly spatially-resolved SECM image of triangular Au nanoplate shows that electron-transfer sites distribute heterogeneously and the corner sites have the fastest electron transfer rate, which demonstrates a linear increase with the particle size. Correlation analyses further reveal that the heterogeneous electron transfer process of individual Au nanoparticles can attribute to the electrochemical potential of the surface sites in electrolyte condition. This study provides an insight into the electron transfer dynamics for the heterogeneous electrocatalysis at single nanoparticle level in electrolyte condition.

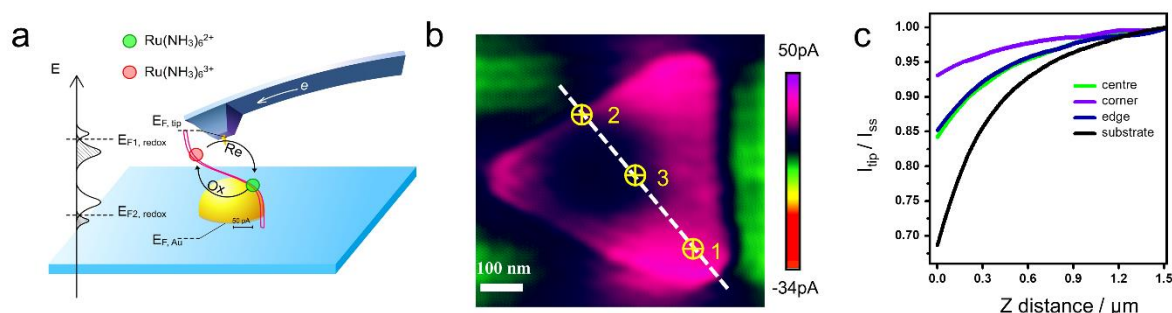


Figure 1. a. Schematic of local feedback mode of the AFM-SECM in redox mediator, b. SECM image of single Au nanoplate, c. Approach curves of different sites of Au nanoplate.

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Poster 6 (Korea)

## Design and development of multifunctional cell for electrochemical/photoelectrochemical application

Dharmesh Hansora, Jin Hyun Kim, Jae Sung Lee\*

*Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea*

Email: dhansora210@unist.ac.kr

There are sustainable ways for solar fuel production. Most of these paths are by solar driven such as photocatalytic (PC), photoelectrochemical (PEC), photovoltaic (PV)-electrolysis (EC) and photobiolysis. But practically, PV-EC and PEC are showing extensive researches on developing primary efficient components such as light absorbers and electrocatalysts. Apart from these components, other important components such as electrolyte, membranes, photovoltaics and cell architectures are required for developing a full practical system. Cell architecture plays a major role for developing one practical system by integrating above all components [1], e.g. PV-EC system and PEC system<sup>1-3</sup>. We focus here for design and development of prototype multifunctional cell for EC/PEC application. Modeling and simulation of each components were studied to optimize the operating parameters of prototype EC/PEC cell. We also study a detailed engineering of EC/PEC cell to bottleneck in to large scale production systems. This simulation and experimental research will boost the future solar hydrogen technologies by water splitting for their industrialization.

**Keywords:** Design and development, Modeling and simulation, prototype EC/PEC cell.

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Poster 7 (China)

## EPR study of paramagnetic species in SrTiO<sub>3</sub> semiconductor photocatalyst for water splitting

Xianwen Zhang, Can Li and Hongxian Han\*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian 116023, China

Email: hxhan@dicp.ac.cn

Light-induced charge separation in SrTiO<sub>3</sub> photocatalyst was investigated by electron paramagnetic resonance (EPR) under air atmosphere and vacuum conditions. Under vacuum conditions, it was found that the photogenerated electrons were transferred from O<sup>2-</sup> to Ti<sup>4+</sup> to generate reduced paramagnetic Ti<sup>3+</sup> centers and O<sup>-</sup> species by trapping holes on lattice O<sup>2-</sup> ions. Simultaneous observation of Ti<sup>3+</sup> and O<sup>-</sup> under steady state EPR experimental conditions revealed that the photoexcited charge separation state of Ti<sup>3+</sup>-O<sup>-</sup> species in SrTiO<sub>3</sub> was profoundly long-lived, which is consistent with the highly efficient charge separation of SrTiO<sub>3</sub> observed by time-resolved spectroscopy<sup>[1]</sup>. Under the atmosphere condition, photoexcitation of SrTiO<sub>3</sub> generates surface bound Ti<sup>4+</sup>-O<sub>2</sub><sup>-</sup> superoxide radicals via reduction of O<sub>2</sub> adsorbed on the surface by photoreduced Ti<sup>3+</sup>. Prolonged photoirradiation may reverse the electron transfer between superoxide radical and surface Ti<sup>4+</sup>, leading to quenching of the superoxide species. This work demonstrates that the Ti<sup>3+</sup>-O<sup>-</sup> is the crucial photoexcited charge separated species for understanding the photocatalytic water splitting processes of SrTiO<sub>3</sub>, and EPR is the powerful tool for the investigation of charge separation and transfer in photocatalysis.

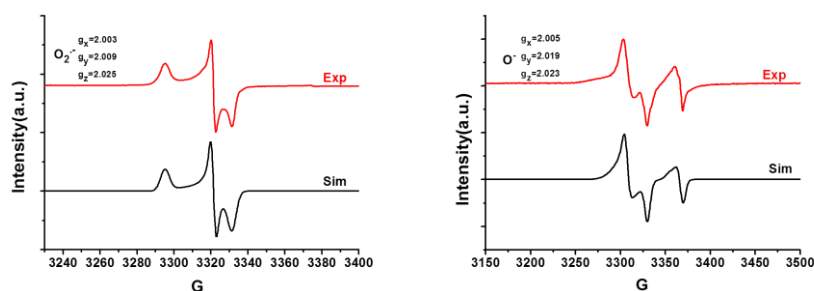


Figure 1. The EPR experimental spectrum and simulated spectrum.

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## Liquid fuel production by CO<sub>2</sub> hydrogenation - Bi-functional catalysts

Eun Cheol Ra, Jae Sung Lee\*

Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea

Email: euncheol93@unist.ac.kr

The main sources of energy for vehicles such as automobiles, airplanes and ships are gasoline, diesel and jet fuel, which are derived from fossil fuels and are now a key energy source in all industries. Easy to transport, energy efficient, and rich in reserves, the use of fossil feedstock has grown geometrically for decades, and CO<sub>2</sub> emissions from using these fuels have led to serious global warming problems. While many alternative energy sources are being developed to address this problem, fossil fuels still account for a significant portion of energy consumption. The catalytic process of converting CO<sub>2</sub> back to liquid fuel can be an important solution to solve global warming and environmental problems. Through a Fischer Tropsch process over an iron-based catalyst, a methane rich hydrocarbon mixture is obtained which can be fed as blending mixture into existing natural gas infrastructure. While CO hydrogenation, FT process, has been studied in various methods, the hydrogenation of CO<sub>2</sub> has less number of processes and catalysts. The here post shows the work has been studied and suggests an approach that could potentially be advantageous for the product of hydrocarbons by CO<sub>2</sub> hydrogenation process.

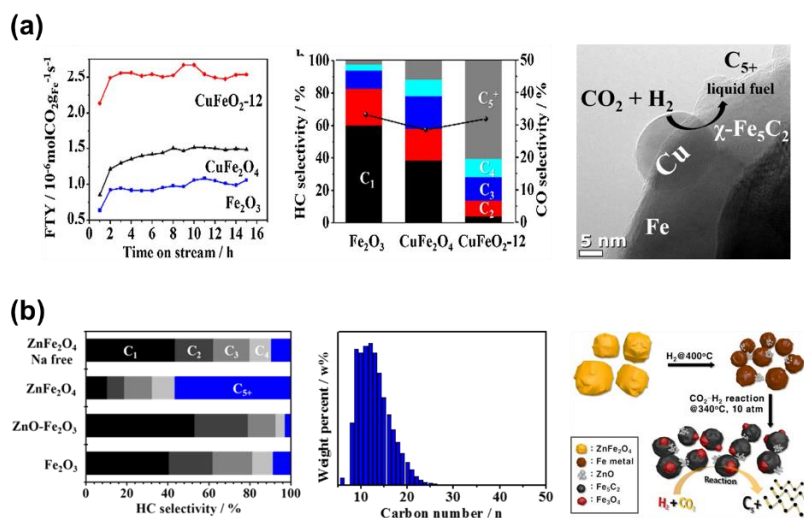


Figure 1. Activity and selectivity of CO<sub>2</sub> hydrogenation for the production of liquid hydrocarbons: (a) Delafossite-CuFeO<sub>2</sub> and (b) ZnFe<sub>2</sub>O<sub>4</sub> catalysts.

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## Electrochemical behavior of vanadium redox couples on carbon electrode

Mingyao Liu<sup>a,b</sup>, Zhenxing liang<sup>a</sup>, Jingying Shi<sup>b</sup>, Canli<sup>b\*</sup>

<sup>a</sup> South China University of Technology (SCUT), Guangzhou, 510641, Guangdong, China

<sup>b</sup> Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, Dalian, 116023, China

Email: mingyaoliu@dicp.ac.cn

Enormous work has been devoted to the vanadium redox flow battery (VRFB) in recent years; however, the electrochemical behavior of the vanadium redox couples has not been well understood. In this work, the redox reaction of vanadium ions ( $V^{2+} \leftrightarrow 3+ \leftrightarrow 4+ \leftrightarrow 5+$ ) on nitrogen-doped ordered mesoporous carbon (NOMC) and Vulcan XC72 carbon black (XC72) was extensively investigated by electrochemical methods. It is found that both the electronic structure modulated by nitrogen doping and the enriched electrochemically active functional groups on NOMC favor the three electrochemical transitions between the adjacent couples, *viz.*  $V^{2+} \leftrightarrow 3+ \leftrightarrow 4+ \leftrightarrow 5+$ , as compared with XC72. Salient findings are as follows. First, the transition of  $V^{3+} \leftrightarrow 2+$  is the same on the two distinctly different carbons, which indicates that this reaction is an outer-sphere charge transfer reaction. Second, the transition of  $V^{5+} \leftrightarrow 4+$  shows a quasi-reversible behavior. Simulation of cyclic voltammogram (CV) reveals that the standard rate constant and the adsorption equilibrium constant are  $(7.0 \pm 0.9) \times 10^{-3} \text{ cm s}^{-1}$  and  $0.70 \pm 0.09$  (both  $V^{4+}$  and  $V^{5+}$ ), respectively. Third, the transition of  $V^{4+} \leftrightarrow 3+$  is recognized in the CV curve, which proceeds in a quasi-reversible reaction. The preceding adsorption of the symmetrical ions ( $V^{3+}$ ) is found to play a key role in determining the kinetics. The above findings not only reveal the applicability of the nitrogen-doped carbon to be used as an electrode material in flow batteries, but also offer an in-depth understanding of the reaction mechanism of vanadium redox couples.

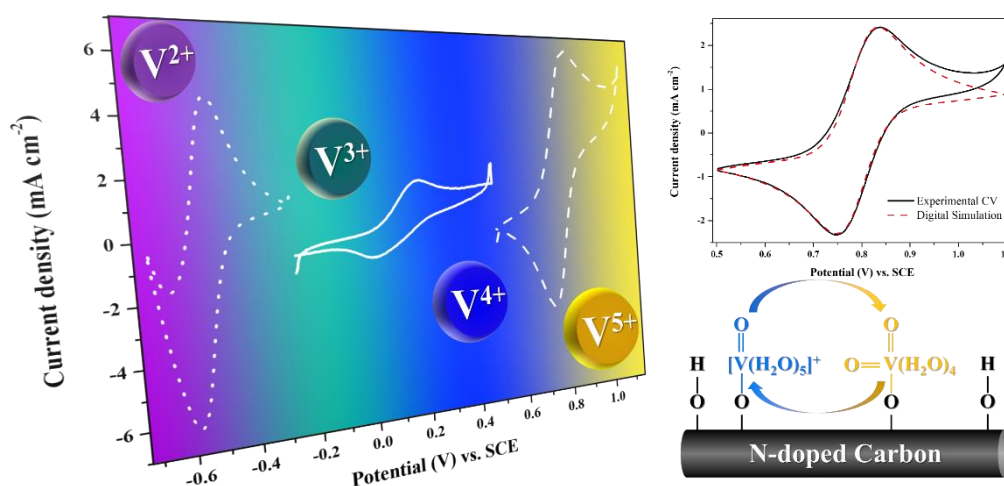


Figure 1. Demonstration of the redox reactions of the vanadium redox couples.

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Poster 10 (Korea)

**Direct CO<sub>2</sub> hydrogenation to formic acid using carbon nitride in neutral media**

Eunhyup Kim, Jae Sung Lee\*

*Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea*

Email: tag1304@unist.ac.kr

Formic acid is stable and clean chemicals. It can be used as raw material for synthesis of various kinds of chemicals such as methanol, acetic acid, etc., which have large demand on the chemical industry. Formic acid is also considered as storage of hydrogen, because it is stable liquid state in room temperature and atmospheric pressure. The volumetric capacity of pure formic acid (53 g<sub>H<sub>2</sub></sub>L<sup>-1</sup>) is outstandingly large enough without high pressurize supplies, which is commonly required for many other hydrogen storage technologies. Furthermore, formic acid is easily decomposed to hydrogen and carbon dioxide under mild condition. For hydrogen storage, both formic acid synthesis and decomposition reactions should be developed. CO<sub>2</sub> hydrogenation to formic acid is thermodynamically unfavorable ( $\Delta G^0 = +33 \text{ kJ mol}^{-1}$ ). So, formic acid synthesis reaction is main barrier. Palladium is promising metal for hydrogen adsorbent. And N doped carbon is widely known as good CO<sub>2</sub> adsorbent. Therefore, carbon nitride can be good CO<sub>2</sub> adsorbent. The modification of carbon nitride can be effective to improve CO<sub>2</sub> adsorption property and formic acid productivity. It can change CN(Carbon Nitride) property such as surface area and defect sites.

Figure 1. Activity comparison: Pd/CN catalysts about Precursor & Synthesis method & acid treatment

**Highly Efficient c-Si based Photoanode for Photoelectrochemical Water Oxidation**Jiangping Ma<sup>1,2</sup>, Tingting Yao<sup>1\*</sup> and Can Li<sup>1,2\*</sup>*1 state Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian 116023, China.**2 College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730070, China.*

Email: ttyao@dicp.ac.cn; canli@dicp.ac.cn

Manipulating the interfacial energetics of composite photoelectrodes through adjusting the interface layers to promote the charge separation and transportation is crucial for achieving high photoelectrochemical (PEC) efficiency. In this work, a passivation layer (MO) and a metal layer (MA) with high work function were introduced within the n-Si photoanode to minimize the adverse effect of defects and increase the barrier height of the heterojunction, effectively leading to an enhanced fill factor and negatively shifted onset potential for water oxidation. Eventually, the n-Si/MO/MA/NiFeOx photoanode could afford a photovoltage of ~600mV, present an onset potential of 0.90 V (vs. RHE) and a saturated photocurrent density of 32mA cm<sup>-2</sup> for PEC water oxidation. The applied bias photon-to-current efficiency (ABPE) and fill factor reached to 3.71% and 0.75, respectively.

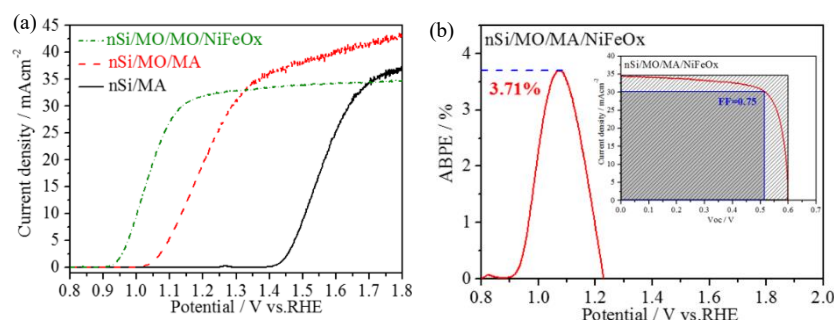


Figure 1. (a) J-E curves of nSi photoanode modified with different overlayer in 1.0M KOH under illumination (AM 1.5G, 100mW cm<sup>-2</sup>). (b) The applied bias photon-to-current efficiency of nSi/MO/MA/NiFeOx (inset: fill factor).

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Poster 12 (Korea)

## Nickel gallium intermetallic compounds derived from layered double hydroxides for electrochemical CO<sub>2</sub> reduction

Jin Ho Lee, Youn Jeong Jang, Jae Sung Lee\*

Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea

Email: miraculum@unist.ac.kr

CO<sub>2</sub> conversion is a promising way to reutilize CO<sub>2</sub> which leads to global warming for sustainable fuel production. Ni element has a catalytic ability for CO<sub>2</sub> conversion into useful fuel, but it has a drawback in low CO<sub>2</sub> adsorption sites and imperfect electrical binding strength of CO<sub>2</sub>. On the other hand, Ni based alloy, for instance Ni-Ga intermetallic compounds (IMCs), has shown the desired catalytic property in multiple CO<sub>2</sub> activation sites and modified its electrical binding strength. NiGa IMCs showed good activity, selectivity for ambient CO<sub>2</sub> Hydrogenation to methanol<sup>1</sup>. This catalytic activity for CO<sub>2</sub> reduction is connected with electrocatalytic activity for CO<sub>2</sub> conversion<sup>2</sup>.

Furthermore, two-dimensional layered double hydroxides (LDHs;  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^n)_{x/n} \cdot mH_2O$ ), where M is divalent metal cation or trivalent metal cation and A is charge-balancing anion has been expected strong capacity for CO<sub>2</sub> adsorption in the interlayer space. By using LDHs as precursor for intermetallic compounds, as-prepared nanostructured IMCs will be expected to have high surface area and other catalytic properties. Herein, Nickel Gallium Intermetallic Compounds(NiGa-IMCs) derived from NiMgGa LDHs was suggested for electrochemical CO<sub>2</sub> conversion and its physicochemical characteristics and catalytic performances were evaluated.



Figure 1. The schematic illustration of synthesizing Nickel Gallium intermetallic compounds derived from layered double hydroxides.

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## Effects of hole-extracting layer on the activity and stability of polymer-based photocathodes toward photoelectrochemical hydrogen production

Wenwen Shi,<sup>a,b</sup> Jingying Shi,<sup>\*a</sup> Can Li<sup>\*a</sup>

<sup>a</sup>Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, China; <sup>b</sup>University of Chinese Academy of Sciences, Beijing 100049, China

E-mail: jingyingshi@dicp.ac.cn; canli@dicp.ac.cn

High-efficiency organic photocathodes, based on donor/acceptor bulk heterojunction sandwiched between charge-selective layers, are emerging as efficient and low-cost devices for solar hydrogen production via water splitting.<sup>[1,2]</sup> However, the detailed effects of hole-extracting layer (HEL) on the activity and stability of the organic photocathodes remains unclear. In this work,  $\text{CuO}_x$ ,  $\text{MoO}_3$  and  $\text{NiO}_x$  were used as HEL to fabricate polymer based organic photocathodes, and their effects on the photoelectrochemical (PEC) performance of hydrogen production were systematically study. The results show that the activity is directly correlated with the hole extraction ability of the HEL material, while the stability of photocathode is more related to the hole transfer capability of the HEL material. The most active photocathode generates a photocurrent of  $10 \text{ mA cm}^{-2}$  at  $0 \text{ V}$  vs. RHE, excellent energetics with  $+0.75 \text{ V}$  vs. RHE onset potential and considerable activity in one hour. This work demonstrates high hole extraction and rapid hole transport are required for fabricating an efficient and durable organic photocathode.

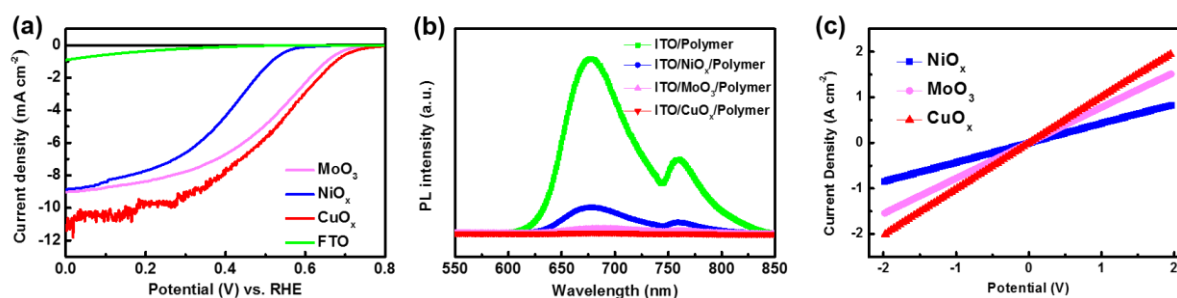


Figure 1. (a) Current-potential curves of organic photocathodes with different HEL materials; (b) PL spectra of polymer with different HEL materials; (c) Conductivity of different HEL materials.

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## Fluorine doping on manganese oxides to achieve enhanced oxygen evolution catalysis

Yimeng Sun<sup>1,2</sup>, Ailong Li<sup>1,2</sup>, Can Li<sup>1</sup> and Hongxian Han<sup>1\*</sup>

<sup>1</sup>State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

<sup>2</sup>University of Chinese Academy of Sciences, Beijing 100049, China

E-mail: hxhan@dicp.ac.cn

**Abstract:** Development of low cost, highly active and durable noble metal-free electrocatalyst for oxygen evolution reaction (OER) remains one of the major challenges for large scale application of PEM water electrolyzer to produce hydrogen. <sup>[1]</sup> Experimental studies have demonstrated that abundant 3d metals (Fe, Co, Ni, or Mn) are unstable due to their dissolution in acidic media. <sup>[2]</sup> Recently, we have reported that earth-abundant metal oxides ( $\gamma$ -MnO<sub>2</sub>) can catalyse the OER with the overpotential around 500mV at 10mA cm<sup>-2</sup>. <sup>[3]</sup> In this work, enhanced electrocatalytic OER performance was further achieved by anionic dopant fluorine (F), exhibiting an overpotential of ~ 400 mV at 10 mA cm<sup>-2</sup>.

**Keywords:** Acid stable electrocatalysts, Manganese oxides, Fluorine anion

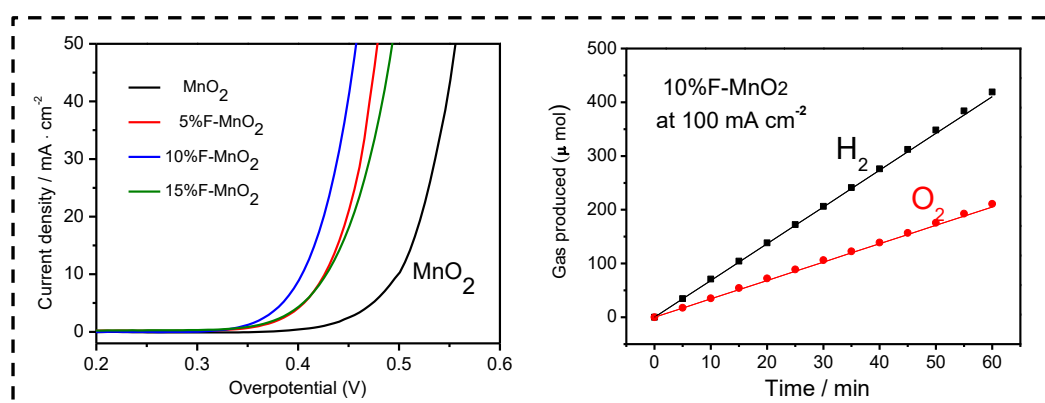


Figure 1. a) Linear sweep voltammograms of different F doping electrodes on FTO in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Scan rate: 5 mV s<sup>-1</sup>. Overpotential = E<sub>RHE</sub> - iR - 1.23V. b) Faradaic efficiency of 10%F-MnO<sub>2</sub> sample at 100 mA cm<sup>-2</sup>.

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**Direct CO<sub>2</sub> hydrogenation to formic acid using carbon nitride in neutral conditions**Ju Hyeong Lee<sup>a</sup>, Hunmin Park<sup>b</sup>, Jae Sung Lee<sup>a,\*</sup><sup>a</sup>Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea<sup>b</sup>Pohang University of Science & Technology (POSTECH), Pohang, 790-784, Republic of Korea

Email: jhlee0415@unist.ac.kr

Formic acid (HCOOH) is a molecule that can be synthesized from CO<sub>2</sub> hydrogenation and is considered as a stable and safe H<sub>2</sub> storage medium with a large volumetric hydrogen capacity (53 gH<sub>2</sub> L<sup>-1</sup>). Moreover, HCOOH is easily decomposed to H<sub>2</sub> and CO<sub>2</sub> on Pd catalysts under mild conditions (<100 °C, ambient pressure) without CO evolution, which is an essential requirement for fuel cell applications. By unifying the HCOOH synthesis and decomposition reactions, a carbon neutral H<sub>2</sub> cycle can be completed.

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is 2-dimension structure. g-C<sub>3</sub>N<sub>4</sub> is applied as a support of the Pd catalyst for direct HCOOH synthesis by CO<sub>2</sub> hydrogenation under neutral conditions. The high CO<sub>2</sub> affinity of g-C<sub>3</sub>N<sub>4</sub> is responsible for the enhanced catalytic activity and stability relative to the inert support such as a carbon nanotube.

The total Pd time yield of 1.4Pd/g-C<sub>3</sub>N<sub>4</sub> is 12 times higher than that of Pd/CNT with a similar Pd particle size. Notable, no HCOOH species was detected in the reaction solution when bare g-C<sub>3</sub>N<sub>4</sub> was used without Pd. Since H<sub>2</sub> is activated on the Pd surface, HCOOH formation reaction should take place at the interface with g-C<sub>3</sub>N<sub>4</sub>, where CO<sub>2</sub> activation occurs.

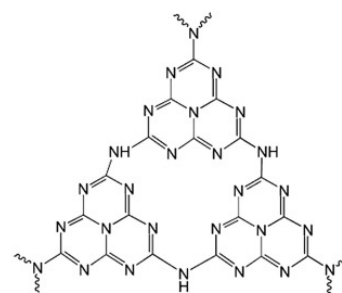
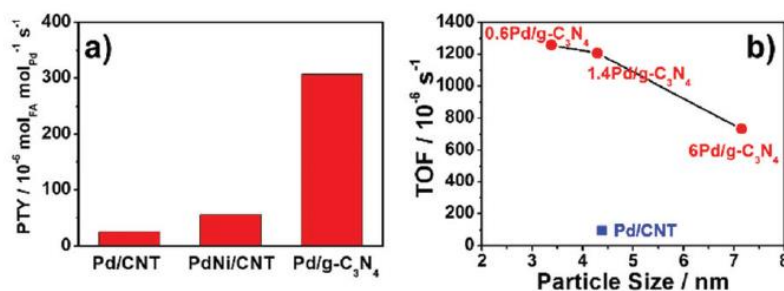
Figure 1. g-C<sub>3</sub>N<sub>4</sub>

Figure 2 (a) Total Pd time yield of Pd/CNT and Pd/g-C<sub>3</sub>N<sub>4</sub> in HCOOH synthesis. (b) The effect of the Pd particle size on TOF for Pd/g-C<sub>3</sub>N<sub>4</sub>

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## Surface activation treatment of lower temperature calcined hematite for efficient photoelectrochemical water oxidation

Changtong Ma, Can Li and Hongxian Han\*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian 116023, China

Email: hxhan@dicp.ac.cn

Hematite is an extensively studied model semiconductor photocatalyst for photoelectrochemical (PEC) water oxidation.<sup>[1]</sup> As the PEC performance of the as-prepared hematite at 550°C is so low, the hematite photoanodes are usually activated at higher temperature of 750°C. The enhancement of the PEC water oxidation activity is ascribed to the increased crystallinity and the diffusion of Sn from the FTO substrate.<sup>[2]</sup> However, the high temperature annealing induces the increase of the FTO substrate resistance and even damage of the FTO substrate. In this case, it is necessary to activate (annealing) hematite at relatively low temperature to balance between the activity of the catalyst and stability of the substrate. In this work, the as-prepared hematite photoanodes were activated with Na<sub>2</sub>WO<sub>4</sub> solution at 550°C. After such treatment, the PEC performance of hematite can be enhanced remarkably, which is better than that of hematite photoanode activated at 750°C. Various spectroscopic and electrochemical characterization results demonstrate that the enhancement of the PEC performance of W-Fe<sub>2</sub>O<sub>3</sub>-550°C is due to increased charge transfer rates at the semiconductor/liquid interface and longer life time of the photogenerated charges.

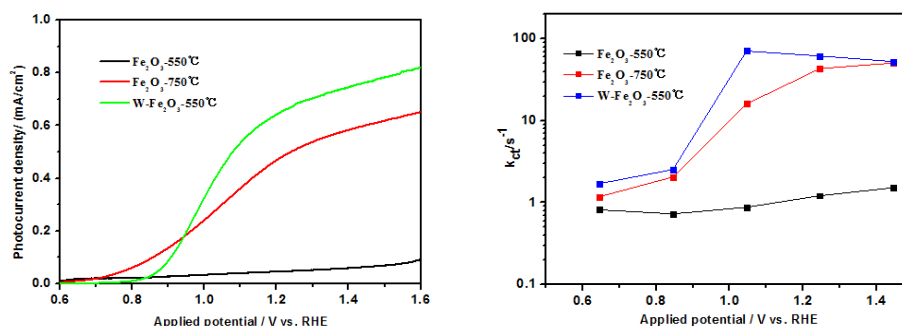


Figure 1. The photocurrent density and charge transfer rates of Fe<sub>2</sub>O<sub>3</sub>-550°C, Fe<sub>2</sub>O<sub>3</sub>-750°C, W-Fe<sub>2</sub>O<sub>3</sub>-550°C.

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Poster 17 (China)

**Bandgap engineering of dual acceptor-containing naphthalene diimide polymers for all-polymer solar cells**

Dandan Tu<sup>1,2</sup>, Xuan Liu<sup>1,2</sup>, Jing Zhang<sup>1,2</sup>, Qing Yang<sup>1,2</sup>, Shuwen Yu<sup>1</sup>, Xin Guo<sup>1,\*</sup> and Can Li<sup>1,\*</sup>

<sup>1</sup>*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian 116023, China*

<sup>2</sup>*University of Chinese Academy of Sciences, Beijing 100049, China*

Email: guoxin@dicp.ac.cn; canli@dicp.ac.cn

Naphthalene diimide (NDI)-based polymers, as non-fullerene acceptors for all-polymer solar cells (all-PSCs), are usually investigated by manipulating electron-donating units, which have a narrow bandgap showing absorption spectra mostly overlapping with high-performance donor polymers like PTB7-Th. In order to gain complementary absorptions between NDI-based polymers and PTB7-Th, we report three NDI-based polymers (P1-P3) designed by a dual-acceptor strategy and systematically study their effect on the bandgap, molecular configuration, and charge transport property. The absorption bands of these polymers range from 300 to 800 nm; in particular, P1 with a maximum absorption at 530 nm exhibits a good complementary absorption with the PTB7-Th. The device based on the PTB7-Th:P1 blend provides higher  $J_{sc}$  and efficiency than those based on other two polymers. The result suggests that the dual-acceptor strategy is effective to design acceptor polymers with adjustable absorption and molecular configuration for the all-PSCs.

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## Solution based synthesis of copper bismuth oxide and NiO hole transport layer

Jeehye Kim, Jin Hyun Kim, Jae Sung Lee\*

Ulsan National Institute of Science & Technology (UNIST), Ulsan, 44919, Republic of Korea

Email: jhkim15@unist.ac.kr

Copper bismuth oxide (CBO) is a p-type semiconductor material which has 1.8eV band gap and 19.7mA/cm<sup>2</sup> of theoretical photocurrent density. The p-type Conductivity comes from the copper vacancy states near the valence band edge. CBO fulfills several requirements for the photoelectrochemical water splitting photocatalyst, 1) proper band gap (1.8eV) 2) appropriate band alignment for hydrogen reduction and 3) earth abundant and low cost of fabrication. But CBO has poor charge transfer activity, slow kinetics and photocorrosion caused by trapping of photoelectrons in the Cu 3d band. To overcome disadvantages, 1) optimizing the synthesis method, 2) improve charge transfer activity by using dopant or junction, and 3) passivation layer for stability are required.

Nickel Oxide (NiO) is a wide-band gap p-type material which has been used as hole transport layer (HTL) in various semiconductor devices. NiO underlayer can act as effective hole selective back contact for CBO and FTO interfaces.

In this study, CBO and NiO underlayer were synthesized with solution-based method and improved photocurrent density was observed.

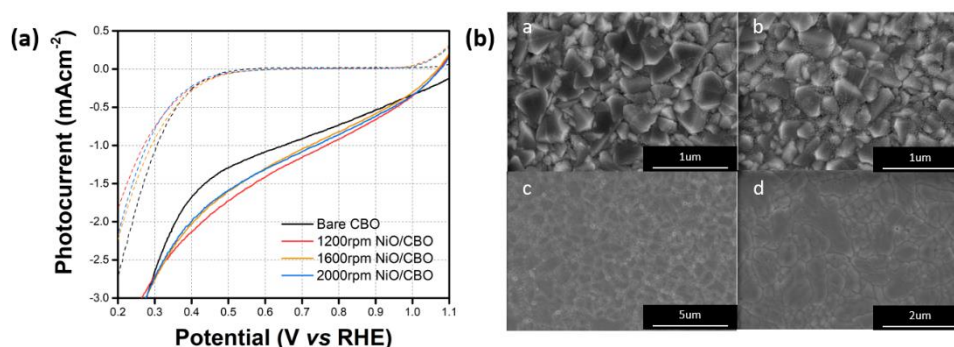


Figure 1. (a) Photocurrent density of CBO and NiO/CBO in 0.2M Potassium Phosphate pH adjusted at 7 and 0.3M Potassium sulfate electrolyte with H<sub>2</sub>O<sub>2</sub>, (b) SEM images of NiO underlayer and CBO film.

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## Crystal facet engineering of novel $\text{Sr}_2\text{CoTaO}_6$ double perovskite for efficient water oxidation

Ahmed Mahmoud Idris<sup>a,b</sup>, Can Li<sup>a</sup>, and Hongxian Han<sup>a,c\*</sup>

<sup>a</sup>State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, China;

<sup>b</sup>University of Chinese Academy of Sciences, Beijing 100049, China

Email: hxhan@dicp.ac.cn

Semiconductor photocatalysts with specific morphologies are very important for enhancing photocatalytic water splitting activity. We have reported fabrication of highly efficient photocatalysts by spatially loading oxidation and reduction cocatalysts on the different facets of semiconductor based on the facet charge separation. In this work, we report synthesis of different facet exposed  $\text{Sr}_2\text{CoTaO}_6$  double perovskite by simple flux method strategy at relatively low temperature. By carefully control of the synthesis conditions, the morphology of the  $\text{Sr}_2\text{CoTaO}_6$  can be tuned from spherical to 18-facet nanocrystals that expose different crystal facets. By using photodeposition method, reduction and oxidation co-catalysts were successfully loaded separately on the different facets of the anisotropic 18-facet  $\text{Sr}_2\text{CoTaO}_6$ , which resulted in high water oxidation activity.

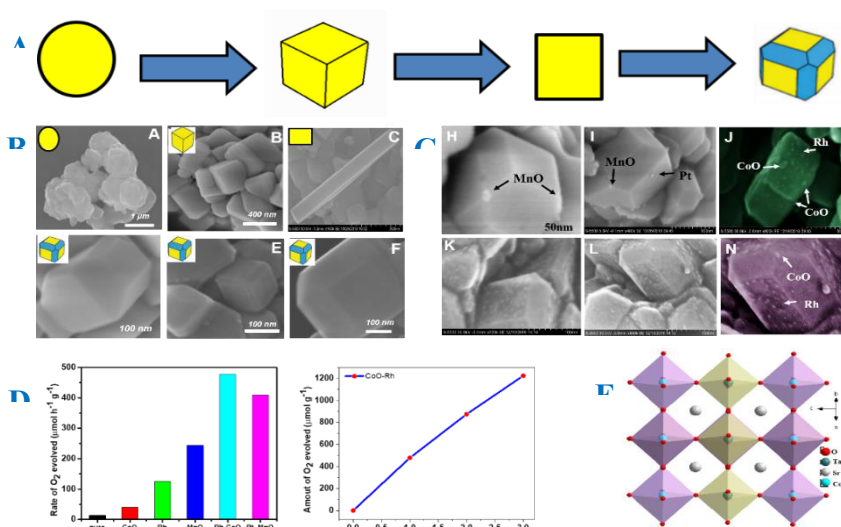


Figure. 1 A. The morphology engineering strategy of  $\text{Sr}_2\text{CoTaO}_6$ . B. (A–F) the different morphologies of  $\text{Sr}_2\text{CoTaO}_6$  nanocrystals. C. (H–N) morphologies of  $\text{Sr}_2\text{CoTaO}_6$  nanocrystals after loading redox co-catalysts. D.(A,B)Photocatalytic O<sub>2</sub> evolution with different Co-catalysts and time course of 0.5wt% of CoO-Rh. E. The schematic description of  $\text{Sr}_2\text{CoTaO}_6$ .

Poster 20 (China)

**Decorating polymer backbone with benzyl alcohol and its dual functions  
for inverted perovskite solar cells**

Xuchao Wang, Qing Yang, Xin Guo, \* and Can Li\*

*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
Dalian National Laboratory for Clean Energy, The Collaborative Innovation Center of Chemistry for  
Energy Materials (iChEM) Dalian, 116023 (P. R. China)*

Email guoxin@dicp.ac.cn; canli@dicp.ac.cn

Low-temperature-processed inverted perovskite solar cells (PSCs) attract increasing attentions because they can be fabricated on rigid and flexible substrates. For these type devices, hole-transporting (HT) layers play an important role in device fabrication and device performance. Here we designed and synthesized a new polymer (P15) with the benzyl alcohol decorated backbone. It can easily form a HT layer with the hydroxyl (OH) groups on the surface. As a result, the complete perovskite film can be easily deposited on this layer, which is good for fabrication of scalable PSCs. Moreover we prove that P15 chemically interacts with lead ions and iodide ions by XPS and solid state H NMR spectrum, and thus be able to passivates undercoordinated defect sites of the perovskite surface. Compared to P10 without such OH group, the defect healing of P15 has proved by the improved PL life time and the decrease of the total tDOS value. Therefore, as new dopant-free hole-transporting materials, the inverted device based on P15 show a very impressive PCE of 20.12% with good reproducibility, which is much higher than P10 (16.34%). More importantly, it is also much higher than the PCE of the reference devices based on the benchmark organic materials PTAA (18.08%) and PEDOT:PSS (12.84%) under the same condition. These in-depth insights provide a good guideline for design effective HTMs to development of inverted planar perovskite solar cells.

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## CdIn<sub>2</sub>S<sub>4</sub>/TiO<sub>2</sub> nanorod heterostructured photoanode: an advanced material for photoelectrochemical applications

Love Kumar Dhandole<sup>a</sup>, Mahadeo A. Mahadik<sup>a</sup>, Hee-Suk Chung<sup>b</sup>, Weon-Sik Chae<sup>c</sup>, Min Cho<sup>a\*</sup> and Jum Suk Jang<sup>a\*</sup>

<sup>a</sup>*Division of Biotechnology, Chonbuk National University, Iksan 570-752, Republic of Korea*

<sup>b</sup>*Korea Basic Science Institute, Jeonju 54907, Republic of Korea*

<sup>c</sup>*Korea Basic Science Institute, Daegu 41566, Republic of Korea*

Email: love.dhandole86@gmail.com

A highly three-dimensional CdIn<sub>2</sub>S<sub>4</sub> deposited TiO<sub>2</sub> (CdIS/TONR/FTO) heterostructured photoanode has been fabricated via a two-step hydrothermal process to enhance the visible light photoelectrochemical (PEC) performance. In this work, bare TiO<sub>2</sub> nanorods are grown successfully on the fluorine-doped tin oxide (FTO) substrate via a hydrothermal method (TONR/FTO), and a second-step hydrothermal synthesis is used to grow CdIn<sub>2</sub>S<sub>4</sub> flower nanostructured layer over the top surface of the bare TONR/FTO. Structural, morphological, optical, and elemental analysis of CdIS/TONR/FTO heterostructure photoanode is investigated in detail. PEC performances are studied in 0.2 V *versus* Ag/AgCl in mixed sulfide-based electrolyte for various concentrations of CdIn<sub>2</sub>S<sub>4</sub> deposited photoanodes. The photocurrent density for optimized (×4)-CdIS/TONR/FTO heterostructure photoanode is observed to be three times higher than that of the bare TONR/FTO photoanode. This excellent PEC performance is ascribed to the way that the deposited CdIn<sub>2</sub>S<sub>4</sub> layer and TiO<sub>2</sub> nanorods synergistically allow the absorption of a wide portion of the solar spectrum under back illumination, and provide efficient separation of the electron-hole pairs in the photoanode architecture. The EIS and IMPS analysis also reveal the significance of CdIn<sub>2</sub>S<sub>4</sub> layer that provides the lowest charge-transfer resistance at the interface and high electron-transfer rate in CdIS/TONR/FTO photoanode. Mainly, the deposited CdIn<sub>2</sub>S<sub>4</sub> layer significantly broadens the optical absorption capacity, and provides efficient electrons-holes transfer that reduces the recombination losses of the charge carriers. The proposed charge transfer mechanism in CdIS/TONR/FTO heterojunction is well studied.

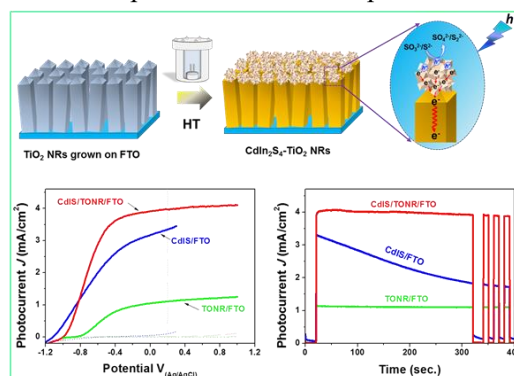


Figure 1. Synthesis and PEC performance of CdIS/TONR/FTO.

## Effect of cocatalyst on photocatalytic water oxidation activity of BiFeO<sub>3</sub>: ferroelectric semiconductor photocatalyst

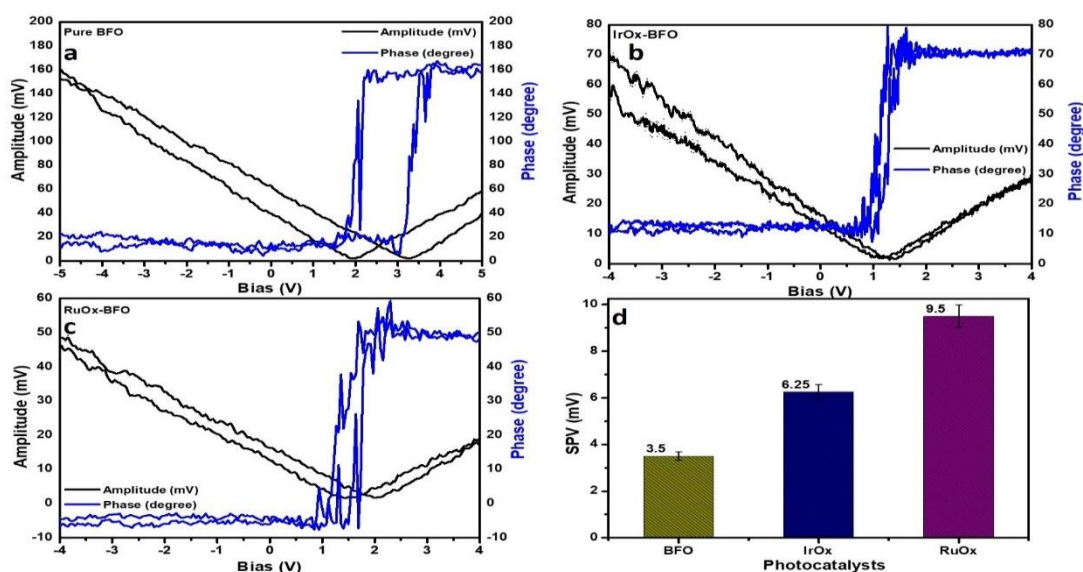
Jafar Hussain Shah<sup>1</sup>, Can Li<sup>1</sup> and Hongxian Han<sup>1,2\*</sup>

1 State Key Laboratory of Catalysis; Dalian National Laboratory for Clean Energy; Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China.

2 The Collaborative Innovation Center of Chemistry for Energy Materials (iChEM),

Email: hxhan@dicp.ac.cn

Ferroelectric materials are considered to be the most promising materials due to their inner built-in electric field. Loading of as transition metals oxides as oxidation cocatalysts on ferroelectrics such as BFO has never been explored. In this work the effects of cocatalysts on photocatalytic water oxidation activity and ferroelectricity of BFO were studied by loading different oxygen evolution reaction (OER) cocatalysts, including RuO<sub>x</sub>, CoO<sub>x</sub>, MoO<sub>x</sub>, and IrO<sub>x</sub>, etc. The RuO<sub>x</sub>/BFO showed OER rate of 680 μmol h<sup>-1</sup> g<sup>-1</sup>, which is the best results reported so far for BFO based water oxidation catalysts. The XPS and EPR study of the BFO after RuO<sub>x</sub> loading showed that the Fe in BFO was partially reduced to low valence Fe species, probably due to the formation of oxygen vacancies that facilitate the charge separation and transfer. PFM and ferroelectric measurements reveals that the as-synthesized BFO and loaded with cocatalysts, have spontaneous polarization and a high SPV thereby demonstrating the ferroelectric nature. This indicates that such ferroelectric BFO should provide promising opportunity for photovoltaics devices. The photocatalytic water oxidation based on RuO<sub>x</sub>-BFO showed quantum efficiency ca. 5.36% at 560 nm. This significant improvement in water oxidation performance is attributed to the promotion of charge separation caused by the internal electric field of BFO, and superior RuO<sub>x</sub> as an oxidation cocatalyst.



## Crystal engineering of bismuth vanadate photocatalysts for efficient water oxidation

Yue Zhao <sup>a,b</sup>, Rengui Li <sup>a</sup> and Can Li <sup>a,\*</sup>

*a* State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences;  
Dalian National Laboratory for Clean Energy, Dalian, 116023, China.

*b* University of Chinese Academy of Sciences, Beijing, 100049, China.

Email: yzhao@dicp.ac.cn, canli@dicp.ac.cn

Photocatalytic water oxidation is much more difficult to occur during photocatalytic water splitting process because the formation of one molecule of oxygen needs 4 holes to oxidize water<sup>1,2</sup>. To achieve high efficiency photocatalytic water oxidation is very important to achieve high solar energy conversion efficiency. Rationally control the morphology of semiconductors is one of the useful strategies for improving the efficiency of solar energy conversion system<sup>3</sup>. In this work, BiVO<sub>4</sub> with different ratio of {010}/{110} was synthesized after comprehending the transformation of the crystalline structure in deep. It is found that the performance of photocatalytic water oxidation of BiVO<sub>4</sub> photocatalyst is demonstrated to be strongly dependent on the proportion of the exposed facets. It is because that the reaction rates of oxidation and reduction reaction can be optimized to achieve a balance rate via controlling the ratio of {010} and {011} facets for BiVO<sub>4</sub> crystals. And after the optimum of the proportion of the exposed facets, an AQE up to 71% can be achieved. The studies show that the high quantum efficiency of BiVO<sub>4</sub> crystals was attributed to not only the high efficiency charge separation caused by the unique spatial charge separation between different facets but also nearly 100% forward reaction with almost no reverse reaction. Further investigations show that the reverse reaction is blocked because of the electrostatic interaction between the reactants and the BiVO<sub>4</sub> surface accumulated by photogenerated charges.

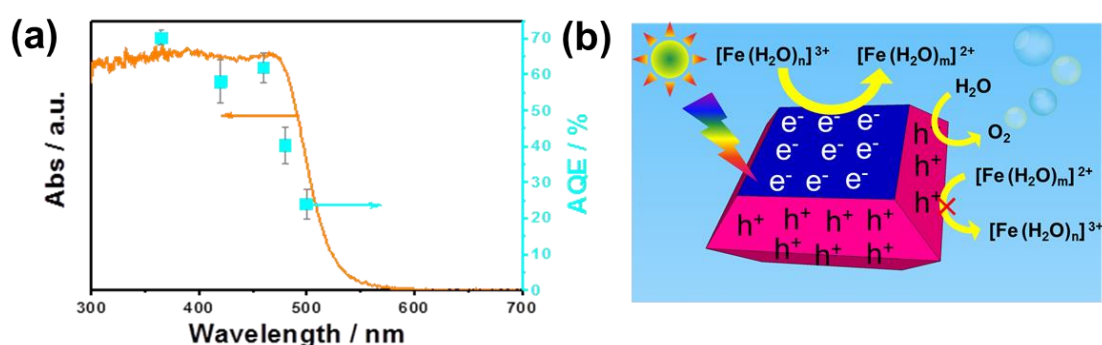


Figure 1. (a) Relationship between apparent quantum efficiency and the absorption spectrum of BiVO<sub>4</sub> photocatalyst. (b) Scheme for surface reaction process for decahedron BiVO<sub>4</sub> crystal in Fe<sup>3+</sup> solution

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## Crystalline polymeric carbon nitride for solar fuel production

Woo Jin Byun, Jin Hyun kim, Jae Sung Lee\*

Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea

Email: wjenergy@unist.ac.kr

Polymeric carbon nitride (PCN) is a promising candidate for photocatalytic hydrogen production, but suffers from insufficient light absorption and sluggish charge carrier transfer.<sup>1</sup> Herein, we synthesized crystalline polymeric carbon nitride by ionothermal method and it was obtained from the thermal polycondensation of urea by using the salt melt of lithium chloride and potassium chloride as a novel heat transfer media.<sup>2</sup> The crystalline carbon nitride showed decreasing trend in PL intensity compared to bulk carbon nitride. And efforts to tune the electronic structure of carbon nitride by introducing metal ions affected on light absorption property, contributing to greater visible light absorption. As a result, the crystalline polymeric carbon nitride exhibited efficient photocatalytic solar fuel production performance with enhanced optical absorption, charge transfer and exciton dissociation.

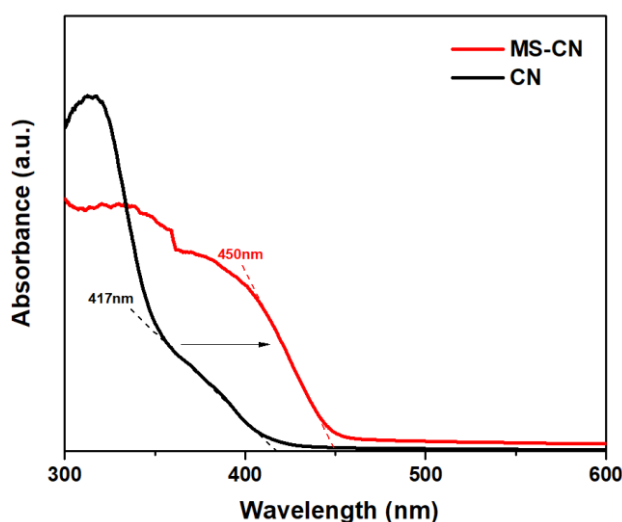


Figure 1. The UV-vis DRS of carbon nitride (CN) and carbon nitride synthesized with molten salts (MS-CN).

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## Synthesis $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ photoanodes for enhanced water splitting performance

Jin Uk Lee<sup>a</sup>, Jae Sung Lee<sup>a,\*</sup>

<sup>a</sup>Ulsan National University of Science & Technology (UNIST), Ulsan, 689-798, Republic of Korea

Email: leejs6588@unist.ac.kr

Solar water splitting using photoelectrochemical cells (PECs) has emerged as a method of storing and utilizing solar energy to produce hydrogen and oxygen as a clean and renewable fuel source. Various semiconductors that have been considered as photoelectrodes for use in PECs. Especially, oxide-based photoanodes are particularly attractive because of their stability in aqueous media. In addition, inexpensive and facile processing compared to other types of semiconductors.<sup>1</sup> Nevertheless, photoanodes are an important limitation on the development of this system because of poor charge carrier separation and transport. Thus, developing efficient and stable photoanodes is a necessary choice to promote the practical application of PEC water splitting.<sup>2</sup> Ternary oxides provide more opportunities to change the composition and electronic structure of the photoelectrode compared to binary oxides. Therefore, they can provide more various the photoelectrochemical properties. In addition, atomic doping method increase the majority carrier density of a material.<sup>1</sup>  $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$  is a copper-based oxide semiconductor. This material has narrower band gap than  $\text{CuWO}_4$  and can absorb larger range of visible light spectrum. It can obtain high solar to hydrogen conversion efficiency. The Mo/W atomic ratio of  $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$  could be changed for reducing band gap and enhanced water splitting performance.<sup>2</sup>

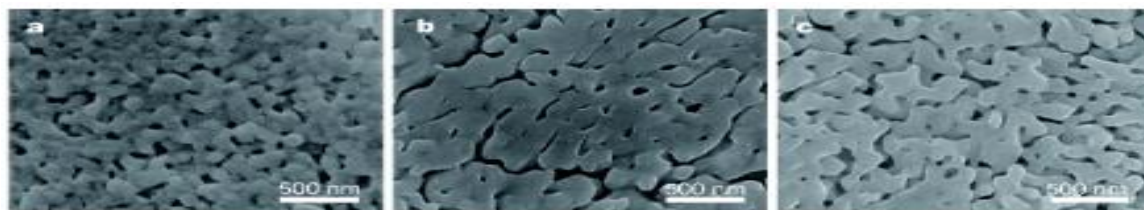


Figure 1. The SEM images of  $\text{CuWO}_4$  and  $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ : (a)  $\text{CuWO}_4$ , (b)  $\text{CuW}_{0.65}\text{Mo}_{0.35}\text{O}_4$  and (c)  $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$

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## Interfacial engineering for modulating photoexcited “hot” carriers in plasmonic photocatalysts

Bin Zeng<sup>1,2</sup>, Shengyang Wang<sup>1,2</sup>, Rengui Li<sup>1,2</sup>, Can Li<sup>1,2,\*</sup>

<sup>1</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,

<sup>2</sup> Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy

Zhongshan Road 457, Dalian, 116023

Email: bzeng@dicp.ac.cn

Efficient collection of photoexcited “hot” carriers in plasmonic photocatalysts holds great promise in solar energy conversion owing to broadly tunable optical properties and large absorption cross section. However, the complex process of hot carriers extraction across the interface, as well as the exceedingly short lifetime of hot carriers, results in quite low efficiency of plasmon-induced photocatalytic reactions, especially for interfacial water oxidation reaction. Here, an interfacial engineering strategy via constructing an insulated layer (e.g. Al<sub>2</sub>O<sub>3</sub>) was introduced to precisely manipulate the interface between plasmon metal (Au) and semiconductor (rutile TiO<sub>2</sub>), which exhibits a remarkable enhancement of photocatalytic water oxidation activity compared with Au/TiO<sub>2</sub>. The resulting Au/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> photocatalyst exceeds an apparent quantum efficiency (AQE) of 1.33% at 520 nm for photocatalytic water oxidation, which is one of the highest AQE in plasmon-induced water oxidation so far. We experimentally demonstrated that the interfacial layer between Au and TiO<sub>2</sub> is of great significance in promoting interfacial charge separation of hot carriers and improving the thermodynamic driving force for water oxidation. Theoretical simulation also revealed that the interfacial layer acts as nucleation center to anchor plasmonic Au particles on TiO<sub>2</sub> surface as well as introducing interface trapping states with more deeper oxidation levels. Our work provides a new avenue towards designing highly efficient plasmonic systems for solar energy conversion and plasmon-induced optoelectronic devices.

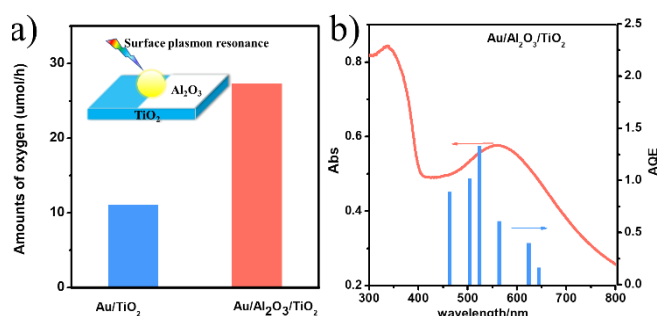


Figure 1. (a) Photocatalytic water oxidation performance of Au/TiO<sub>2</sub> and Au/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, (b) Action spectra and apparent quantum efficiency of Au/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>.

## Photoelectrochemical hydrogen peroxide production via delafossite CuFeO<sub>2</sub> photocathode

Hyo Eun Kim, Jae Sung Lee\*

*Ulsan National University of Science & Technology (UNIST), Ulsan, 44919, Republic of Korea*

Email: hyoeunkim@unist.ac.kr

Photoelectrochemical solar fuel generation is a promising strategy can get H<sub>2</sub> from water, formic acid or other carbon-based fuels from CO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> from oxygen and water in the context of global warming and energy economy. Among them, hydrogen peroxide is one of the most important chemicals in a high industrial demand. The current production of H<sub>2</sub>O<sub>2</sub> involves multi-step procedures and its production cost is high due to the use of precious-metal catalysts and high-pressure of hydrogen.

Photoelectrochemical H<sub>2</sub>O<sub>2</sub> generation via the oxygen reduction reaction (ORR) is an attractive method that enables low-cost, eco-friendly, continuous, and on-site production of H<sub>2</sub>O<sub>2</sub>. Recently, p-type CuFeO<sub>2</sub> has focused as a talented candidate photocathode for solar fuel production system as it has favorable light absorption properties, small band gap (1.5 eV), and high flat-band potential which suggests the capability to develop a high photovoltage. However, this material has poor HER and CO<sub>2</sub>R activity due to its poor charge transport and separation kinetics. Nevertheless, CuFeO<sub>2</sub> shows a cathodic current about 0.8 mA/cm<sup>2</sup> at 0.4 V versus RHE in the presence of oxygen as a sacrificial electron acceptor. From this point of view, we report that CuFeO<sub>2</sub> thin films have activity for H<sub>2</sub>O<sub>2</sub> production.

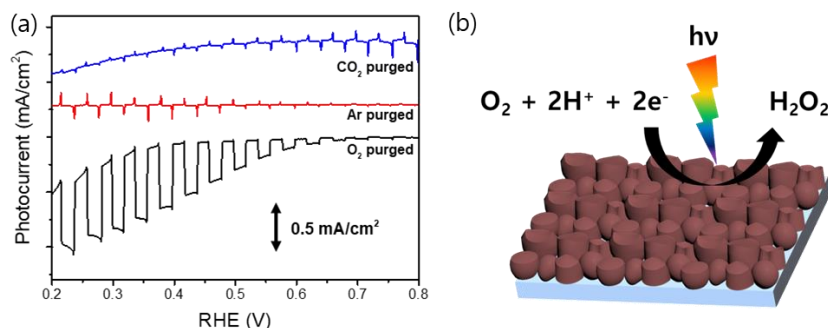


Figure 1. (a) Linear sweep voltammogram of CuFeO<sub>2</sub> electrode in 0.1 M KOH, one sun illumination (scan rate: 10 mV/s) (b) Brief schematic diagram of hydrogen peroxide production via CuFeO<sub>2</sub> photocathode

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## Effect of the interfacial defects on plasmon-induced water oxidation

Hao Li,<sup>1,2</sup> Shengyang Wang,<sup>1</sup> and Can Li<sup>1,\*</sup>

<sup>1</sup>State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian 116023, China

<sup>2</sup>University of Chinese Academy of Sciences, Beijing 100049, China

Email: canli@dicp.ac.cn

The plasmon-mediated photochemistry reaction based on the metal-semiconductor heterojunctions has been extensively researched for its efficient light capture and intriguing hot carrier transfer. In the metal-semiconductor plasmonic photocatalytic systems, the interfacial structure is vital for the charge separation and photocatalytic reaction. The interfacial defect in the metal-semiconductor heterostructure is a ubiquitous phenomenon. However, the effect of interfacial defects in the plasmonic system, especially in hole-participated water oxidation reaction is still not understood. Herein, we adopt the way of hydrogen reduction to generate oxygen vacancies at the interface of Au/TiO<sub>2</sub>. The water oxidation activity of reduced samples decreased with the increase of oxygen vacancies present in the interface, and the activity of reduced samples can restore after eliminating the defects via post-oxidation. It was elucidated that defect states in the plasmonic system caused mid-gap states below the conduction band of the TiO<sub>2</sub>. The existence of defect states enhances the charge recombination through backward electron transfer, leading to the short lifetime of hot holes which are harmful for the kinetics-sluggish water oxidation. This find highlights that the interface of plasmonic catalyst is sensitive to defect states, and the interfacial defects may play crucial roles in plasmon-induced reduction reaction and oxidation reaction.

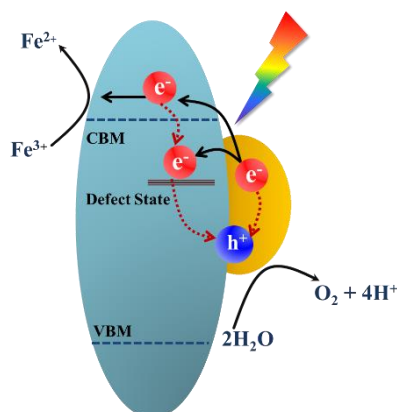


Figure 1. The OER activity of Au/Rutile and reduced Au/Rutile with different reduction temperature (Left) and the schematic diagram of charge separation and utilization in reduced Au/Rutile (Right).