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# A Photoelectrochemical Fixation of Carbon Dioxide.
## Spontaneous Up Quality Conversion of Organic Compound

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A photosynthetic semiconductor electrochemical cell with Mg electrode as a sacrificial anode was assembled. This photoelectrochemical cell spontaneously fixes carbon dioxide into organic molecule such as benzyl chloride to form phenyl acetic acid which costs 7.5 times more than the sources. Among the semiconductor electrodes investigated, p-GaP showed highest current efficiency, 47%.

An artificial carbon dioxide fixation attracts the great interests in ecological background. Electrochemical and photochemical fixations of $CO_2$ have been extensively studied.1-7,9,10) However, most of the studies concentrate on direct reduction of carbon dioxide on the electrode. The practical system requires the breakeven between the cost for the input energy to drive the cell and the value of the products. The products of direct electrolysis of $CO_2$ are CO1), formic acid1,2), methanol,1,3) and so on, which are not so valuable. Thus, it is more attractive to synthesize valuable organic compounds electrochemcally by fixing carbon dioxide into organic substances. Electrochemical $CO_2$ reduction requires fairly negative potential and therefore, there have been many attempts to reduce the overpotential by using suitable catalysts. For example, Komeda et al. electrochemically fixed $CO_2$ into $CH_3C(O)SEt$ and $C_6H_5C(O)SEt$ and obtained $CH_3C(O)COO^-$ and $C_6H_5C(O)COO^-$ respectively, using $(Et_4N)_3[Mo_2Fe_6S_8(SEt)_9]$ as a catalyst.4) Colloidal semiconductor microcrystallites are often used as a photocatalyst. Kanemoto et al. demonstrated that $CO_2$ and benzophenone photochemically yield benzilic acid in the presence of colloidal CdS microcrystallites as photocatalyst and triethylamine as a sacrificial electron donor.5) Inoue et al. photochemically fixed $CO_2$ into oxoglutanic acid using CdS as a photocatalysts, isocitrate dehydrogenase as a catalysts, methyl viologen as an electron mediator and triethanolamine as an electron donor.6)

Electrochemical reduction of benzyl chloride in the presence of $CO_2$ led directly to benzyl phenylacetate by using a Pt as the anode.8) On the other hand, if one uses Mg as an anode, the reductive intermediate of the benzyl chloride captures $CO_2$ to form phenyl acetic acid. In this case, anodic process is the dissolution of $Mg^{2+}$. It is well recognized that the rate of $CO_2$ insertion process is dramatically enhanced in the presence of freshly prepared $Mg^{2+}$ion, which is commonly prepared by anodic dissolution of Mg counter electrode.9,10) It has been well known that electrical energy required to drive various electrochemical reactions are reduced quite significantly by using illuminated semiconductor electrodes.7,11,12)

In this article, we demonstrate that the combination of p-type semiconductor electrodes and magnesium counter electrode spontaneously photoconverts benzyl chloride to phenyl acetic acid without the external electric power.

A conventional three electrode system was used for the electrochemical measurements with Pt and $Ag/Ag^+$

as the counter and the reference electrodes, respectively. The electrode potential is represented with respect to SCE in this article. The photo-excitation of semiconductor electrodes was conducted by 500 W xenon arc lamp through proper combination of optical filters.

The aprotic solvents used for electrolyte preparation were acetonitrile and dimethyl formamide dried over $P_4O_{10}$ under continuous stirring for at least 24 h. The solvents were transferred to the freshly prepared descant by trap to trap distillation under vacuum. This process was repeated for three times. The oxygen dissolved was removed by freeze-pump-thaw cycles. Supporting electrolyte used was a tetra-n-butylammmonium tetrafluoroborate which was dried under vacuum.

In the photosynthetic experiments, a two electrode cell consists of p-type semiconductor electrode and Mg counter electrode was used. Two electrodes were connected through zero-shunt ammeter so that current flow during photo-electrolysis could be measured. The product was analyzed by JASCO HPLC system with combination of 870-UV optical detector.

The typical electrochemical behaviors of the direct reduction of $CO_2$ on Pt and p-GaP electrode in acetonitrile solution are depicted in Fig. 1. The cathodic current for $CO_2$ reduction started to flow around -2.0 V and -1.0 V at Pt and photoexcited p-GaP, respectively. With the presence of benzyl chloride, the cathodic current started around -0.5 V as presented in Fig. 2. The electrochemical behavior of Mg electrode is also shown in Fig. 2.

The anodic dissolution of Mg started at -1.8 V. As the anodic dissolution of Mg proceeds at more cathodic potential than the photoelectrochemical reduction of benzyl chloride, the combination of p-type semiconductor and Mg counter electrode forms a photoelectrochemical cell. Because the anodic dissolution current of Mg is larger than the cathodic photocurrent of p-type semiconductor electrodes, the potential of the semiconductor electrodes under the photoelectrochemical cell operation are close to the onset potential of the Mg dissolution reaction, i.e., -1.8V.

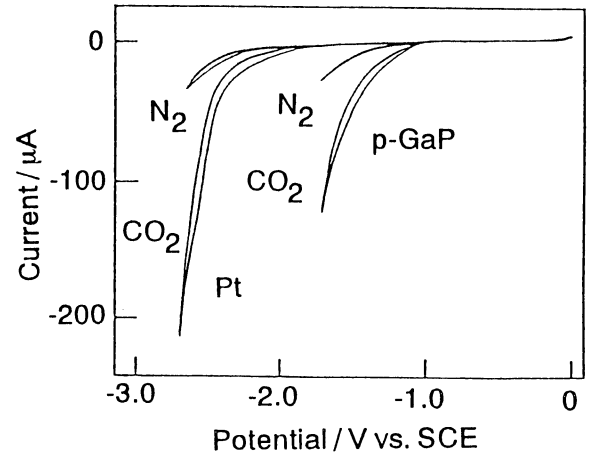

Fig.1. Direct electrochemical reduction of $CO_2$ at Pt and illuminated p-type GaP electrodes in acetonitrile solution.

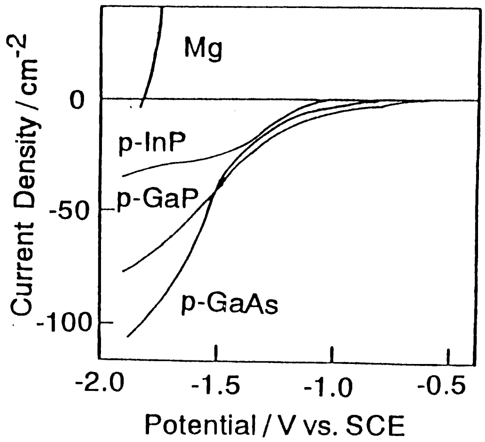

Fig.2. Electrochemical behaviors of p-type photoexcited semiconductors and Mg electrodes in $CO_2$ saturated acetonitrile solution with 50 mM of benzyl chloride.

The short circuit current of the cell was measured as a function of both the concentration of benzyl chloride and irradiation intensities as shown in Fig.3. The photocurrent increases linearly with the light power up to certain point and then the deviation from the linear relation was observed. The higher concentration of benzyl chloride shifts the point to higher light intensity where the deviation starts. This result suggests that the electron transfer occurring on the electrode is not direct reduction of $CO_2$ but reduction of benzyl chloride.

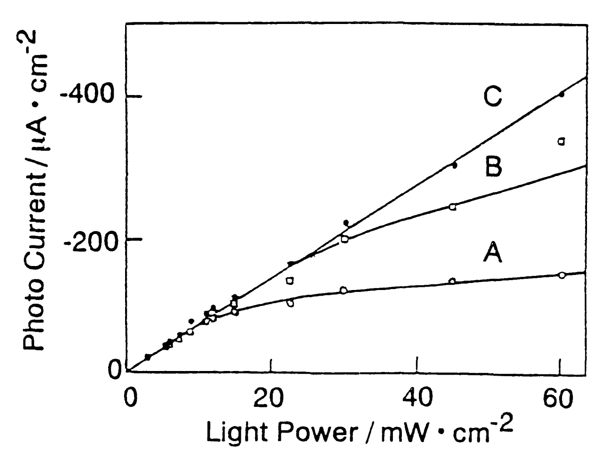

Fig.3. Short circuit photocurrent of p-GaP synthetic photocell as a function of benzyl chloride concentration and irradiation intensity under $CO_2$ saturated condition. The concentration of benzyl chloride are 50, 100, and 500 mM for curve A, B, and C, respectively.

After the continuous photo-electrolysis under $CO_2$ bubbling, the product analysis was carried out. The major product is phenyl acetic acid. The amount of the phenyl acetic acid and the current efficiency of the reaction are shown in Table 1 for three p-type semi-conductor photocathodes. Although the data scatters to some

Table 1. Current yield of phenyl acetic acid in various p-type semiconductor synthetic photocell in acetonitrile solution at 25 ℃

| Electrode | Current<br>μA | Time<br>h | Amount of Product<br>nmol | Current Efficiency<br>% |
|---|---|---|---|---|
| p-GaP | | | | |
| (50 mM)$^{a)}$ | 3 | 20 | 530 | 44 |
| (2 M)$^{a)}$ | 2 | 24 | 360 | 47 |
| p-GaAs | | | | |
| (50 mM)$^{a)}$ | 4 | 20 | 630 | 42 |
| (2 M)$^{a)}$ | 7 | 16 | 1000 | 42 |
| p-InP | | | | |
| (50 mM)$^{a)}$ | 0.2 | 20 | —— | —— |

a) Concentration of benzyl chloride.

extent, the yield increases in the order of p-type InP, GaAs and GaP, successively. Only the trace amount of phenyl acetic acid was produced at InP electrode. From the flatband potentials measured in the dark and the band gap energy of the semiconductors, the energy of the photocreated electrons on the conduction band is determined as 1.10, -1.01 and -2.09 V vs. SCE for p-type InP, GaAs and GaP, respectively. The reactivity of the electrodes has no relation with the energy of electrons in the conduction band.

The current efficiency was improved by 40% by carrying the reaction at 275K. The temperature effect must be mainly due to the increase of the saturation concentration of $CO_2$ in the aprotic electrolytes.

As a comparison, the potentiostatically controlled photoelectrolysis was conducted also with a platinum counter electrode at -1.8V vs. SCE. After the continuous electrolysis, the analysis of the solution revealed that only trace amount of phenyl acetic acid was produced. Even by adding magnesium sulfate in the solution, the phenyl acetic acid was not detected.

These results shows that the photoelectrochemical carbon dioxide insertion to benzyl chloride is initiated by the reduction of benzyl chloride on p-type semiconductor electrode and carbon dioxide is captured by the reductive intermediate of benzyl chloride, which is drastically accelerated by the presence of freshly prepared magnesium ion in the solution. The detailed study of the mechanism is under way in this laboratory.

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