Photocatalytic hydrogen production and enhancement of reactivity using electron irradiation over carbon coated TiO_2

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1. Introduction

Hydrogen has been noticed as a clean and renewable energy source. Fossil fuel, which is the most widely used energy source, has two defects. One is CO_2 emission causing global warming.[1] The other is exhaustion. On the other hand, hydrogen causes no CO_2 emission and can be made from water, renewable and easily obtainable source.

However, about 95% of hydrogen is derived from fossil fuel.[2] It means that hydrogen is not an energy source, but just energy carrier. To maximize the merits of hydrogen, renewability and no CO_2 emission, it is needed to enhance the technology to produce the hydrogen using water splitting without using fossil fuel. The photocatalytic water-splitting is one of the potent options. Photocatalytic water-splitting that uses hole/electron pairs of semiconductor is expectable way to produce clean and renewable hydrogen from solar energy.[3]

Electron irradiation can modify the band position of semiconductor materials. Applying this phenomena in photocatalytic hydrogen production, We tried to enhances photocatalytic reactivity of carbon coated TiO_2

2. Methods and Results

2.1 Preparation of Carbon Coated TiO_2

Figure 1 shows the schematic figure of fabrication processes of electron irradiated C_{60}/TiO_2. The details are as follow.

For the preparation of C_{60} coated TiO_2, Chlorobenzene was used as a solvent. 36 mg of C_{60} powder was suspended in the 50mL chlorobenzene. 500mg of porous TiO_2 was added. The solution was stirred on the magnetic stirrer for 5hrs. Using additional chlorobenze, the mixture of C_{60} and TiO_2 was washed three times to remove impurities. To get rid of residual chlorobenzene solvent, the washed sample was dried in the 10^{-2}torr vacuum for 2hrs. The color of TiO_2 particle turned from white to brown after C_{60} coating. In order to investigate the effect of C_{60} coating, pure TiO_2 and C_{60}/TiO_2 was prepared. The samples were coated with platinum using UV irradiation method. Pt was loaded from 15% of methanol aqueous solution in the presence of H_2PtCl_6. 250mg of Catalyst was dispersed in the 250mL methanol solution containing H_2PtCl_6. The solution was magnetic stirred for 1hr to disperse the particles uniformly. The solution containing the dispersed particles was illuminated for 1hr with UV light using 200W Hg-Xe lamp. The color of three samples changes from white or brown to dark grey after Pt loading.

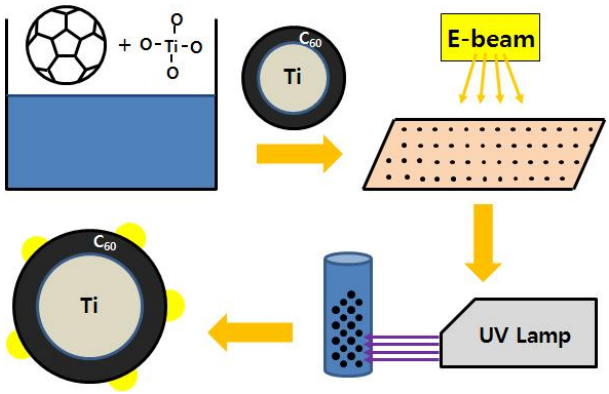

Fig. 1. Schematic figure of preparation of electron irradiated C_{60}/TiO_2 photocatalyst for hydrogen production.

2.2 Electron Irradiation

The effect of electron irradiation on photocatalytic reactivity was also investigated. The precursors, TiO_2 based photocatalysts, were irradiated with an electron beam generated from a thermionic electron gun. Such modification processes were carried out at the room temperature in vacuum of less than 2×10^{-5} Torr. The electron beam was irradiated on the samples spread on the silicon wafer surface with uniform energy fixed at 50keV. The beam diameter was 10 cm. Pt loading of the electron irradiated samples was carried out after electron irradiation.

2.3 Hydrogen Production

Closed-loop photocatalytic hydrogen production device was installed to analyze reactivity of synthesized catalysts. The device consists of three parts; lamp, chamber, and cooler part as shown in figure 2 below. 500W Xe lamp was used as a visible light and UV source. The Xe lamp equipped on the top of the device irradiated top of the reaction chamber. The reaction cell was vacuumized prior to the hydrogen production reaction. A volume of evolved gas was recorded every ten minutes from the pressure changes measured by

pressure gauge directly connected to reaction chamber. To avoid temperature increase which influences pressure change even in the situation without hydrogen production, water circulation cooler was installed surrounding reaction chamber. Magnetic stirrer was set up inside reaction chamber in order to spread photocatalyst particles during the hydrogen production experiment.

Water splitting reaction was carried out in methanol aqueous solution. Water splitting reaction over TiO_2 and C_{60}/TiO_2 photocatalysts were carried out to analyze carbon coating effect. Reactivity of electron irradiated samples was also investigated.

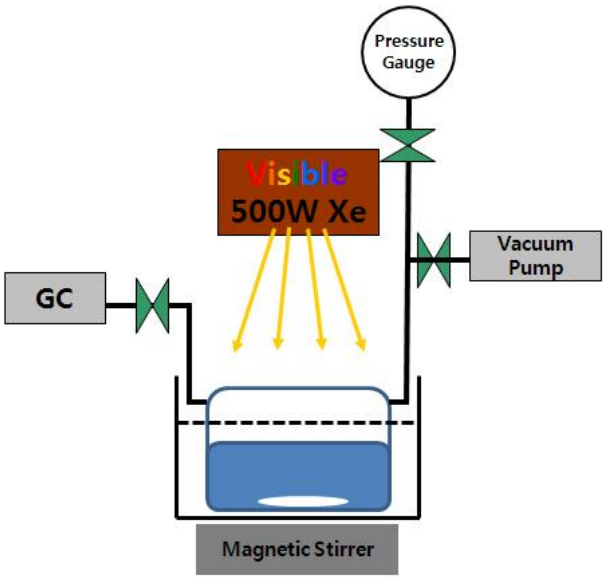

Figure 2. Photocatalytic hydrogen production device

2.4 Results and Discussion

Both carbon coating and electron irradiation enhanced hydrogen production rate of TiO2 photo catalyst. Figure 1 shows the pressure changes driven by hydrogen production with 10minute time interval. At constant temperature, the number of hydrogen molecules produced is directly proportional to the pressure. Table I lists hydrogen production rate of each samples converted from pressure changes shown in figure 1. As the irradiation time increased, hydrogen production rate also increased. It means that electron irradiation modified carbon coated TiO2 and caused positive effect on photocatalytic reactivity.

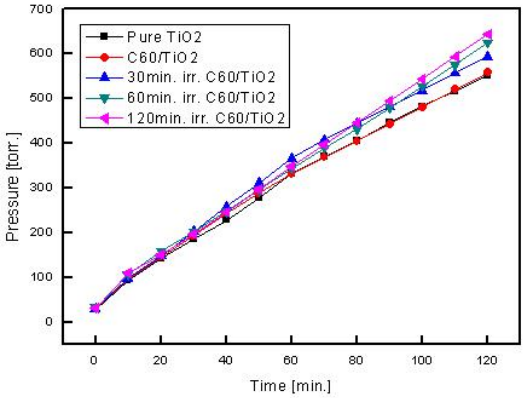

Figure 3. Effects of carbon coating and electron irradiation

Table I: Hydrogen production rate

	Hydrogen production rate (mmol/hr)
TiO_2	3.356
C_{60}/TiO_2	3.369
30min. irradiated C_{60}/TiO_2	3.606
60min. irradiated C_{60}/TiO_2	3.798
120min. irradiated C_{60}/TiO_2	3.913

3. Conclusions

Electron irradiation on carbon coated TiO2 induced hydrogen production rate increases. The longer the electron irradiation time kept, the more hydrogen was produced. These phenomena can be applied to other photocatalyst previously investigated.

REFERENCES

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