

## PHOTOCATALYTIC ACTIVITY OF TiO<sub>2</sub>-SnO<sub>2</sub> SYSTEM

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TiO<sub>2</sub> doped with Sn was prepared by polymerizable complexes method. The solid solution was annealed to make SnO<sub>2</sub> layers within TiO<sub>2</sub> matrix. Electrochemical cell study of the solid solution and TiO<sub>2</sub> samples indicated that the solid solution had higher photocatalytic activity than TiO<sub>2</sub>. The Pt-added TiO<sub>2</sub> powder was also prepared by impregnation method. The experimental results of photocatalytic reaction revealed that amount of gases generated for Pt-added TiO<sub>2</sub> was greater than that for TiO<sub>2</sub> without Pt and it decreased with increasing Pt concentration when the concentration of Pt was high.

Key words : titanium oxide, tin oxide, platinum, photocatalyst, hydrogen

### 1. INTRODUCTION

Fossil fuels, such as oil and coal, used as the main source of energy at present time, are expected to run out. In addition, these fuels when they are burned emit greenhouse gases, such as CO<sub>2</sub> creating the environmental problem. Therefore, it is an important assignment to find a new energy source which substitutes for fossil fuels. Hydrogen has attracted much attention as a new energy source. Hydrogen may store energy when it is reduced from water, and may release energy when it reacts with oxygen. When fossil fuels are burned, they emit NO<sub>x</sub>, CO<sub>2</sub>, H<sub>2</sub>O, etc., while hydrogen emits only water. Therefore the new energy system, which uses hydrogen as an energy source, is more promising as the energy source of future. The methods such as electrolysis could be used to produce hydrogen from water. However, a problem for the electrolysis of water is how we get electric power without emitting greenhouse gasses.

In 1972, Honda and Fujishima<sup>1)</sup> reported photoelectrolysis of water using single-crystal TiO<sub>2</sub> to produce hydrogen and oxygen. This method utilizes the fact that holes and electrons are photogenerated on TiO<sub>2</sub> surface when exposed to

solar radiation. The electrons migrate to the Pt cathode, and water is decomposed by the potential difference between TiO<sub>2</sub> anode and Pt cathode. Since this report, TiO<sub>2</sub> has been studied as photocatalyst. However the yield of hydrogen has not been improved.

For photoelectrolysis of water, the following conditions have to be satisfied.<sup>2)</sup> (1) The potential of photogenerated electron must be lower than the H<sup>+</sup>|H<sub>2</sub> potential. (2) The potential of photogenerated hole must be higher than the O<sub>2</sub>|OH<sup>-</sup> potential. (3) The material must not be decomposed by reacting with water during exposure to solar radiation. (4) The rate of recombination of photogenerated electron-hole pair must be sufficiently slower than the rate of reaction of water decomposition. We think that TiO<sub>2</sub> is the best material which satisfies these conditions. One of the problems<sup>2)</sup> associated with TiO<sub>2</sub> is that the electron-hole pair is not generated by visible light irradiation, because the band gap of TiO<sub>2</sub> is 3.0 eV. TiO<sub>2</sub> absorbs only ultraviolet light, and utilizes only a few percent of all sunlight energy even if quantum efficiency is 100%. Another problem is that the activity would be lowered by recombination of photogenerated

electron-hole pairs.

In this study,  $\text{SnO}_2\text{-TiO}_2$  solid solution is fabricated as photocatalyst of electrochemical cell.  $\text{SnO}_2$  with higher electronic conductivity was doped into  $\text{TiO}_2$ , and spinodal decomposition was allowed to take place. The existence of  $\text{SnO}_2$  will slow down the recombination of photogenerated electron-hole pairs. As a different kind of experiment, Pt was deposited on the surface of  $\text{TiO}_2$  powder with impregnation method as catalyst for generation of  $\text{H}_2$ . This sample was also tested as photocatalyst.

## 2. EXPERIMENTAL

The solid solution of  $\text{TiO}_2$  doped with Sn was prepared by polymerizable complexes method.<sup>3)</sup> In this method, titanium tetra-iso-propoxide and tin (IV) chloride were used as starting materials. Titanium tetra-iso-propoxide was dissolved into ethylene glycol, and citric acid was added into the solution. This solution was stirred at  $60^\circ\text{C}$  for 1.2h to yield yellow solution. Tin (IV) chloride was then added into the solution. The solution was stirred at  $60\sim 70^\circ\text{C}$  for 70h, and then stirred at  $160\sim 170^\circ\text{C}$  for 20min. The solution was esterified at  $180^\circ\text{C}$ , and carbonized at  $250^\circ\text{C}$  to form oxide precursor. The precursor was calcined at  $750^\circ\text{C}$  to obtain the mixture of  $\text{SnO}_2\text{-TiO}_2$ . This mixture was well ground with agate mortar and uniaxially pressed into pellet. The pellet was sintered at  $1400^\circ\text{C}$  for 5h to form  $\text{TiO}_2\text{-SnO}_2$  solid solution. The solid solution was annealed at  $1000^\circ\text{C}$  for 1h, during which spinodal decomposition took place. This sample contained  $\text{SnO}_2$  layer within  $\text{TiO}_2$  matrix and was used as an electrode material.

The electrochemical cell used in this study to test solid solution sample consisted of a Pt cathode and a  $\text{SnO}_2\text{-TiO}_2$  solid solution anode. For preparation of anode, In-Ga alloy was placed on one side of the  $\text{SnO}_2\text{-TiO}_2$  solid solution sample, and using soft solder a copper wire was attached to In-Ga alloy. The copper wire was covered with a glass tube, and the wire attached to the side of the sample was insulated with epoxy. For anode side,

4M KOH electrolyte was placed in quartz glass cell to form electrolytic cell. For cathode side, 4M HCl electrolyte was placed in pyrex glass cell. Two electrolytic cells were connected by salt bridge. The anode was irradiated by sun-light, and potential difference between anode and cathode was measured.

Sample of Pt-deposited  $\text{TiO}_2$  was prepared by impregnation method.  $\text{H}_2\text{PtCl}_6$  aqueous solution was sprayed onto  $\text{TiO}_2$  powder (anatase), and  $\text{H}_2\text{PtCl}_6$  was reduced with HCHO solution for two days. The sample was then heated at  $400^\circ\text{C}$  for 1h to produce Pt on the  $\text{TiO}_2$  surface. The presence of Pt on the sample was confirmed by EDX.

The photocatalytic reaction using the Pt-deposited  $\text{TiO}_2$  was performed with a reactor shown in Fig. 1. The sample and  $\text{CH}_3\text{OH}$  solution were placed into quartz glass cell.<sup>4)</sup> This reactor was irradiated from side of the cell by Hg lamp (365nm wavelength).

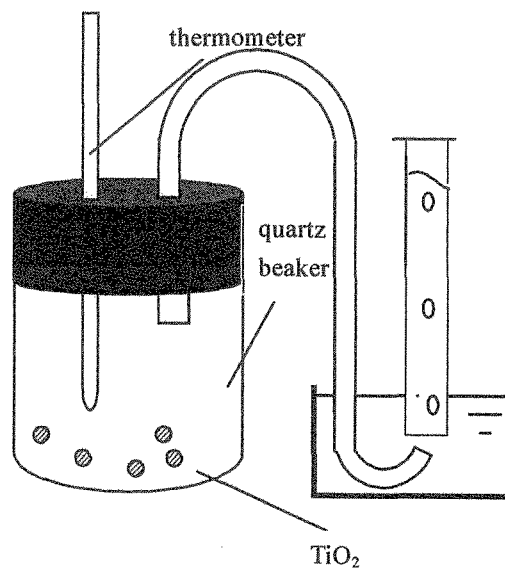


Fig. 1 Reactor for photocatalytic reaction using  $\text{TiO}_2$  powder. In this reactor, solution of  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  ( $\text{CH}_3\text{OH}$ , 40ml,  $\text{H}_2\text{O}$ , 60ml) was used as electrolyte. Light source was 365nm Hg lamp.

## 3. RESULTS AND DISCUSSION

Results of potential difference measurement for sintered  $\text{TiO}_2$  and  $\text{SnO}_2\text{-TiO}_2$  solid solution are

shown in Fig. 2. As the anode material was irradiated by sun-light, the potential difference between anode and cathode increased suddenly for both samples. This result indicates that the electron-hole pair is photogenerated by irradiation and electrons as carrier of n-type semiconductor transfer to Pt cathode. This is photocatalyst reaction. We notice that the potential difference between SnO<sub>2</sub>-TiO<sub>2</sub> anode and Pt cathode is greater than the potential difference between TiO<sub>2</sub> anode and Pt cathode. This suggests that SnO<sub>2</sub> layer generated by spinodal decomposition may prevent electron to recombine with hole. Therefore, the layer of SnO<sub>2</sub>, which has high electronic conductivity, may prevent recombination of electron-hole pairs and this system could be used to increase the efficiency of photoelectrolysis of water. The problem associated with this method was that the reproducibility of data using electrochemical cell was poor. This was caused by the fact that the electrode with the same characteristic was not reproducible. We have to find more reliable method to make electrode.

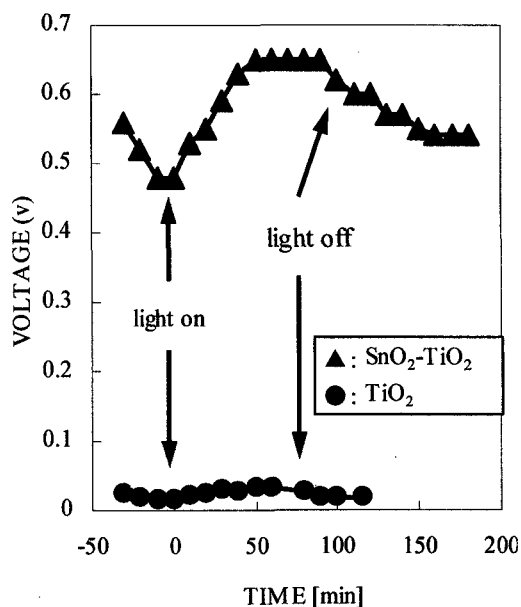


Fig. 2 Potential difference between TiO<sub>2</sub> or SnO<sub>2</sub>-TiO<sub>2</sub> anode and Pt cathode. The light source was sun light, and the thickness of samples were 1.5 mm, and Pt cathode was 20 × 20 × 0.1mm<sup>3</sup>.

One of the methods to make electrochemical cell will be to use powder electrode. In this case the problems are how we attach Pt on TiO<sub>2</sub> and how much. Results of EDX of powder samples are shown in Fig. 3. The figure shows that peak of Cl appears in TiO<sub>2</sub> sample before heating. Since H<sub>2</sub>PtCl<sub>6</sub> is not stable when HCHO is present, it may be reduce to Pt, HCOOH and HCl by HCHO. However, HCl and/or a few H<sub>2</sub>PtCl<sub>6</sub> might remain on the sample. After heating at 400°C, peak of Cl disappeared and only peaks of Pt and Ti existed; only Pt was present on the TiO<sub>2</sub> sample. In addition, result of X-ray diffraction of sample after heating indicates that TiO<sub>2</sub> powder is still in anatase form. Consequently we have successfully deposited Pt on TiO<sub>2</sub> powder.

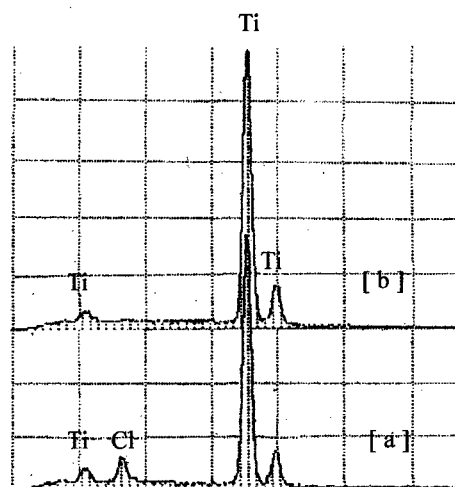


Fig. 3 EDX patterns of Pt-deposited TiO<sub>2</sub> before heating [ a ] and after heating [ b ].

Amount of gases which were accumulated during the exposure of Pt-deposited TiO<sub>2</sub> to 365nm light is shown in Fig. 4 as a function of Pt concentration. The figure indicates that although there are scatters in data, amount of gases generated for Pt-deposited TiO<sub>2</sub> is greater than that for TiO<sub>2</sub> without Pt. In addition the amount of gases generated decreases with increasing Pt concentration in the area where the concentration of Pt is high. Therefore, optimum deposition of

Pt on the surface of  $\text{TiO}_2$  is effective to activate photocatalytic reaction. These results may indicate that area occupied by Pt on  $\text{TiO}_2$  powder increases with increasing amount of Pt deposition, and the area of  $\text{TiO}_2$  powder that is not covered with Pt decreases with that.

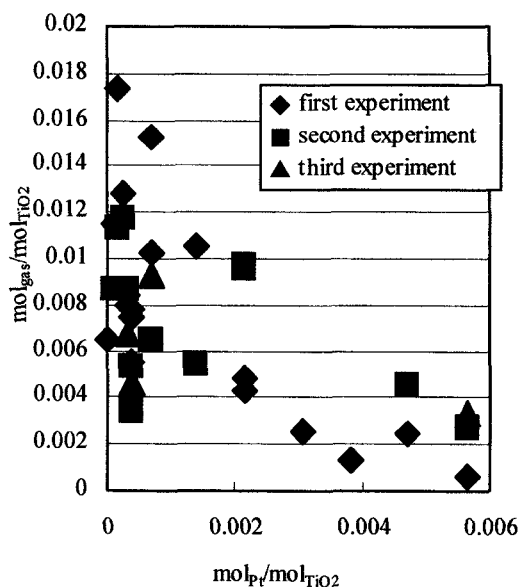


Fig. 4 Amount of gases produced as a function of Pt concentration.

The gases generated were analyzed by gas chromatograph. The gases consisted of  $\text{H}_2$ ,  $\text{O}_2$  and  $\text{N}_2$ . Since the ratio of  $\text{O}_2$  to  $\text{N}_2$  was approximately 1:4, there might be a leakage of air into the system. Consequently, it is clear that only  $\text{H}_2$  was generated in this experiment and  $\text{O}_2$  was not generated. This is caused by the fact that  $\text{CH}_3\text{OH}$  solution was used as electrolyte and is consistent with the results reported by Zou *et al.*<sup>4)</sup>

#### 4. CONCLUSION

$\text{SnO}_2\text{-TiO}_2$  solid solution prevented the recombination of photogenerated electron-hole pairs and showed higher activity as photocatalyst. However, the reproducibility of data with this photoelectrochemical cell was poor. When  $\text{H}_2\text{PtCl}_6$  on  $\text{TiO}_2$  powder was reduced by  $\text{HCHO}$ , both Pt and Cl remained on the surface. By

heating the sample to  $400^\circ\text{C}$ , only Pt was deposited onto  $\text{TiO}_2$  surface. Deposition of small amount of Pt on  $\text{TiO}_2$  powder increased the photocatalytic activity of  $\text{TiO}_2$ , but excess deposition of Pt was harmful.

#### 5. REFERENCES

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