Sunlight-driven Photocatalytic Hydrogen Evolution from Water Using Titanium Phosphorus Oxide

<u>Cheng-Ting Lee,</u>[a] Yu-Chieh Shih,[b] Ling-I Hung,[b] Jeffrey Chi-Sheng Wu,[a,]* Sue-Lein Wang [b]

[a]*Chemical Engineering Department of National Taiwan University, Taipei, 10617, Taiwan*
[b]*Chemical Department of National Tsing Hua University, Hsinchu, 30013, Taiwan*
**Corresponding author: +886-2-2363-1994, cswu@ntu.edu.tw*

Abstract:

This research is dedicated to investigating the potential of titanium phosphorus oxides (TiPO) to do hydrogen evolution reaction from water. These novel TiPO materials have the feature of trivalent titanium, and could absorb visible light. Therefore, these materials were expected to have the photo-catalytic ability to produce hydrogen from water with sunlight irradiation. The hydrogen evolution ability of several TiPO materials were confirmed by gas chromatography machine equipped with Pulsed Discharge Helium Ionization Detector (PDHID). After loading platinum onto these materials by photo-deposition method, the hydrogen evolution rate increased to 2~3 times, which were dependent on the platinum loading amount. Furthermore, this research also tried to do hydrogen evolution reaction from sea water using TiPO materials, and the long time stability tests have been done.
Keywords: Titanium Phosphorus Oxides, Trivalent Titanium, Hydrogen Evolution.

1. Introduction

Burning the conventional fossil fuels to generate energy has caused serious environmental pollution and global warming. Therefore, hydrogen becomes a promising energy source, because no carbon dioxide is produced after burning hydrogen, and the heating value of hydrogen is higher than other commonly-used fuel. Steam reforming is a hydrogen production method which is commonly used by industry, but it needs high temperature and pressure, and its byproduct, carbon dioxide, becomes a problem. Therefore, photo-catalytic hydrogen evolution from water using sunlight irradiation is worth developing.

Among the photo-catalyst, TiO_2 is often used to do hydrogen evolution reaction. However, the visible light absorption ability of TiO_2 is bad. Therefore, a lot of research focus on developing new Ti^{3+} materials because of their good visible light absorption ability[1,2]. Marco et al., have proposed a new kind of mixed valence Ti^{3+}/Ti^{4+} phosphate material which can do hydrogen evolution reaction with visible light irradiation[3].

This research focused on investigating the potential of several new kinds of TiPO materials to do hydrogen evolution reaction from water. In addition, the photo-deposition method was used to load metal onto TiPO materials, and the effect of the loading metal on these materials was discussed.

Because the sea water and the sunlight are very abundant resource on the earth, this research also tried to do hydrogen evolution reaction from sea water using TiPO materials with sunlight irradiation. The abundant chloride ions in sea water were expected to act as the hole scavenger[4], preventing Ti^{3+} in catalyst from oxidizing.

2. Experimental

Batch photo-reactor was used to do hydrogen evolution reaction. 300W Xenon lamp with AM1.5 filter was the light source to simulate the sunlight irradiation. Certain amount of the catalyst and water (pure water or seawater) were placed in the Pyrex glass reactor and sonicated for 10 min. Among some reactions, 2mM of iron(II) chloride was added into solution as sacrificial agent, and the pH value was adjusted to 2.4 by sulfuric acid. After that, stainless steel cover was used to seal the reactor, and then the reactor was purged with helium gas to expel the remaining air in the reactor. After these settings were completed, 300W Xenon lamp with a distance of 5cm from reactor was turned on to start the photo-catalytic reaction. The gas sample in the reactor was taken every hour, and analyzed by the gas chromatography machine equipped with Pulsed Discharge Helium Ionization Detector (PDHID) to calculate the hydrogen production amount.

The TIPO materials were synthesized by National Tsing Hua University in Taiwan, and the material were analyzed by several equipment, including Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), to know a lot of information such as visible light absorption ability, atomic valence ratio, surface property, crystalline structure.

3. Results and discussion

From XPS data, the existence of Ti^{3+} in TiPO materials was confirmed. The hydrogen production rates of several TiPO materials were confirmed by gas chromatography machine equipped with PDHID detector. The blank tests were conducted without catalyst to make sure that the hydrogen was generated by photo-catalytic reaction of TiPO catalyst. After loading platinum onto TiPO materials by photo-deposition method, the existence of the Pt nanoparticles and the amount ratio were confirmed by TEM and ICP-MS, and the hydrogen evolution rate of TiPO materials increase 2 to 3 times, which is dependent on the platinum loading amount. There is a best loading amount because the enhancement of hydrogen production ability is dependent on both the number of surface Pt sites and the nanoparticle dispersion. The dispersion may decrease with the metal loading amount[5]. In addition, a series of optimization tests have been done in order to find the best reaction condition for hydrogen evolution. Furthermore, the longtime stability tests confirmed that these TiPO materials could to hydrogen evolution reaction from sea water for long time.

4. Conclusions

In this research, the TiPO materials were confirmed to have the feature of trivalent titanium, and exhibited hydrogen evolution ability. TiPO materials loaded with platinum by photo-deposition method showed a great enhancement in photo-catalytic activity of hydrogen evolution. Furthermore, these TiPO materials could to hydrogen evolution reaction from sea water for long time.

References

1. R. Ren, Z. Wen, S. Cui, Y. Hou, X. Guo, J. Chen, Controllable Synthesis and Tunable Photocatalytic Properties of Ti^{3+}-doped TiO_2. Scientific Reports, 2015.
2. N. Feng, F. Liu, M. Huang, A. Zheng, Q. Wang, T. Chen, G. Cao1, J. Xu, J. Fan, F. Deng, Unravelling the Efficient Photocatalytic Activity of Boron-induced Ti^{3+} Species in the Surface Layer of TiO_2. Scientific Reports, 2016.
3. M. Serra, H. G. Baldovi, F. Albarracin, H. Garcia, Visible light photocatalytic activity for hydrogen production from water–methanol mixtures of open-framework V-doped mixed-valence titanium phosphate. Applied Catalysis B: Environmental 183, 2016, 159–167.
4. L. Huang, R. Li, R. Chong, G. Liu, J. Hanab, C. Li, Cl^{-} making overall water splitting possible on TiO2-based photocatalysts. Catal. Sci. Technol., 2014, 4, 2913.
5. Z. Jiang, Z. Zhang, W. Shangguan, M. A. Isaacs, L. J. Durndell, C. M. A. Parlettb, A. F. Lee, Photodeposition as a facile route to tunable Pt photocatalysts for hydrogen production: on the role of methanol. Catal. Sci. Technol., 2016, 6, 81.