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CO_2 conversion with light and water by GaN photo-electrode

Satoshi Yotsuhashi[1], Masahiro Deguchi[1], Yuji Zenitani[1], Reiko Hinogami[1], Hiroshi, Hashiba[1], Yuka Yamada[1], and Kazuhiro Ohkawa[2]

[1.] Advanced Technology Research Laboratory, Panasonic Corporation, 3-4 Hikaridai, Seikacho, Sôraku-gun, Kyoto 619-0237, Japan
Phone: +81-98-774-2566 E-mail: yotsuhashi.s@jp.panasonic.com
[2.] Department of Applied Physics, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

1. Introduction

As atmospheric carbon dioxide (CO_2) has risen to a critical level due to high rates of combustion of hydrocarbon fuels, it is highly desirable to realize an energy conversion system reducing the CO_2. One of the main research targets for chemical conversion from solar energy is an inorganic photo-catalyst which has been a focus of considerable research interest since evolution of hydrogen was demonstrated using a TiO_2 photo-electrode.[1] Here, semiconductor photo-electrode is used as an anode to create separate electrons and holes by photo-absorption. The holes assist with the oxidation of water and the residual electrons move to the cathode, leading to the reduction reaction, such as hydrogen generation or CO_2 reduction. The schematic picture is described as Fig. 1 (a). The researches for photo-catalysts have been mainly focused on the direct water splitting generating hydrogen.[2-4] Meanwhile, there have been a few approaches for CO_2 conversion by photo-catalyst.[5-6] This is because it is difficult to satisfy the conditions for accommodating high energy required for CO_2 reduction. For CO_2 reduction, calculating the energy required for the reaction is somewhat complicated, since it depends on which products the reaction involves. For example, a cathodic potential of approx. –0.61 V (vs. SHE) is needed to produce formic acid (HCCOH) from protons and electrons. This energy cannot be reached by most oxide materials, including TiO_2, whereas it can be accommodated in the band gap of GaN as shown in Fig. 1 (b).

In this study, we report on direct CO_2 conversion by using gallium nitride (GaN) photo electrode. CO_2 reduction is realized without extra power input except for illumination with light. GaN has attracted attention for its potential application to highly efficient optical and power devices for energy saving; but recently, its potential has been revealed to extend beyond solid devices: more specifically, that it can be used to generate hydrogen.[7-9] In a chain of experiments, it has turned out that the energy of conduction band of GaN is higher than that of most oxides, which is preferable for CO_2 reduction. Here, we show that this material can be adapted to a system for CO_2 conversion by light and water.

2. Methods and Results

The engine of the reaction is the photo-absorption process that leads to electron-hole separation. High crystalline quality is needed to facilitate the reaction efficiently. Single-crystal GaN was grown by atmospheric-pressure metal organic vapor-phase epitaxy (MOVPE) on (0001) sapphire substrate with low-temperature GaN buffer layers. Silicon was chosen as the dopant for n-type GaN. The growth temperature of the n-type GaN was 1025 ˚C. The GaN layer thickness and carrier concentrations at room temperature were 3.0 μm and n = 3.0 x 10^{17} cm^{-3}, respectively. The thickness was measured using a secondary electron microscope. The van der Pauw method was adopted for measuring electrical properties. The crystalline quality was confirmed by full width at half maximum of an X-ray rocking curve for the (0002) reflection of the GaN layer.

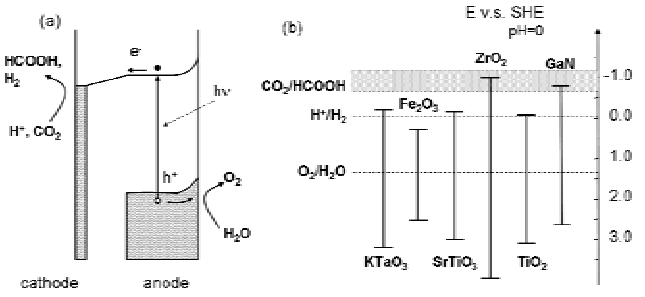

Fig. 1 Schematic illustrations for (a) the mechanism of CO_2 reduction empowered by the photo electrode and (b) band structures of several oxides and GaN. The reduction energy of CO_2 is higher than that of hydrogen generation.

The electrons, excited illumination by light of the GaN, move to the counter electrode, where they drive the CO_2 reduction reaction. For the counter electrode, we use Cu plate of 99.9999% purity. In the electrochemical reduction of CO_2, copper is the only transition metal that delivers a range of reaction products, such as CO, HCOOH, CH_4, etc.[10-11]

A 300-W Xe arc lamp with a UV spectroscopic mirror was focused through a quartz optical fiber onto the surface of the cell. The cell for the cathode electrode was sealed, and CO_2 was introduced in the electrolyte by gas bubbling before the photo-electrolysis. Both the gas and liquid samples were analyzed, using gas and liquid chromatography respectively, after the photo-electrochemical reduction. Hydrogen was determined using a thermal conductivity detec-

tor (TCD) and CO, CH_4, C_2H_4, C_2H_6 were determined using the flame ionization detector (FID) attached to the gas chromatograph. Liquid chromatography was used for detecting HCOOH.

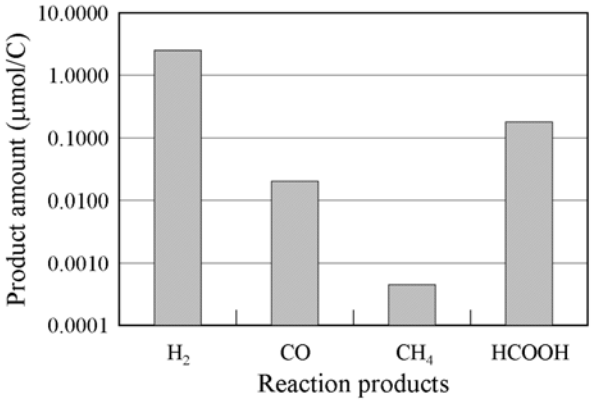

Fig. 2 Comparison of the production amount of each component is shown. The values are normalized by electric charge passed during the electrolysis. Faradic efficiency of HCOOH is ~ 3%.

The comparative data for product amount for each component are shown in Figure 2. These data were obtained after 10 C of photo-electrolysis. The Faradic efficiency for HCOOH was 3.2 %. We calculated the Faradic efficiencies from the total charge passed during electrolysis. It should be noted that the main product from CO_2, formic acid, is potentially a renewable energy source for transport and storage. Whereas recent studies are based mainly on various materials such as complex molecules [12-13] or silica-based materials,[14-17] our system uses only inorganic materials.

3. Conclusions

We have shown the direct CO_2 conversion using Cu and GaN electrodes. With this system, we realized CO_2 reduction without extra power input except for illumination with light. The generation of formic acid (HCOOH) from CO_2 and H_2O with 3% Faradic efficiency was confirmed by light illumination alone. This result demonstrates a possibility for direct CO_2 conversion in a system comprising only inorganic materials. GaN can be widely expanded due to its tunable band gap and carrier concentration. A well-defined and quantitative band engineering of this material will be relevant for improving the ability to control the ratios of its reaction products.

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