The Challenge to Develop an Artificial Photosynthesis Device that Fixes CO_2 Using the Sun

Yuya Uzumaki, Sayumi Sato, Akihiro Kohno, and Takeshi Komatsu

Abstract

Interest in reducing greenhouse gases, especially carbon dioxide (CO_2), as a measure against climate change is increasing not only in countries but also in companies around the world. The NTT Group has formulated a new vision for zero environmental impact and declared its intention to achieve carbon neutrality by 2040. We expect artificial photosynthesis that converts CO_2 and water (H_2O) into hydrocarbons and molecular oxygen (O_2) using solar energy to be a technology that contributes to CO_2 reduction. To introduce this technology to the market, it is necessary to improve its efficiency and durability. We propose a gas-phase CO_2 reduction reaction system to improve solar-to-hydrocarbon conversion efficiency η_{STC} and conducting basic research on electrodes that make up this system. We studied a nickel oxide/indium gallium nitride (NiO/InGaN) photoanode to achieve both high efficiency and long lifetime. We also studied a copper (Cu)-fiber cathode to improve efficiency. In our system using these electrodes, formic acid (HCOOH) was produced in 140 hours of continuous light irradiation, resulting in an η_{STC} of 0.16%.

Keywords: CO_2 reduction, renewable energy, GaN

1. Introduction

Climate-change awareness is growing worldwide, even with the COVID-19 pandemic. In 2021, the World Economic Forum reported that both the likelihood and expected impact of environmental risks, for example, climate-action failure, extreme weather, and biodiversity loss, are greater than those of economic, geopolitical, societal, or technological risks [1]. Greenhouse gas reduction in particular is being promoted as a measure against climate change. Japan announced at COP26* that in 2030 it will have reduced its greenhouse gas emissions by 46% from those in 2013 and by 2050 will have become a carbon-neutral society. Therefore, in Japan, renewable energies, such as solar power, wind power, geothermal power, small and medium-sized hydropower, and biomass conversion, are attracting increasing interest as promising and diverse energy sources. The NTT Group has formulated a new vision called "NTT Green Innovation Toward 2040" for achieving zero environmental impact through the combination of increasing the use of renewable energy and decreasing energy consumption with IOWN (Innovative Optical and Wireless Network) technologies.

Our team is conducting basic research on *artificial photosynthesis* to contribute to carbon dioxide (CO_2) reduction. Artificial photosynthesis is a technology that converts CO_2 and water (H_2O) into hydrocarbons (formic acid (HCOOH), methane (CH_4), alcohols, etc.) and molecular oxygen (O_2) using solar energy. Currently, CO_2 capture and storage is expected to reduce CO_2, but it is a large-scale system and its

* COP26: The 26th session of the Conference of the Parties to the United Nations Framework Convention on Climate Change.

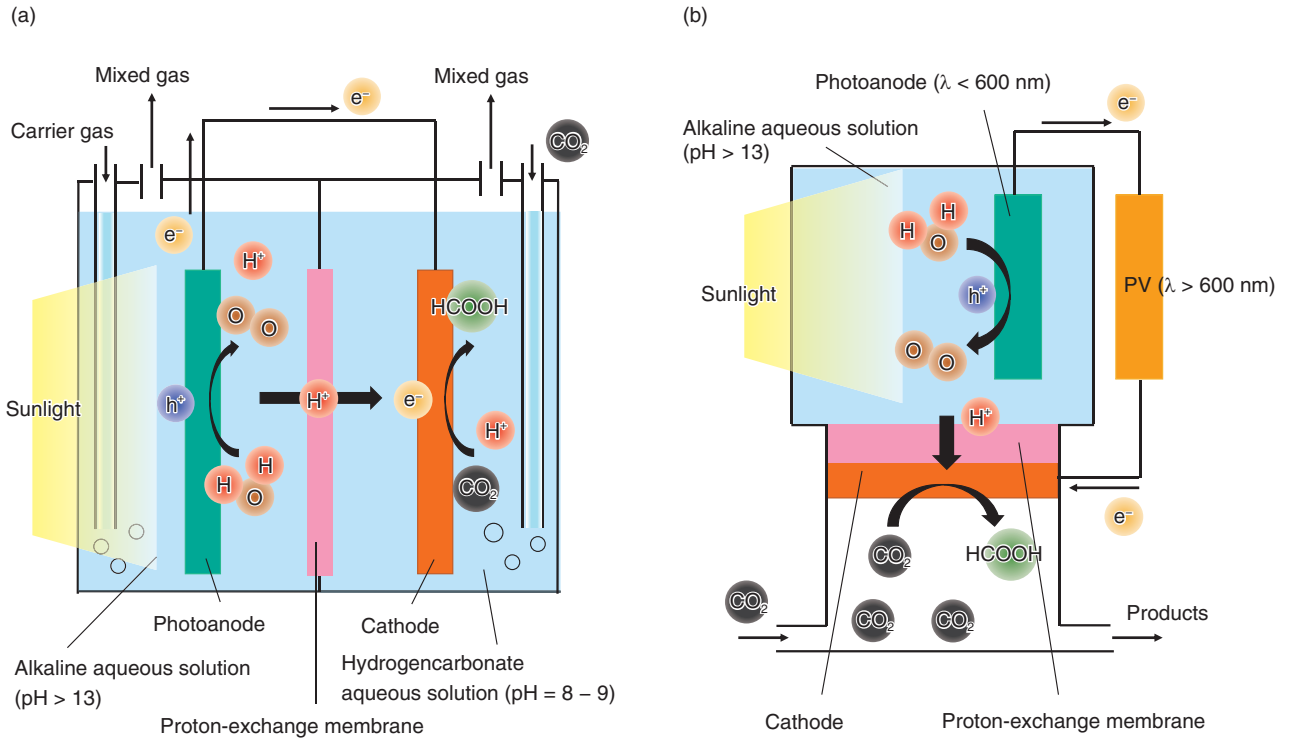


Fig. 1. Schematic illustrations of artificial photosynthesis systems: (a) conventional system using dissolved CO_2 as a reaction material, (b) our system using gas-phase CO_2 as a reaction material.

installation location is limited, especially in Japan. Artificial photosynthesis, which has scalability and is driven by sunlight, is expected to be a new method for CO_2 reduction. With the development of artificial photosynthesis technology, we envision that artificial photosynthesis systems can be attached to buildings, vehicles, etc. to fix CO_2 from the atmosphere, resulting in a more sustainable society.

2. Artificial photosynthesis for CO_2 reduction

An artificial photosynthesis system is mainly composed of a photoanode (negative electrode), cathode (positive electrode), and proton-exchange membrane (electrolyte), as shown in **Fig. 1(a)**. When the photoanode, which is a semiconductor called a photocatalyst, is irradiated with light having an energy larger than the band-gap energy of the semiconductor, electron-hole pairs are generated in the semiconductor, resulting in an oxidation-reduction (redox) reaction. The principle of this system is based on the Honda-Fujishima effect [2]. When high-concentration CO_2 gas is supplied to this system and light is applied to the photoanode, a water-oxidation reaction and CO_2-reduction reactions can proceed as follows:

Oxidation reaction: $2H_2O + 4h^+ \rightarrow O_2 + 4H^+$,
Reduction reactions:
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$,
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$,
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$,
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$,
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$.

The target performance for market introduction is 10% solar-to-hydrocarbon conversion efficiency η_{STC} and 10-year durability in the 2030s. The η_{STC} of CO_2-reduction reactions is written as follows:

$$\eta_{STC} = \{(n_{HCOOH} \times Q_{HCOOH}) + (n_{CO} \times Q_{CO}) + \cdots\} / (\text{solar energy}) \times 100\%,$$

where n is the amount of product and Q is the heat of formation. Some research institutes have achieved an efficiency of 10% [3], but most teams have achieved percentages less than that. In addition, no research institute has reported that both efficiency and durability are compatible. Achieving both high efficiency

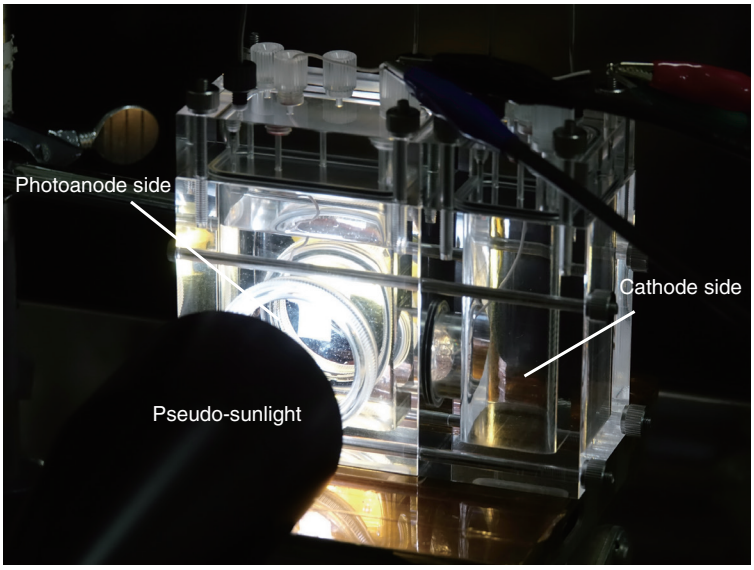


Fig. 2. Light irradiation experiment in our laboratory (photoanode area = 1 × 1 cm^2).

and long lifetime of artificial photosynthesis systems is therefore an important issue in research and development.

To improve the η_{STC}, it is important to increase the Faradaic efficiency of the CO_2-reduction reaction by increasing the CO_2 supply to the reaction area for suppressing the side-reaction ratio [$H^+ + e^- \rightarrow H_2$]. The Faradaic efficiency is the ratio of the number of electrons consumed in the objective reaction to that generated in the photoanode. Even if many electrons are generated in the photoanode, if the CO_2 supply is insufficient at the surface of the cathode, they will be consumed as the side reaction proceeds. In the conventional reaction system shown in Fig. 1(a), CO_2 is dissolved in an aqueous solution and supplied to the reaction area on the surface of the cathode. The amount of CO_2 supplied is limited by the solubility and diffusion coefficient of CO_2 in the solution, and it is difficult to suppress the side reaction.

We propose a gas-phase CO_2-reduction reaction system to solve this issue, as shown in **Fig. 1(b)**. It is easier to increase the concentration and diffusion coefficient of CO_2 in the gas phase than it is to increase them in the dissolved phase. Thus, this system can increase the CO_2 supply to the reaction area and improve the Faradaic efficiency of CO_2-reduction reactions. In addition, a photovoltaic (PV) power generator that uses the light transmitted through the photoanode is connected in series to increase the photocurrent by applying a voltage corresponding to the overvoltage (**Fig. 2**). We are conducting basic research to improve the η_{STC} and lifetime, focusing on the materials and structures of the photoanode and cathode.

2.1 NiO/GaN-based photoanode

The photoanode in an artificial photosynthesis system generates electrons for the proton and CO_2-reduction reactions and generates holes for the water-oxidation reaction. The surface of the photoanode is also a water-oxidation reaction area. We focus on a gallium-nitride (GaN)-based photoanode [4]. The band-gap energy of GaN is 3.4 eV, and the top of the valence band is lower than the oxidation potential of water, and the bottom of the conduction band is higher than the reduction potential of protons and CO_2 (**Fig. 3**). An aluminum gallium nitride (AlGaN)/silicon (Si)-doped GaN (n-GaN) heterostructure and indium gallium nitride (InGaN)/n-GaN heterostructure can improve the η_{STC} because of enhanced electron-hole separation due to the large polarization field in AlGaN and enhanced electron-hole generation due to the wide absorbable wavelength range in InGaN. Thus a GaN-based photoanode is expected to generate O_2 and hydrocarbons. However, there are still issues with improving the η_{STC} and durability toward the target performance.

To improve the η_{STC}, we investigated how to increase the light absorption of the photoanode material. Indium gallium nitride is a mixed crystal of GaN

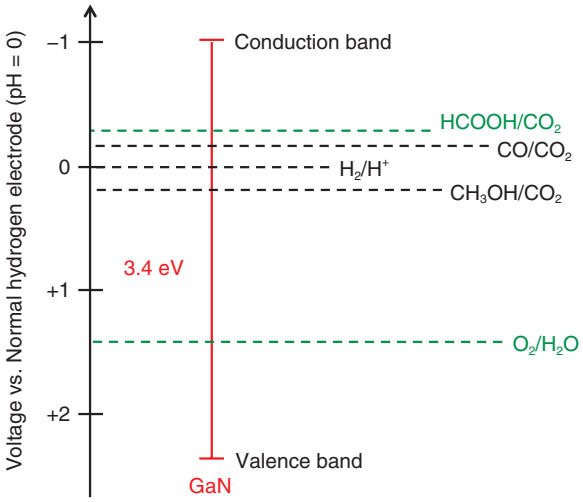


Fig. 3. Band-gap of GaN and redox-reaction level of CO_2-reduction reactions using water as an electron source.

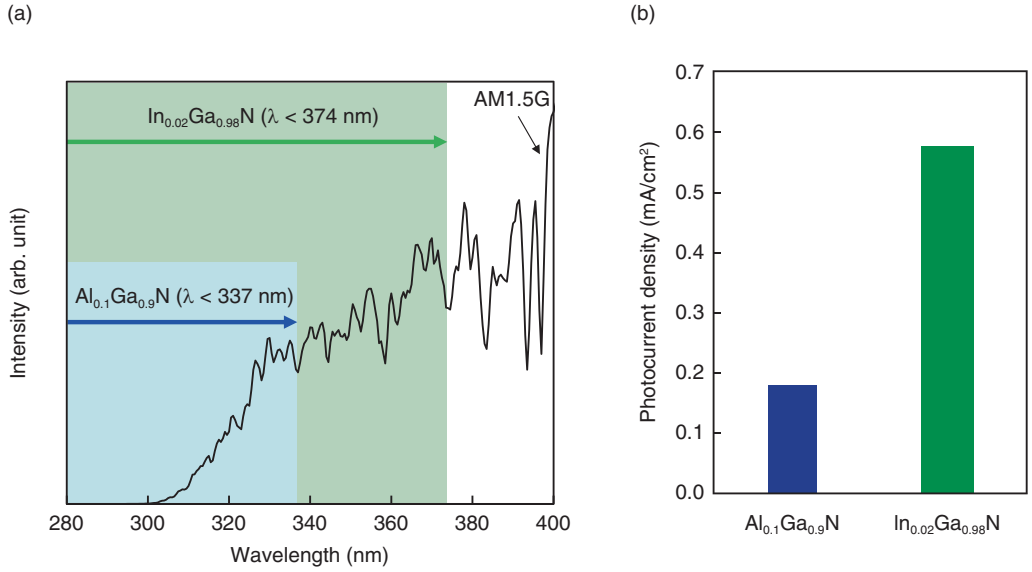


Fig. 4. (a) Theoretical absorption wavelength ranges of $In_{0.02}Ga_{0.98}N$ and $Al_{0.1}Ga_{0.9}N$ with the solar spectrum (AM1.5G) and (b) photocurrent densities measured using $In_{0.02}Ga_{0.98}N$ and $Al_{0.1}Ga_{0.9}N$ photoanodes 1 min after light irradiation.

and indium nitride (InN), and its band-gap energy can be adjusted by changing its In composition. Therefore, as shown in **Fig. 4(a)**, InGaN can use a wider wavelength range for the redox reaction than AlGaN. We prepared an $In_{0.02}Ga_{0.98}N$ photoanode by growing an $In_{0.02}Ga_{0.98}N$/n-GaN heterostructure on a sapphire substrate. We measured the photocurrent in the hydrogen (H_2)-production system, which is the simplest reduction-reaction system using platinum (Pt) as a cathode, under pseudo-sunlight irradiation. The photocurrent density, which is photocurrent per unit light-irradiation area, measured using a 100-nm-thick $In_{0.02}Ga_{0.98}N$ photoanode, was higher than that measured using a 100-nm-thick $Al_{0.1}Ga_{0.9}N$ photoanode (**Fig. 4(b)**) [5]. This suggests that expanding the wavelength range increases the photocurrent and that narrowing the band-gap energy of the photoanode material can further increase the photocurrent. We

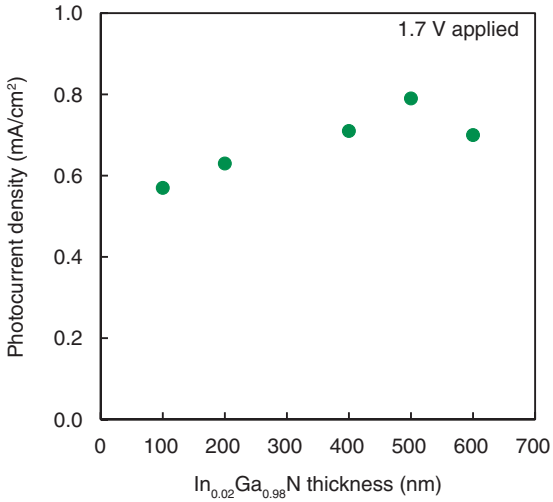


Fig. 5. Photocurrent-density dependence on $In_{0.02}Ga_{0.98}N$ layer thickness 1 min after light irradiation.

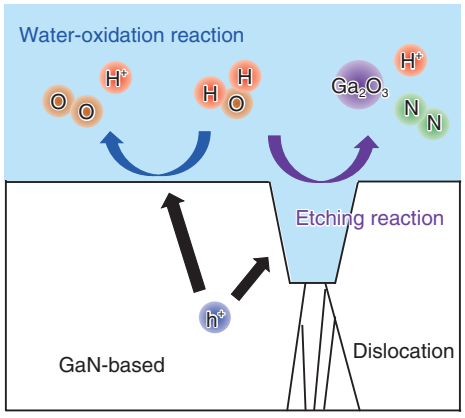


Fig. 6. Schematic illustration of etching process of GaN-based photoanode.

also studied the photoanode structure to further increase light absorption. The light absorption of an $In_{0.02}Ga_{0.98}N$ layer increases with increasing layer thickness because of decreasing light transmittance. **Figure 5** shows the dependence of photocurrent density on $In_{0.02}Ga_{0.98}N$-thickness in an H_2-production system to which 1.7 V was applied under pseudo-sunlight irradiation [6]. The photocurrent density increased with increasing $In_{0.02}Ga_{0.98}N$ thickness, and the maximum density was at 500 nm. Increasing the $In_{0.02}Ga_{0.98}N$ thickness increases the photocurrent density by increasing the amount of electron-hole pairs. It also promotes electron-hole pair recombination caused by the lattice defects in $In_{0.02}Ga_{0.98}N$, thus reducing the photocurrent density. It is thought that the photocurrent density maximized at 500 nm due to the balance between increasing and decreasing the amount of electron-hole pairs.

To improve durability, we investigated how to prevent the etching reaction [$2GaN + 3H_2O + 6h^+ \rightarrow Ga_2O_3 + 6H^+ + N_2$]. The etching reaction is driven by holes generated in GaN-based photoanodes and continues at the interface between the GaN and aqueous solution, as shown in **Fig. 6**. As this reaction progresses, electron-hole pair recombination is promoted by the decrease in the crystallinity of GaN, thus, decreasing the photocurrent. We therefore formed a protective layer on the GaN-based photoanode to eliminate the interface between the GaN and aqueous solution [7, 8]. Nickel oxide (NiO), which is known to transport holes, was used for the protective layer. The thin film of NiO, about 2 nm thick, was formed to sufficiently transmit light. The reaction using NiO/InGaN photoanodes continued for about 20 hours, even though that using bare-InGaN photoanodes had been inactivate for several hours. We also studied the photoanode structure to find how to further suppress the etching reaction [9, 10]. The etching reaction continues with dislocations near the InGaN surface as the starting point. Thus, we prepared a photoanode with reduced dislocations by growing an $In_{0.02}Ga_{0.98}N$/n-GaN heterostructure on a GaN substrate instead of a sapphire substrate, as shown in **Fig. 7(a)**. The dislocation density of the $In_{0.02}Ga_{0.98}N$/n-GaN heterostructure estimated from the full width at half maximum measured with an X-ray rocking curve decreased by an order of magnitude, and the surface roughness also improved. The stability of the photocurrent improved significantly, and the reaction continued for over 100 hours, as shown in **Fig. 7(b)**.

2.2 Metal-fiber cathode on proton-exchange membrane

The cathode catalyzes the CO_2-reduction reaction. Some metals have been reported to catalyze CO_2-reduction reactions, and it is known that the type of hydrocarbons produced differs depending on the type of metal. In our gas-phase CO_2-reduction system, the CO_2-reduction reaction continues in a triple-phase-boundary, as shown in **Fig. 8(a)** [11]. Therefore, it is also necessary to control the CO_2 diffusivity in the cathode to increase the amount of CO_2 supplied to the triple-phase boundary. When the cathode was formed on the proton-exchange membrane by using the plating method, the H_2-generation reaction was dominant

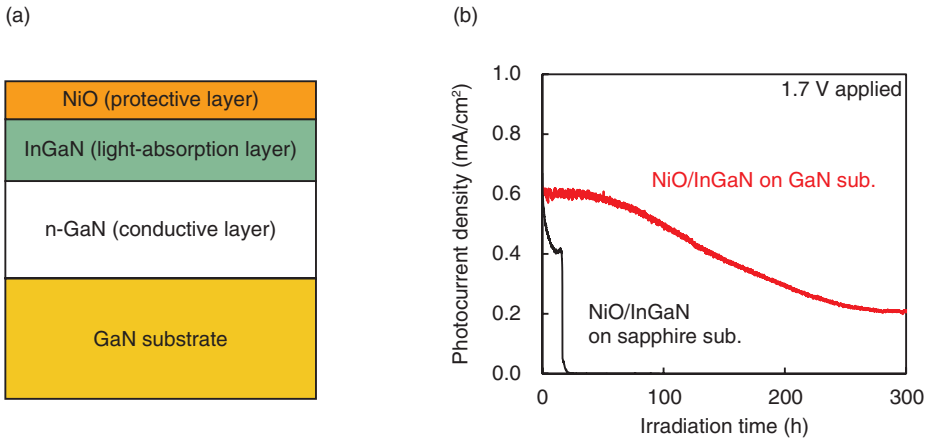


Fig. 7. (a) Structure of NiO/$In_{0.02}Ga_{0.98}N$ photoanode and (b) photocurrent densities in H_2-production system of NiO/$In_{0.02}Ga_{0.98}N$ photoanodes grown on GaN and sapphire substrates. Values obtained with 1.7 V applied under pseudo-sunlight irradiation.

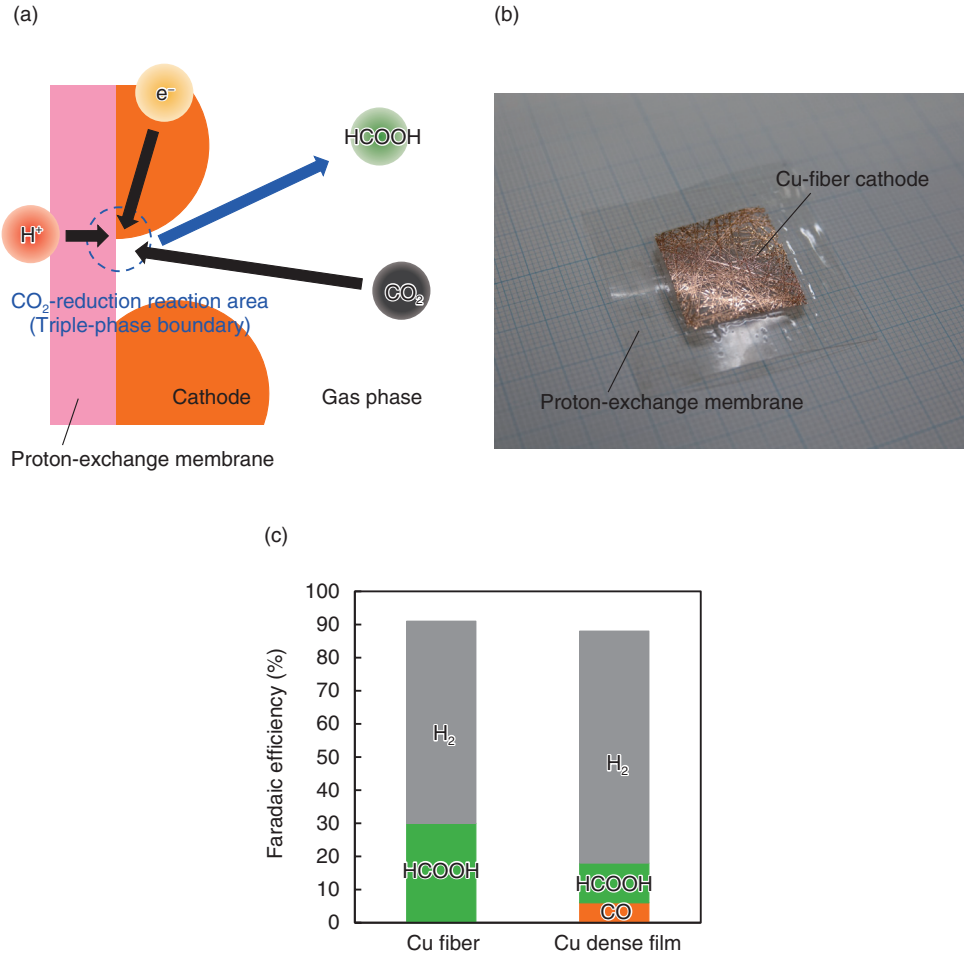


Fig. 8. (a) Schematic illustration of gas-phase CO_2-reduction reaction process at the triple-phase boundary as the reaction area, (b) appearance of Cu-fiber cathode on proton-exchange membrane, and (c) Faradaic efficiency of each product obtained using Cu-fiber and Cu-dense cathodes and a NiO/$Al_{0.1}Ga_{0.9}N$ photoanode.

and η_{STC} was low. This was because the CO_2 supply to the triple-phase boundary was insufficient due to the dense electrode.

To improve the η_{STC}, we studied the metal structure to increase CO_2 diffusivity in the cathode. Gas diffusivity generally depends on the porosity in the electrode. Thus, we focused on a metal-fiber structure with a large void easily controlled by changing the fiber diameter. The metallic fiber is formed on the proton-exchange membrane with a hot press under a condition that maintains the fiber structure, as shown in **Fig. 8(b)** [12]. **Figure 8(c)** shows the Faradaic efficiency of each product obtained using the copper (Cu) fibers and Cu dense film as the cathode in our gas-phase CO_2-reduction reaction system. In this system, HCOOH was mainly generated in the CO_2-reduction reaction and H_2 was also generated as a by-product. The Faradaic efficiency of HCOOH obtained using the Cu-fiber cathode improved compared with that of HCOOH and CO obtained using a Cu-dense-film cathode.

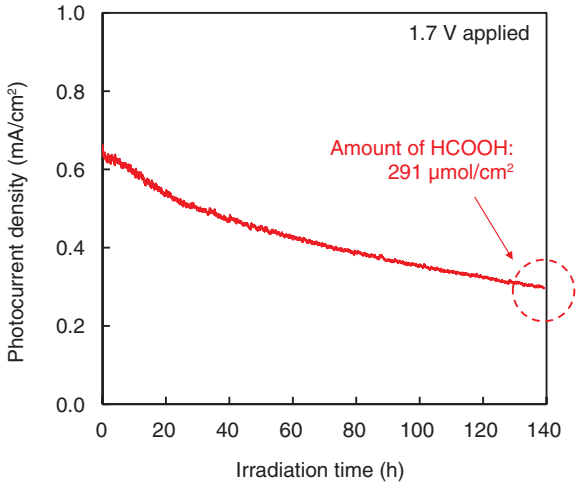


Fig. 9. Photocurrent density using NiO/$In_{0.02}Ga_{0.98}N$ photoanode and Cu-fiber cathode in our gas-phase CO_2-reduction system with 1.7 V applied under pseudo-sunlight irradiation.

2.3 Gas phase CO_2-reduction reaction using NiO/InGaN photoanode and Cu-fiber cathode

We conducted photoelectrochemical measurement using a NiO/$In_{0.02}Ga_{0.98}N$ photoanode grown on a GaN substrate and a Cu-fiber cathode on a proton-exchange membrane in our gas-phase CO_2-reduction reaction system. As shown in **Fig. 9**, the photocurrent density with 1.7 V applied decreased to about half the initial value after 140 hours of light irradiation. The reduction products were HCOOH and H_2. The amount of HCOOH produced 1 and 140 hours after beginning light irradiation were respectively 3.79 and 291 μmol. The η_{STC} and Faradaic efficiency of HCOOH 1 hour after beginning irradiation were respectively 0.25 and 28%, and the average η_{STC} and Faradaic efficiency of HCOOH 140 hours after beginning irradiation were respectively 0.16 and 24%. The amount of fixed carbon per unit light-irradiation area calculated using the chemical reaction formula for HCOOH production was 3.5 mg/cm^2.

3. Conclusion

We proposed the gas-phase CO_2 reduction system to improve the solar-to-hydrocarbon conversion efficiency η_{STC} of artificial photosynthesis. Focusing on the materials and structures of the photoanode and cathode in this system, we are conducting basic research to improve its characteristics. We studied an InGaN photoanode and its thickness to improve the η_{STC} by increasing the light absorption. We also studied a NiO protective layer and lower dislocations of InGaN to improve durability by suppressing the etching reaction of InGaN.

We studied a metal-fiber cathode for improving the η_{STC} by increasing CO_2 diffusivity in the cathode. Using our gas-phase CO_2-reduction reaction system with a NiO/InGaN photoanode grown on GaN substrate and Cu-fiber cathode, HCOOH was produced in 140 hours of continuous light irradiation, and the η_{STC} was 0.16%. For future work, we will study the combining PV as the visible-light response elements with our system for improving the η_{STC} and the system design for improving durability. We aim to achieve CO_2-fixation performance better than that of a plant.

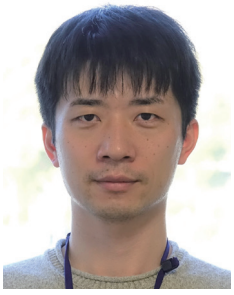
References

[1] World Economic Forum, "The Global Risks Report 2021, 16th Edition," 2021.
[2] A. Fujishima and K. Honda, "Electrochemical Photolysis of Water at a Semiconductor Electrode," Nature, Vol. 238, pp. 37–38, 1972.
[3] N. Kato, Y. Takeda, Y. Kawai, N. Nojiri, M. Shiozawa, S. Mizuno, K. Yamanaka, T. Morikawa, and T. Hamaguchi, "Solar Fuel Production from CO_2 Using a 1 m-square-sized Reactor with a Solar-to-formate Conversion Efficiency of 10.5%," ACS Sustainable Chem. Eng., Vol. 9, pp. 16301–16037, 2021.
[4] M. Deguchi, S. Yotsuhashi, H. Hashiba, Y. Yamada, and K. Ohkawa, "Enhanced Capability of Photoelectrochemical CO_2 Conversion System Using an AlGaN/GaN Photoelectrode," Jpn. J. Appl. Phys., Vol. 52, 08JF07, 2013.
[5] Y. Uzumaki, Y. Ono, K. Kumakura, and T. Komatsu, "Electrochemical Properties of Water Splitting Reaction with NiO/$In_xGa_{1-x}N$/n-GaN

Photoanodes," The 85th Electrochemical Society of Japan Spring Meeting, 1Q22, 2018 (in Japanese).
[6] Y. Uzumaki, S. Sato, A. Kohno, and T. Komatsu, "Photoelectrochemical Properties in Water Splitting Reaction Using NiO/InGaN Photoanodes with Different InGaN Layer Thickness," The 89th Electrochemical Society of Japan Spring Meeting, 1B15, Mar. 2022 (in Japanese).
[7] Y. Ono, Y. Uzumaki, K. Kumakura, and T. Komatsu, "Photoelectrochemical Properties of AlGaN/n-GaN Photoanode with NiO Layer," Proc. of 2017 International Conference on Artificial Photosynthesis, pp. 4–17, 2017.
[8] Y. Uzumaki, Y. Ono, K. Kumakura, and T. Komatsu, "Impedance Analysis of Water Oxidation Reaction with NiO Thin Film/GaN-based Photoanode," The Electrochemical Society of Japan Fall Meeting, 1L32, 2017 (in Japanese).
[9] Y. Uzumaki, S. Sato, Y. Ono, K. Kumakura, and T. Komatsu, "Suppression of Degradation of Artificial Photosynthesis System Using GaN-based Thin Film with Different Dislocation Densities as Photoanodes," The Electrochemical Society of Japan Fall Meeting, 1B06, 2019 (in Japanese).
[10] Y. Uzumaki, S. Sato, Y. Ono, K. Kumakura, and T. Komatsu, "Stability of GaN-based Photoanode for Water Splitting Reaction under Light Irradiation for 300 h," International Conference on Artificial Photosynthesis, P1–61, 2019.
[11] S. Sato, Y. Uzumaki, Y. Ono, and T. Komatsu, "Photoelectrochemical Gas-phase CO_2 Reduction Reaction on Cu Cathode Formed on Proton Exchange Membrane," International Conference on Artificial Photosynthesis, P1–55, 2019.
[12] S. Sato, Y. Uzumaki, A. Kohno, and T. Komatsu, "Photoelectrochemical CO_2 Reduction Reaction with Cu Fiber Electrodes on Proton Exchange Membrane," The 89th Electrochemical Society of Japan Spring Meeting, 1B14, Mar. 2022 (in Japanese).

Yuya Uzumaki
Researcher, NTT Device Technology Laboratories.
He received a B.E. and M.E. in environmental studies from Tohoku University, Miyagi, in 2012 and 2014. He joined NTT Energy and Environment Systems Laboratories in 2014, where he started research and development of a backup system with a combination of power-generating units. He is currently with NTT Device Technology Laboratories, where he is engaged in the research and development of an artificial photosynthesis system for achieving zero environmental impact. His research interests include electrochemical analysis and electrode material and structural design. He is a member of the Electrochemical Society of Japan (ECSJ).

Sayumi Sato
Researcher, NTT Device Technology Laboratories.
She received a B.E. and M.E. in physics from Waseda University, Tokyo, in 2015 and 2017. She joined NTT Device Technology Laboratories in 2017, where she is engaged in the research and development of an artificial photosynthesis system. Her current interests are catalyst for redox reaction and electrode structural design. She is a member of ECSJ.



Akihiro Kohno
Research Engineer, NTT Device Technology Laboratories.
He received a B.E. and M.E. in applied chemistry from Tohoku University, Miyagi, in 2008 and 2010. He joined NTT Energy and Environment Systems Laboratories in 2010 and studied image-restoration algorithms for application to the growth of microalgae. He is currently engaged in the research and development of an artificial photosynthesis system at NTT Device Technology Laboratories. He is a member of the Institute of Electronics, Information and Communication Engineers (IEICE) and the Japan Society of Applied Physics (JSAP).

Takeshi Komatsu
Project Manager, Social Device Technology Laboratory, NTT Device Technology Laboratories.
He received a B.S. and M.S. in physics from Yokohama City University, Kanagawa, and Ph.D. in engineering from Nagaoka University of Technology, Niigata, in 1996, 1998, and 2007. He joined NTT in 1998 and until 2010 conducted research on fuel cells, in particular, a solid-oxide fuel cell. He was with the NTT Environmental Protection Office from 2010 to 2013. He was transferred to NTT Device Technology Laboratories in 2013, where he is currently working on the development of social device technologies that will revolutionize the user experience and overcome social challenges predicted from social trends, such as energy and environment, smart healthcare, and advanced infrastructure maintenance. He is a member of ECSJ.