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優勝作品專輯

作品編號 **030018**

參展科別 **化學**

作品名稱 **Artificial Photosynthesis -Formic Acid Generated from Carbon Dioxide by Using Photocatalyst-**

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1. Introduction

Reduction of carbon dioxide is desired as an environmental problem of global warming. The study of generation of formic acid from carbon dioxide was performed under irradiation of ultra violet to photocatalyst. Ta_2O_5 could reduce carbon dioxide, but the band gap of Ta_2O_5 was 4.0 voltage. In this research, it was found that tantalum oxide / tantalum plate responds to visible radiation. Therefore, the reason of visible light response was examined. It was studied to make efficient tantalum oxide / tantalum plate.

2. Experimental

2.1. Synthesis of Ta_2O_5 and Ta_3N_5 film electrode

By burning tantalum plate in air by electric furnace, oxygen and nitrogen by cylindrical electric furnace, changing the time and temperature (600、800、1000 ℃), different thickness of Ta_2O_5 and Ta_3N_5 film was made easily on the surface of tantalum.

Fig.1. Cylindrical electric furnace

2.2 Two electrode system

Light from xenon lamp was irradiated to Ta_2O_5 in 0.1mol/L Na_2SO_4. Voltage and electric current were measured with Pt counter electrode. Current density-voltage curve was made and energy conversion efficiency was calculated.

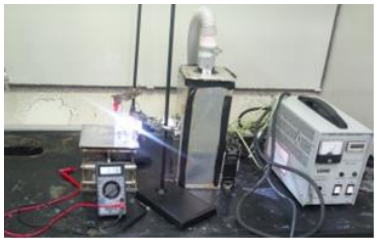

Fig.2. Xenon lamp

2.3 Three electrode system

The electric potential of the conduction band of photocatalyst was checked by using potentiostat, and wavelength dependence was checked using visible light LED (violet, blue, green and red).

2.4. Generation of Formic Acid

Ultra violet was irradiated to photocatalyst with silver as the counter electrode in 0.1mol/L Na_2SO_4 saturated with CO_2. Formic acid was measured by HPLC (column ODS-80Ts 4.6 mm I.D. ×25 cm, eluent water/acetonitrile（98/2）+0.1% phosphoric acid, flow velocity 1mL/min, detector 235nm UV).

3. Results and Discussion

3.1. Synthesis of Ta_2O_5 and Ta_3N_5 film electrode

Ta_2O_5 and Ta_3N_5 film electrode was made by burning tantalum plate in air by electric furnace, oxygen and nitrogen by cylindrical electric furnace (fig.3 ～Fig.7).

Fig.3. In air at 600℃（Ta plate）for 10, 20 and 30 min.

Fig.4. In air at 800℃（Ta plate） for 2, 5, 7, 9 and 12 min.

Fig.5. In air at 1000℃（Ta plate）for 1, 2, 3,5 and 7 min.

Fig.6. In N_2 at 800℃ for 15 and 90 min.

Fig.7. In O_2 at 600℃ 5 min.

In N_2, Ta_3N_5 was synthesized at 800 degrees Celsius.

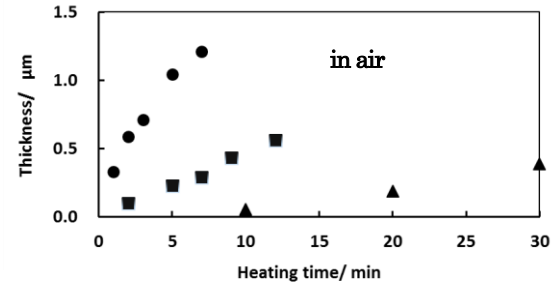

Fig.8. Heating time in air and thickness of thin film

▲600℃ ■800℃ ●1000℃

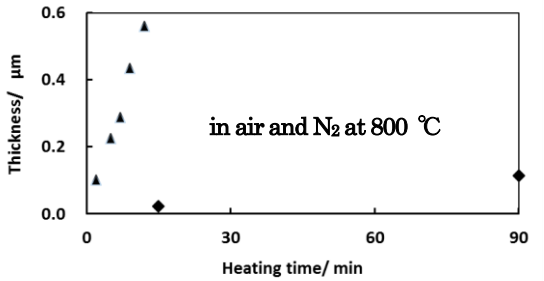

Fig.9. Heating time and thickness of thin film

▲800℃ in air ◆ 800℃ in N_2

The film thickness became thick by burning more and high temperature. The film thickness in the oxygen increased fast compared with in air. The film was black when thin, but it became white gradually as the thickness increased.（Fig.3～Fig.5 Fig.8）。

The thickness increased slowly in nitrogen compared with air (Fig.9), and the film became thick quickly in the oxygen (Fig.10).

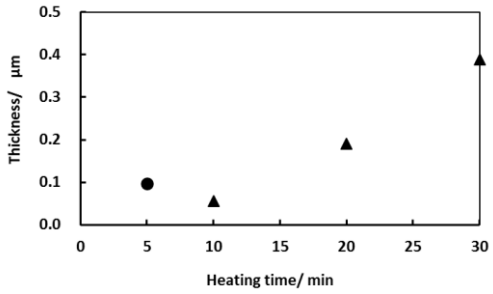

Fig.10. Heating time and thickness of thin film

▲600℃ in air ● 600℃ in O_2

3.2. Film Thickness Dependence and Light Response

(1) Open circuit voltage and short circuit current

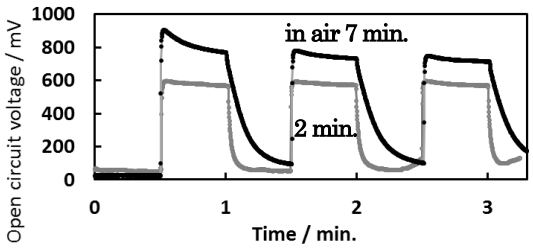

Fig.11. . Light responce of Ta_2O_5/Ta. in air and irradiation of Xe lamp

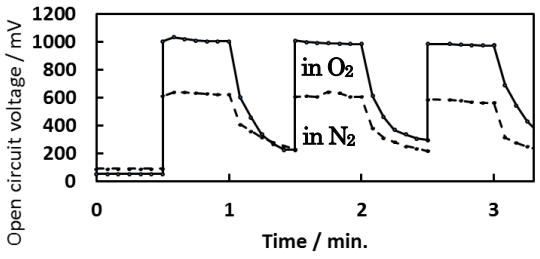

Fig.12. Light responce of Ta_2O_5/Ta. irradiation of Xe lamp

—●— 5min 600℃ in O_2 - - -▲- - - 15min 800℃ in N_2

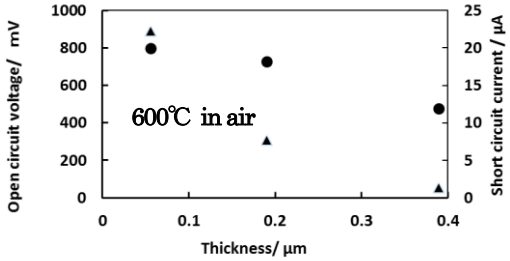

Fig.13 Property of Ta_2O_5 thin film borned in air at 600℃, Xe lamp irradiation

● Open circuit voltage ▲ Short circuit current

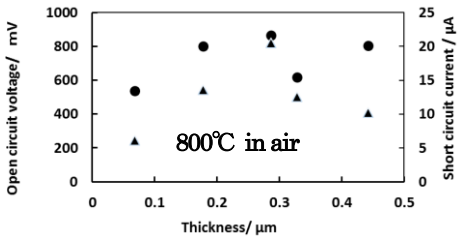

Fig.14. Property of Ta_2O_5 thin film borned in air at 800℃、Xe lamp irradiation

● Open circuit voltage ▲ Short circuit current

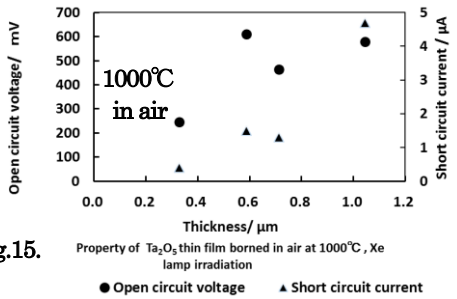

Fig.15.

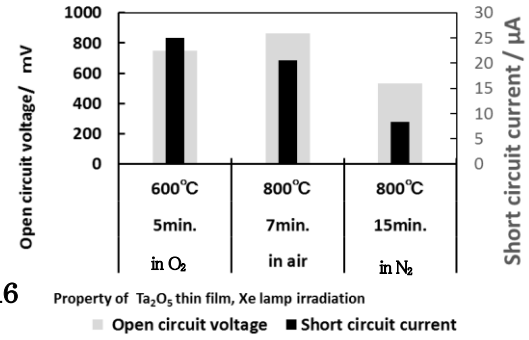

Fig.16

It was found out that the plate baked during 600 ℃ for 10 minutes (Fig.13), during 800 ℃ for 7 minutes (Fig.14) and during 1000 ℃ f or 5 minutes (Fig.16) were fine in air.

The most shown optical response during all the photocatalyst was the one baked during 600 degree oxygen for 5 minutes.

(2) Current density-voltage curve

Xe lamp (100 mW/cm^2) was applied and the current density and the voltage were measured. The electric power density was 0.02 mW/cm^2 by using film plate which was burned at 600 ℃ for 5 minutes in O_2 (Fig17).

The energy conversion efficiency of Ta_2O_5/Ta in O_2 was 0.02%.

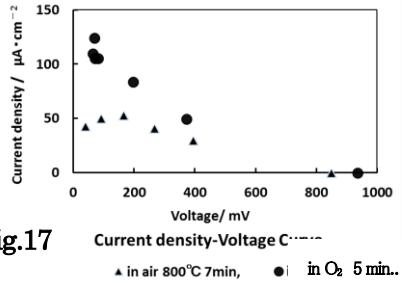

Fig.17

3.3. Three-Electrode System and Wavelength Dependence

Optical response current was measured by a potentiostat in 0.1mol/L Na_2SO_4 and Ag/AgCl reference electrode. It was measuresd for 30 seconds at light on –off, by changed electric potential.

(1) Conduction band

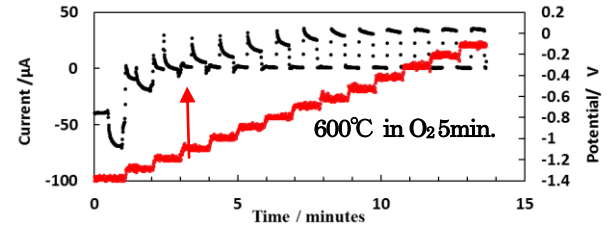

Fig.18 Ta_2O_5 : Xe lamp, Pt ,0.10 mol/L Na_2SO_4
- Light response of electrode at light off-on
- Potential (refarence Ag/AgCl)

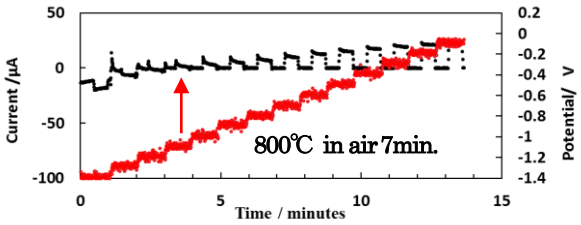

Fig.19 Ta_2O_5 : Xe lamp, Pt ,0.10 mol/L Na_2SO_4
- Light response of electrode at light off-on
- Potential (refarence Ag/AgCl)

It was confirmed that semiconductor was n type, because the oxidation current with optical response flowed at nobleness (+) electric potential.

It was found out that conduction band of Ta_2O_5/Ta was at -1.1V vs. Ag/AgCl (Fig.18,19) and conduction band of Ta_3N_5/Ta was at - 0.5 V vs. Ag/AgCl (Fig.20). Therefore, this showed that Ta_2O_5/Ta could reduce carbon dioxide.

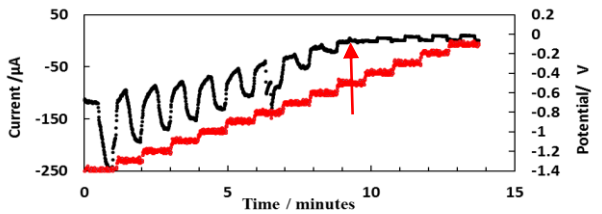

Fig.20 Ta_3N_5 : Xe lamp, Pt ,0.10 mol/L Na_2SO_4
- Light response of electrode at light off-on
- Potential (refarence Ag/AgCl)

(2) Visible light response

Ta_2O_5/Ta responded to ultraviolet rays and visible light at two electrode system with Pt counter electrode. By irradiation from violet LED (3.1 eV), blue LED (2.6 eV), green LED (2.4 eV) and red LED (1.9 eV), oxidation current was measured at 0 V vs. Ag/AgCl using potensiostat.

However, the bandgap of Ta_2O_5 was 4.0 eV and it was impossible for Ta_2O_5 to respond to visible light. However, impurity were doped during Ta_2O_5/Ta.

First, nitrogen in the air expected to be doped. The band gap was 2.1eV for Ta_3N_5 and 2.5eV for TaON. Ta_2O_5/Ta burned in oxygen, which wasn't include nitrogen, also responded to visible light. Therefore, it was thought that the impurity doped to Ta_2O_5/Ta wasn't nitrogen The purity of tantalum plate was 99.98 % as table 1, and included small amount of other metals. The biggest amount of impurity was 0.01 % of tungsten. It was considered that the cause of visible light response was tungsten doped to Ta_2O_5/Ta.

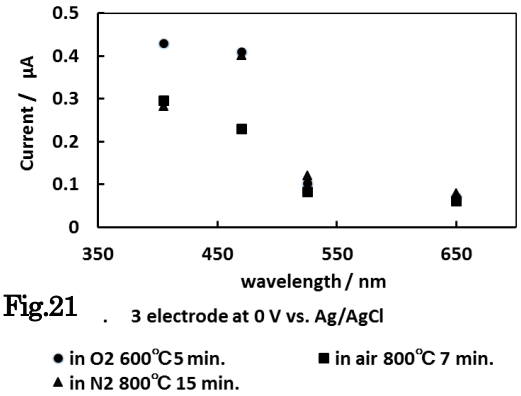

Fig.21 . 3 electrode at 0 V vs. Ag/AgCl

Table 1. Chemical composition of tantalum plate (%)

Nb	Fe	Ti	W	Si	Ni	Mo	Ta
<0.001	<0.001	<0.001	<0.01	<0.001	<0.001	<0.001	99.98

3.4. Generation of formic acid

Ultra violet was irradiated to Ta_2O_5/Ta burned at 600 ℃ for 5 minutes in O_2 with silver wire at pipe tee as the counter electrode in 0.1mol/L Na_2SO_4 saturated with CO_2. Formic acid was measured by HPLC (column ODS-80Ts 4.6 mm I.D. ×25 cm, eluent water/acetonitrile (98/2)＋0.1% phosphoric acid, flow velocity 1mL/min,).

Fig.22. Silver wire and pipe tee

Fig.23. Irradiation to Ta_2O_5/Ta.

Formic acid was absorbed under 240 nm (fig.24). Wavelength of UV detector was selected at 225 nm and 235 nm. The pike of formic acid was recorded at 10 seconds later for 3 minutes. At 225 nm, it was recorded at shoulder of another pike (fig. 25). So, it was recorded at a single pike at 235 nm (fig. 26).

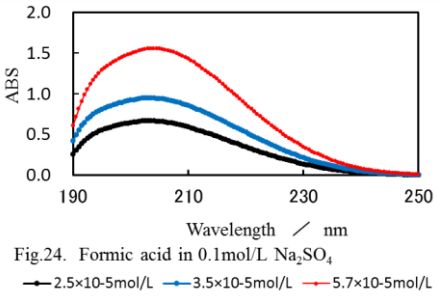

Fig.24. Formic acid in 0.1mol/L Na_2SO_4

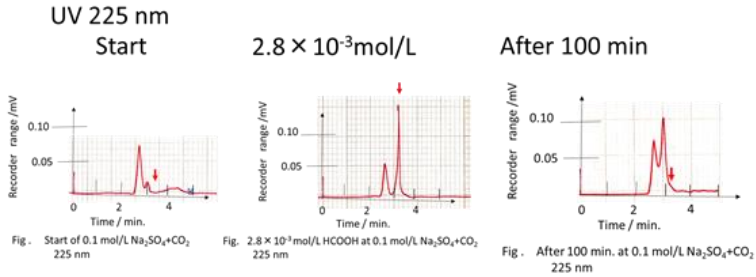

Fig.25. HPLC detected at 225 nm

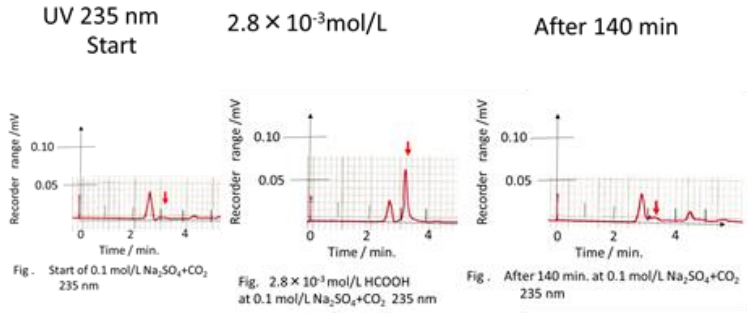

Fig.26. HPLC detected at 235 nm

The generation of formic acid from experiment was evaluated 2.2×10^{-4} mol/L. Theoretical value was calculated 4.8×10^{-7} mol and from 11 μA and 140 minutes and reaction of formic acid generation $CO_2+2H^++2e^-\rightarrow HCOOH$. The concentration was 4.8×10^{-3} mol/L by volume of 0.1 mL. Generation rate was 4.5 %.

4. Conclusion

1) By burning tantalum, changing the time and temperature, different thickness Ta_2O_5/Ta, Ta_3N_5/Ta was made easily.

2) The biggest short-circuit current and open voltage was seen by irradiating light to Ta_2O_5 made in 600 ℃ O_2 for 5 minutes, and the conversion efficiency was 0.02%.

3) The conduction band of Ta_2O_5/Ta was in the level which can reduce carbon dioxide and generate formic acid.

4) Ta_2O_5/Ta responded to ultraviolet rays and visible light. However the reason of light response is that there are impurities doped inside.

5) By irradiating xenon lamp to Ta_2O_5/Ta, and by using a silver wire, formic acid was generated from carbon dioxide.

5. Future Prospects

1) Make W doped Ta_2O_5 and backup my consideration of visible light response.

2) Develop the conversion efficiency of photocatalyst by doping various metals and gases.

3) Generate formic acid from sun light after developing the conversion efficiency of photocatalyst.

4) Zirconium is less expensive than tantalum. Therefore, use zirconium instead of tantalum, to make the cost lower.

6. Acknowledgements

We are greatly indebted to Yutaka Amao professor and Tomoko Yoshida professor (Osaka city university Research Center for Artificial Photosynthesis), for information that Ag was suitable for co-catalyst of Ta_2O_5.

7. References

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【評語】030018

Carbon Dioxide by Using Photocatalyst-Artificial Photosynthesis

The candidate delivers a report about using Ta_2O_5 and Ta_3N_5 as the active materials for reduction of CO_2 to formic acid. In the design, Ta_2O_5 and Ta_3N_5 have been prepared from a Ta plate. Although theoretically Ta_2O_5 should only be responsive to UV light, the candidate discovered that the material prepared by her method is also responsive to visible region. She also successfully demonstrated the possible if making formic acid by reduction of CO_2 through an electrochemical process. The candidate has received perfect training and has excellent performance. I should express congratulation to her and her mentors.