

# MANA E-BULLETIN



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INTERNATIONAL CENTER FOR MATERIALS NANOARCHITECTONICS

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## FEATURE

# Making Fuel from Sunlight and CO<sub>2</sub>

## An interview with Jinhua Ye

MANA Principal Investigator,  
Group Leader of  
Photocatalytic Materials Group

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# Making Fuel from Sunlight and CO<sub>2</sub>

*An interview with Jinhua Ye, MANA Principal Investigator*

Since joining WPI-MANA in 2007, Dr. Jinhua Ye has focused on research and development of photo-functional materials and their applications in the fields of environment preservation and new energy production. In addition to her position at WPI-MANA, she is an adjunct professor of Hokkaido University, and a fellow of the Royal Society of Chemistry. Dr. Ye is a highly cited researcher, having published over 600 papers in high-quality research journals, which have been cited more than 50,000 times.

## Photo-functional materials offer a new way to combat climate change

**Thank you for meeting with us today. To start with, could you give us a rundown of your current research?**

Basically, I am studying photo-functional materials and their applications in the fields of environment preservation and new energy production. I'm developing catalysts for converting CO<sub>2</sub> into hydrocarbons, using sunlight to power the reactions. For this I am focusing on finding materials to act as catalysts for the reactions, and broadening our understanding of how to make these reactions more efficient and selective.

It's a three-step process. First we ask, "How can we absorb more light?" In particular visible light and infrared, not just UV. To do that, we need to tune the band gap of the material. If it's too wide, it will only absorb a small part of the UV light. But if it's too narrow, the generated electron hole reduction activity or oxidation activity will be limited. So we need to find some kind of compromise.

And then also, if it is to help the reaction, we need the reduction energy of this conduction band to be more negative than some reaction. On the other hand, we also need to adjust the valence band position. So we think about all these things, and then we can have a guideline for what kind of electronic structure or element is better, or what kind of crystallinity or conductivity it should have. The second step is to keep the electron and hole separated and move to the surface, so we need to have some way to create a potential gradient from the inside of the nanoparticle to the surface. We usually construct some kind of nanometer-scaled hybrid structure with a nanometal on the surface which has a larger work function to capture photoexcited electrons easily. This nanometal is called a "co-catalyst," which is the critical point in the third step: accelerate surface reaction and tune selectivity.

## Inspired by nature

**Do you ever use a biomimetic approach?**

Oh, sure. We have tried a bio-hybrid system of PS II and WO<sub>3</sub> to do artificial photosynthesis. In fact, several approaches are running in parallel right now. The photocatalytic materials we are doing are one of the major trends; photo-biocatalysis is also attracting increasing attention. Each approach has its own advantages and disadvantages, but at the moment, we cannot see that any is overwhelmingly

better than the other. But for photocatalytic materials, it's basically oxide semiconductor materials, so they are more stable and easier in terms of fabrication, cost and control.

I was recently invited to write a review paper on CO<sub>2</sub>. So I wrote on carbon recycling using sunlight. I described the possible approaches for tackling the CO<sub>2</sub> issue, and my future view of the technology. I systematically analyzed not only the efficiency, selectivity and durability of each approach, but also its cost and impact on the environment.

**Will the technology you're working on be involved in the sustainability effort? Will it make a difference?**

Reducing CO<sub>2</sub> is now a major concern around the world. We need to keep the economy rolling, but we also need to reduce CO<sub>2</sub>. There are numerous strategies to sequester the CO<sub>2</sub> such as burying it, but I think utilizing sunlight to convert the CO<sub>2</sub> into fuel is a better way. Sunlight is free, and we can utilize it to convert CO<sub>2</sub> into something useful, such as hydrocarbons or some other chemicals, for a new source of energy. We can decrease CO<sub>2</sub> and global warming and create a new form of energy -- we can accomplish two goals with one action.

**Your work on photo-functional materials has a clear relevance to MANA's Four Grand Challenges (Nano Perceptive Systems, Nanoarchitectonic Artificial Brain, Room-temperature Superconductivity and Practical Artificial Photosynthesis). As for MANA in general, what direction should the organization take?**

That is quite difficult to answer because we have lots of experts in different research areas at MANA. This diversity is a real strength of MANA, and everyone has their own research interest. Definitely, all the four Grand Challenges are very important and exciting. For me, how to utilize solar energy to produce renewable energy is my main interest, so I started working on "Practical Artificial Photosynthesis" when I joined MANA 14 years ago. I think that for MANA in general, the direction should be sustainability -- we must do work that can contribute to the realization of sustainability, in energy and other fields.

## High impact research

**You're a highly cited researcher at MANA. This must be a growing field of interest worldwide.**



It's growing very quickly. When I started in this field, I tried to fully utilize my background to bring some new ideas into the traditional catalysis field, and so I used a slightly different approach from others, so we could have some high impact results very quickly. Later on, I continued this kind of effort, so we were able to lead the field and always keep ahead of the game. We have produced a lot of high-impact work, and results published in good journals, so we get lots of citations from others in the field.

### **What sparked your interest in this field?**

I'm a big science fiction fan. I love to watch science fiction movies, over and over. When I was in elementary school, I read a novel by a Chinese science fiction writer, in which he describes a beautiful castle, all made of diamond. And this diamond is converted from graphite.

This is actually possible, though right now, the technology to do it is very limited; you couldn't build such a beautiful castle, or anything of any size. But I realized, "Oh, the same element, carbon, can have totally different properties." I think that strongly affected me and later on, I started my dream of doing scientific research to develop new materials and study phase transformations.



### **A lot of young researchers and students come here. Do you have any advice for people considering a career in this field?**

First of all, it is very important to find something you are really interested in -- something that really excites you -- and someday your dreams will come true. In my case, I started my career researching shape memory alloys and later worked on high temperature superconductors. But finally, I arrived at artificial photosynthesis, which is a dream closer to something I imagined from my childhood.

## Looking ahead

### **What are some future directions of your research?**

Right now we are coming to a good stage, I think. But, of course, we still need to have a deeper understanding of the mechanism. So we will advance and deepen our understanding at the atomic and molecular level of this catalytic reaction. Of course, we will continue to develop new materials based on this understanding of the mechanism. We will also design a prototype reactor. And in several years, I hope, we will be able to show it to the world.

### **Finally, what is your vision for the future?**

My dream is to develop a material that results in a system to convert CO<sub>2</sub> into fuel -- a machine into which we pour CO<sub>2</sub> and water, and fuel comes out the other side, powered just with sunshine. This could be a revolution -- and I hope to make it a reality someday.



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## Artificial Retinal Device Mimics Human Optical Illusions

**A team at WPI-MANA has developed the first-ever artificial retinal device that increases the edge contrast between lighter and darker areas of an image, using ionic migration and interaction within solid. The device has the potential for use in developing compact, energy-efficient visual sensing and image-processing hardware systems capable of processing analog signals.**

Recently artificial intelligence (AI) system developers have shown much interest in research on various sensors and analog information-processing systems inspired by the human senses. Most AI systems require sophisticated software and complex circuit configurations, including custom-designed processing modules. The problem with these systems is that they are large and consume much power.

The team built a multiple ionic device system, each of which had a lithium cobalt oxide channel arranged on a common lithium phosphorus oxynitride electrolyte. Because of the migration of Li-ions between the channels through the electrolyte, the devices were highly interactive, similar to human retinal neurons such as photoreceptors, and horizontal and bipolar cells. Input voltage pulses caused ions within the electrolyte to migrate across the channels, which changed the output channel current.



The device was able to process input image signals and produce an image with increased edge contrast between darker and lighter areas. This is similar to the human visual system's ability to increase edge contrast between brightness differences by means of visual lateral inhibition.

The human eye produces various optical illusions associated with tilt angle, size, color and movement, in addition to darkness/lightness, and this process is believed to play a crucial role in the visual identification of different objects. The artificial retinal device the team created could be used to reproduce these types of optical illusions. They hope to develop visual sensing systems capable of performing human retinal functions by integrating their device with other components, including photoreceptor circuits.

This research was conducted by Tohru Tsuruoka (Chief Researcher, Nanoionic Devices Group, WPI-MANA, NIMS), Kazuya Terabe (MANA Principal Investigator, Group Leader, Nanoionic Devices Group, WPI-MANA, NIMS) and their collaborator.

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Xiang Wan, Tohru Tsuruoka, and Kazuya Terabe  
"Neuromorphic System for Edge Information Encoding: Emulating Retinal Center-Surround Antagonism by Li-Ion-Mediated Highly Interactive Devices"  
Nano Letters 2021, 21, 19, 7938-7945 (13 September 2021)  
DOI : 10.1021/acs.nanolett.1c01990



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# Exfoliation of Zeolites into Solution Produces Porous Monolayers

**A pioneering study at WPI-MANA has resulted in the first direct exfoliation of zeolites into a liquid suspension of monolayers. This breakthrough provides proof of the presence of monolayers, and could lead to their use in the creation of catalysts, nanodevices, drug delivery systems and other products with tailored properties.**

Some two-dimensional (2D) materials, such as graphene, exhibit a variety of unique properties thanks to their molecular thinness and large size, as well as their 2D anisotropy. Catalysts and electrode materials that take advantage of nanosheets' high surface area are a promising field, but the 2D anisotropy prevents efficient transfer of ions and molecules within the materials. Therefore, 2D materials with through-holes are attracting attention, but so far there have been few examples of them.

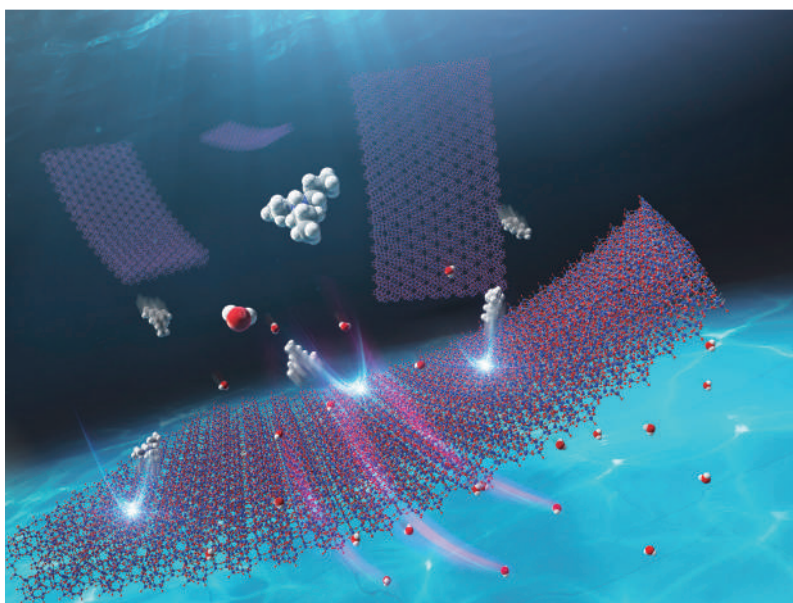
Zeolites are typical porous materials and some of them have a layered structure. So exfoliating them in a single 2D layer could result in nanosheets with a regular pore structure. Although there have been reports of the synthesis of zeolite nanosheets in trace yields, large quantities of the substance have not been obtained at a usable level.

A WPI-MANA group succeeded in synthesizing zeolite nanosheets (MWW and FER types) by exfoliating them into a single layer by greatly swelling the layered zeolite in a solution containing organic ammonium ions.

Dispersing the zeolites into liquids provides the most effective approach to their practical exploitation to fabricate materials with particular activity and functionality. The suspended layers can be deposited on supports or restacked into hierarchical structures alone or in combination with other 2D materials to produce solids with useful properties.

The exfoliation and proof of the presence of monolayers in the colloids open new possibilities of synthesizing functional hybrid and hierarchically structured materials. The researchers also made predictions about potential applications of zeolite monolayer colloids based on the anisotropic physical properties of 2D materials.

This research was conducted by Takayoshi Sasaki (MANA Principal Investigator, Group Leader, Soft Chemistry Group, WPI-MANA, NIMS) and his collaborators.



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Wieslaw J. Roth, Takayoshi Sasaki et al.  
Journal of the American Chemical Society 143, 29, 11052-11062 (15 July 2021)  
DOI : 10.1021/jacs.1c04081  
Science Advances 6 (12), eaay8163 (20 March 2020)  
DOI : 10.1126/sciadv.aay8163



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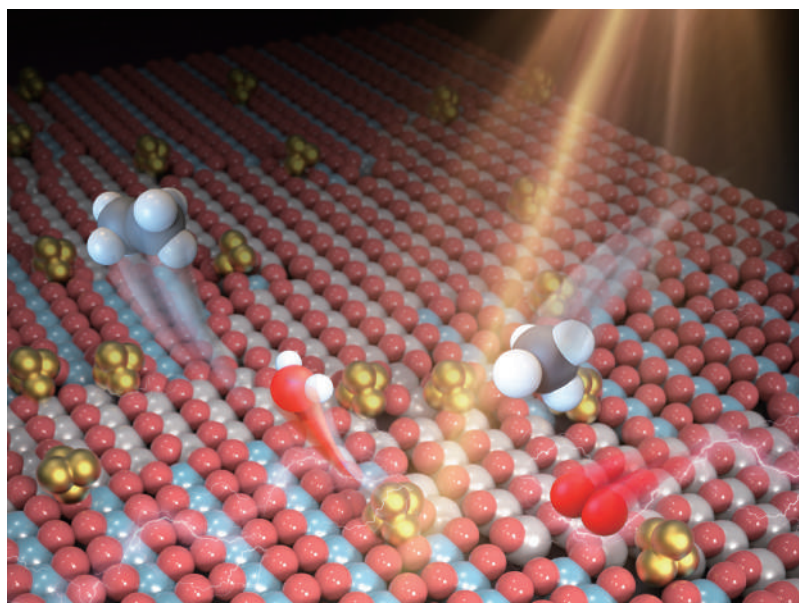
# Selective Hybrid Photocatalyst Allows Oxidative Coupling of Methane to Ethane with Dioxygen

**A team at WPI-MANA has demonstrated that methane can be efficiently and selectively oxidized to ethane with oxygen under light irradiation over an Au-ZnO/TiO<sub>2</sub> hybrid. This achievement opens the door to cheaper and more efficient production of valuable chemicals using methane as a feedstock.**

Methane (CH<sub>4</sub>), the main component of natural gas and shale gas, is not only an abundant and low-cost fuel, but also a powerful greenhouse gas with a potential 28-34 times that of CO<sub>2</sub>. Directly and selectively converting methane to value-added higher hydrocarbons or oxygenates has been attracting substantial interest from both academia and industry, and could reduce society's reliance on crude oil and contribute to carbon neutrality.

However, the high C-H bond dissociation energy and non-polar nature of methane, along with the higher reactivity of the desired products, make selective activation and conversion of methane challenging.

The WPI-MANA group designed an Au-ZnO/TiO<sub>2</sub> hybrid photocatalyst for selectively oxidizing CH<sub>4</sub> to ethane (C<sub>2</sub>H<sub>6</sub>) with oxygen (O<sub>2</sub>). This showed a high C<sub>2</sub>H<sub>6</sub> production rate with high selectivity and excellent durability, which were more than one order of magnitude higher than the state-of-the-art photocatalytic systems.



Mechanistic studies showed that the formation of ZnO/TiO<sub>2</sub> heterojunctions by precisely controlling the ratio and interface structure of ZnO/TiO<sub>2</sub> led to enhanced activity, while maintaining high selectivity owing to the weak overoxidation ability of the main component ZnO. Moreover, using Au nanoparticles as the cocatalyst not only promotes charge separation, but also facilitates methyl (CH<sub>3</sub>) species desorption to form methyl radicals, which promotes the formation of C<sub>2</sub>H<sub>6</sub> and inhibits the overoxidation of CH<sub>4</sub> to CO<sub>2</sub>.

These findings could guide the future design of photocatalysts that could transform methane to ethane with high activity and selectivity. This, along with other technologies such as new reactor designs, could provide an economically viable way to directly convert methane into ethane.

This research was conducted by Jinhua Ye (MANA Principal Investigator, Group Leader, Photocatalytic Materials Group, WPI-MANA, NIMS) and her collaborators.

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"A selective Au-ZnO/TiO<sub>2</sub> hybrid photocatalyst for oxidative coupling of methane to ethane with dioxygen"  
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DOI: 10.1038/s41929-021-00708-9



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