Single step fabrication method of fullerene/TiO_2 composite photocatalyst for hydrogen production

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1. Introduction

Hydrogen is one of the most promising alternative energy sources. 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 emits no CO_2 and can be produced by splitting water which is renewable and easily obtainable source.

However, about 95% of hydrogen is derived from fossil fuel.[2] It limits the merits of hydrogen. Hydrogen from fossil fuel is not a renewable energy anymore. To maximize the merits of hydrogen, renewability and no CO_2 emission, unconventional hydrogen production methods without using fossil fuel are required. Photocatalytic water-splitting is one of the unconventional hydrogen production methods. Photocatalytic water-splitting that uses hole/electron pairs of semiconductor is expectable way to produce clean and renewable hydrogen from solar energy.[3]

TiO_2 is the semiconductor material which has been most widely used as photocatalyst. TiO_2 shows high photocatalytic reactivity and stability in water. However, its wide band gap only absorbs UV light which is only 5% of sun light. To enhance the visible light responsibility, composition with fullerene based materials has been investigated. 1-2 Methano-fullerene carboxylic acid (FCA) is one of the fullerene based materials. We tried to fabricate FCA/TiO_2 composite using UV assisted single step method. The method not only simplified the fabrication procedures, but enhanced hydrogen production rate.

2. Methods and Results

2.1 Preparation of Carbon Coated TiO_2

Figure 1 shows the schematic figure of conventional fabrication processes of FCA/TiO_2. The carbon coating is carried out by stirring fullerene based materials and TiO_2 particle in organic solvent. After the fullerene coating, platinum should be deposited on the surface of the fullerene TiO_2 composite.

The Figure 2 is the scheme of UV assisted single step fabrication method of Pt/FCA/TiO_2. The details are as follow.

For the preparation of Pt/FCA/TiO_2, 20% methanol aqueous solution was used as a solvent. 5 mg of FCA powder was suspended in the 125mL methanol aqueous solution. 100mg of porous TiO_2 was added. 500μ L of H_2PtCl_6 solution is also added into the solution. The solution was stirred on the magnetic stirrer and illuminated for 2hrs with UV loght using 200W Hg-Xe lamp. The sample was dried out in vacuum with 10^{-2}torr for 1hr and washed by pure water to remove residual impurities.

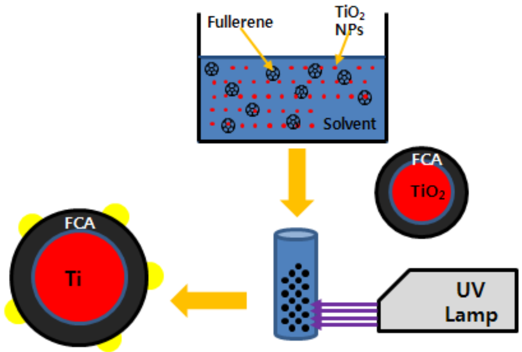

Fig. 1. Schematic figure of conventional fabrication procedure of Pt/FCA/TiO_2 photocatalyst.

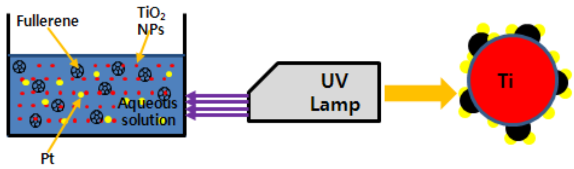

Fig. 1. Schematic figure of UV assisted single step fabrication methods of Pt/FCA/TiO_2 photocatalyst.

2.2 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 3 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.

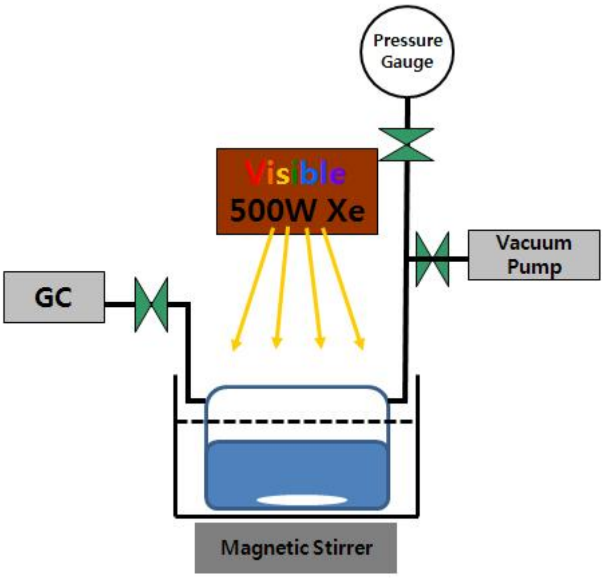

Figure 3. Photocatalytic hydrogen production device

2.3Hydrogen production rate

FCA coating enhanced hydrogen production rate of TiO_2 photo catalyst. Figure 4 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 4. FCA/TiO_2 fabricated by single step method shows higher hydrogen production rate compared with FCA/TiO_2 fabricated by conventional method. The enhancement can be caused by the geometric difference between the samples fabricated by different procedures. As figure 1 shows, the FCA covers most of the TiO_2 surface and platinum is coated on the FCA surface in conventional fabrication method. On the other hand, single step method make platinum be coated on both TiO_2 and carbonaceous material surface. It will enhance the electron charge transfer and can causes enhancement of hydrogen production.

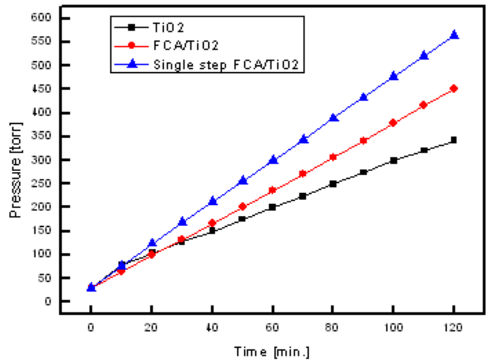

Figure 4. Hydrogen production rate of TiO_2, conventional FCA/TiO_2, FCA/TiO_2 fabricated by single step method.

Table I: Hydrogen production rate

	Hydrogen production rate (mmol/hr)
TiO_2	2.1
Conventional method FCA/TiO_2	2.7
Single step method FCA/TiO_2	3.4

3. Conclusions

We found that UV assisted single step method to fabricate Pt/FCA/TiO_2 can enhance the photocatalytic hydrogen production rate. The enhancement of charge transfer caused by uniform platinum coating on the catalyst surface made enhancement of hydrogen production rate. These phenomena can be applied to other photocatalysts based on the fullerene-TiO_2 composite previously investigated.

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