Research Article

Photoelectrochemical CO₂ Conversion to Hydrocarbons Using an AlGa_N/Ga_N-Si Tandem Photoelectrode

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We report on a qualitatively improved photoelectrochemical CO₂ reduction system which makes it possible to convert CO₂ into hydrocarbons. The key is the tandem photoelectrode, which consists of AlGa_N/Ga_N and Si device with p-n junction. The Si device is located on the back of AlGa_N/Ga_N structure and acts as activation layer that raises cathode potential. Use of a Cu cathode results in change of the main reaction products from CO and HCOOH to hydrocarbons such as CH₄ and C₂H₄. The energy conversion efficiency to hydrocarbons from CO₂ is estimated to be 0.046% under irradiation with concentrated solar light.

1. Introduction

The consumption of fossil fuels, which has been increasing exponentially since the early 20th century, is resulting in a rising concentration of carbon dioxide (CO₂) in the atmosphere and is raising the risk of an economic crisis striking when conventional energy sources run out. To solve these two problems, there has been a great deal of research into how to reduce CO₂ emissions, such as by energy-saving or carbon capture and storage. However, no matter by how much CO₂ emissions can be reduced, the problem of eventual depletion of fossil fuels remains. At present, despite intensive efforts, it is still not possible to produce enough renewable energy to support human activities.

Photocatalytic energy conversion is one of the most intensively researched fields for producing renewable energy. Since photocatalytic water splitting was discovered, numerous photocatalysts have been synthesized for hydrogen production [1–5]. In photocatalytic reactions, the key is to design the band-gap structure of the photocatalyst to deliver the reaction energies needed for water splitting.

Another important photocatalytic reaction is CO₂ reduction: it would enable us to reduce CO₂ and produce carbon-based fuels simultaneously and thus would be a major step towards reducing and recycling CO₂. However, a higher

cathode energy is necessary for CO₂ reduction than for H₂O reduction, and it also involves water oxidation as a counterreaction. Because of the challenging nature of the process, there are far fewer research reports on this subject than those on hydrogen generation [6–11].

The authors have reported that the problem of high cathode potential required for CO₂ reduction can be solved by using gallium nitride (Ga_N) as a photoelectrode [12, 13]. Ga_N is one of the few materials that can create excited electron-hole pairs with sufficient energy for CO₂ reduction and water oxidation, which means it can be operated with no extra bias input or need for sacrificial materials. Recent research has established that the efficiency of the Ga_N photoelectrode can be considerably enhanced by creating an AlGa_N/Ga_N heterostructure in which the main reaction product is formic acid (HCOOH) [14, 15].

Although HCOOH could be used as a renewable energy source, ideally CO₂ should be converted to conventional fuels, such as hydrocarbons and alcohols. There are two requirements for realizing a conversion from CO₂ to hydrocarbons. One is to raise the cathode potential sufficiently to promote a reaction with multiple electrons and protons, which is necessary for converting CO₂ to methane. The other is to adopt a cathode catalyst that is able to drive such a complicated reaction.

For this purpose, to raise the cathode potential, we adopted a tandem structure comprising a photoelectrode with multilayered nitride semiconductors and a Si p-n junction. The Si p-n junction has the role of increasing the cathode potential via the photovoltaic effect. The increased cathode potential achieved by adopting a copper (Cu) electrode as the cathode also creates a qualitative difference. Cu is a CO_2 conversion catalyst whose reaction products vary considerably according to the cathode potential [16, 17]. We succeeded in changing the main reaction products from carbon monoxide (CO) and HCOOH to hydrocarbons such as methane (CH_4) and ethylene (C_2H_4).

2. Materials and Methods

The photoelectrode presented in this study consists of a tandem structure comprising an AlGaN/GaN region and Si with p-n junction as shown in Figure 1. The AlGaN/GaN region was unintentionally doped (uid-) AlGaN and highly Si-doped n^+ -GaN thin film layers grown epitaxially on a conductive GaN substrate: the same structure as described in our previous study [15]. It should be noted that the present study employs a GaN substrate to realize a vertical device with an Si p-n junction. The uid-AlGaN layer plays a role in the efficient conversion of photons to electron-hole pairs that are needed to trigger chemical reactions. This heterostructure appears to show electric polarization in the uid-AlGaN layer, which makes electron-hole separation more effective [14]. NiO co-catalysts are also supported on the GaN in the same manner as described in a previous report [18].

The Si with p-n junction described in Figure 1 is constructed by applying amorphous Si films to an n-Si single-crystal substrate that converts energy from light to electricity. The Si with p-n junction utilizes the light transmitted from the AlGaN/GaN region. The role of Si with p-n junction is to raise the cathode potential using the photovoltaic effect. The cyclic voltammetry measurements of the cathode suggest that the cathodic current should increase when the cathode potential is raised.

Two 300 W xenon arc lamps (Asahi Spectra) with spectroscopic mirrors were focused through quartz optical fibers onto the surface of the photoelectrode. The irradiation area was 9 cm^2 . Each lamp was fitted with UV- and VIS-mirrors and the power was appropriately tuned to imitate that of the real sun. The spectrum of the light used in the present study is shown in Figure 2 together with the spectrum of AM 1.5 (1-SUN, 100 mW/cm^2) for comparison. Although wavelengths over 800 nm are attenuated due to the VIS-mirror, in this paper we define this spectrum as 1-SUN. The efficiency calculated in the latter discussion is based on measurements under the light spectrum described in this Figure 2.

The reaction products of CO_2 conversion include liquid components, such as formic acid and alcohols. To completely prevent these liquid components from following inverse reactions, we used an H-type reactor to separate the cathode and anode by means of a cation exchange membrane (Dupont Nafion 117) that blocks electrolytic intercommunication. The electrons, excited by light illumination on the photoelectrode,

FIGURE 1: The photoelectrode structure, consisting of an AlGaN/GaN region and Si with p-n junction.

FIGURE 2: Spectrum of irradiated light (comparison with AM 1.5).

move to the cathode where they drive the CO_2 reduction reactions. Here, a Cu plate (Nilaco, 99.9999%) was chosen as the cathode for CO_2 reduction, while the photoelectrode was placed at the anode.

The Cu electrode was immersed in 1.0 or 3.0 M KCl electrolyte on the cathode side, and the uid-AlGaN/ n^+ -GaN photoelectrode was immersed in 5.0 M NaOH electrolyte on the anode side. Each electrolyte was selected so as to promote the reactions on each electrode. The photoelectrode is a 2-inch circular device while the surface area of the cathode metal is an 0.8 inch-diameter circle. The cathode and anode were electrically connected via an ammeter.

The cell for the cathode was hermetically sealed, and CO_2 was introduced into the electrolyte by gas bubbling before photoelectrolysis. After the photoelectrochemical reduction, the gas and liquid samples were analyzed using gas and liquid chromatography, respectively. Hydrogen (H_2) was determined using a thermal conductivity detector (TCD); and CO, CH_4 , C_2H_4 , and ethane (C_2H_6) were determined

FIGURE 3: Ratio of products in the photoelectrochemical CO₂ reduction under 8-SUN: (a) without the Si device; (b) with Si device.

using a flame ionization detector (FID) attached to a gas chromatograph (GL Sciences GC-4000). Liquid chromatography was used for detecting HCOOH (Shimadzu LC-2010). Alcohol components such as C₂H₅OH were detected by gas chromatography (Shimadzu GC-17A) connected by a headspace sampler (PerkinElmer Turbomatrix HS40).

3. Results and Discussions

We show the change in the reaction products in the photoelectrochemical CO₂ reduction in Figure 3, with the Si with p-n junction adopted. This result was obtained under 3.0 M KCl electrolyte and 8 × 1-SUN (8-SUN). The production of hydrocarbons (CH₄, C₂H₄) and alcohol (C₂H₅OH) was confirmed after adopting the Si p-n junction, whereas they appeared only in minute quantities in the previous study. The difference in the distribution of reaction products was consistent with the change in the cathode potential from -1.47 V versus Ag/AgCl to -1.74 V versus Ag/AgCl.

The energy conversion efficiency was estimated to be 0.034% under concentrated sunlight and reached 0.046% in case of 1.0 M KCl electrolyte. Here, the denominator for the estimation is 800 mW/cm² (8-SUN) and the numerator is the sum of energies for hydrocarbons (CH₄ and C₂H₄). As discussed above, the energy of the light we used is lower than real sunlight, especially at over 800 nm, which means that it is unlikely to be an overestimate.

This result also confirms that concentrated sunlight effectively raises the cathode potential. To realize hydrocarbon production under real sunlight, we constructed a photoelectrochemical CO₂ conversion system with a lens and a tracking system for concentrating the sunlight. A picture of the system is shown in Figure 4(a). A 30 cm-square Fresnel lens is set in front of the photochemical cell. The measurement was carried out in July in Kyoto, Japan. The photocurrent between anode and cathode was measured during the experiment

(a)

(b)

FIGURE 4: (a) Picture of outdoor experiment. (b) Time course of photocurrent during the measurement.

and is shown in Figure 4(b). On the day, the reaction was often interrupted by passing clouds; however, sufficient photocurrent was observed through measurement of the accumulated electric charges in the system. After 4 hours of photoelectrolysis, the accumulated electric charge was 104 C, and the measurements made using the gas chromatograph showed 285.3 ppm of methane and 251.8 ppm of ethylene, showing that approximately 0.74 μmol of hydrocarbons were generated from CO₂ using real sunlight.

4. Conclusions

We have shown that Si with p-n junction brings about not only a quantitative but also a qualitative improvement in the CO₂ photoelectrochemical system. The idea of using a p-n junction as the back surface of a photoelectrode has been discussed in several reports on hydrogen generation [19, 20]. Those results show its outstanding efficiency for producing hydrogen. In the system presented here, although the efficiency may not be outstanding, it brought a qualitative improvement in that the main reaction products changed from CO and HCOOH to hydrocarbons. The performance of the CO₂ photoelectrochemical system is determined by the balance of several factors which are the properties of the cathode and anode, the electrode size, and light intensity. Further improvements will be accomplished by optimizing the properties of each factor.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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