Hydrothermal Synthesis of Titanium Oxide Nanotube Catalysts and Its Modification for Water Splitting Application

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Abstract. In this study, a hydrothermal method was used to prepare Titanium Oxide nanotube photocatalysts for splitting water into hydrogen [1,2]. Optimizing the hydrogen production efficiency of the TiO$_2$ nanotubes by varying sodium hydroxide concentration and copper content enhances its photocatalytic reactivity. The TiO$_2$ nanotubes impregnated with Cu followed by transfers the photoexcited electrons to the loaded metal particles and decreases electronic-electronic hole recombination. The structural information of the TiO$_2$ nanotubes has been investigated by XRD. FE-SEM, and TEM in order to understand its chemical and physical properties. To test the reactivity of catalysts, a self-assemble reactor equipped with GC-TCD is used to analyze the water splitting efficiency.

Introduction

At present, hydrogen energy has been planned by the International Energy Agency as a clean energy source mainly used in the future. Hydrogen has a very high energy density resource. Its source can be generated by solar energy decomposition water mechanism. Both sunlight and water are the most abundant resources in the nature. The consumption of the hydrogen to produce energy with water as a product, and nor will affect the Earth's environment. Such advantages and development potential results in the gradual attention of the hydrogen energy. In 1972, the Japanese scientists A. Fujishima and K. Honda have found in the UV light irradiating TiO$_2$ electrode can decompose water into hydrogen and oxygen gas, and this photocatalytic reaction has attracted many investigators to work in this research field.

Experimental Section

The schematic studies of the experiment are shown in Figure 1. The two controlling factors (sodium hydroxide concentration and Cu concentration) have been chosen to prepare the TiO$_2$ nanotubes photocatalysts [3,4]. The XRD, FE-SEM, and TEM have been used to investigate surface structural properties. Then, the water splitting hydrogen product experiments are performed to study the hydrogen production efficiency over the TiO$_2$ nanotubes and its modification.
Results and Discussions

XRD Analysis

Fig. 2 (a) shows the XRD patterns of TiO2 nanotubes prepared at different sodium hydroxide concentrations. According to the standard of JCPDS (79-2051), the major characteristic peak of TiO2 anatase phase is 2θ = 25.52° (101). It confirms that the titanium dioxide nanotubes were successfully synthesized. In general, the crystal forms prepared at these three concentrations are very close to each other with all anatase crystal form, and we found that the concentration of 5M possesses a strong characteristic peak of TiO2.

Fig. 2 (b) shows the XRD pattern of CuO/TiO2 catalysts with different content of copper [5,6]. The XRD pattern of CuO/TiO2 shows a copper peak at 2θ = 28.2°, but the signal is not so obviously. However, the peak of CuO can be affected by the strong characteristic peak of TiO2, and the Cu peak value become weak.
SEM&TEM Analysis

Figure 3 shows the SEM images of nanotubes prepared from three different sodium hydroxide concentrations. From Figure 3 (a), it can be seen that at the 5M sodium hydroxide, the main tubular structure has been formed. The tubular structure becomes higher density with increasing sodium hydroxide concentration up to reach 10M. From the above pictures, it can be deduced that the titanium dioxide nanotube has a loose tubular structure, and greatly improve hydrogen production efficiency.

Figure 4 shows the TEM images of the nanotubes prepared at three different concentrations of sodium hydroxide. In the TEM image, it can be observed that the TiO nano-structures can be classified into tubular and lamellar structure with tubing diameter of about 10-20nm. When the NaOH concentration has been increased to 7.5M, the lamellar structure turn into a tubular structure, and the most TiO2 nanotube structure form at higher NaOH concentration of 10M, and the tubular diameter is not obviously changed.

Figure 5 is the different proportions of copper nitrate modified titanium dioxide nanotube structure. From the SEM surface analysis, it can be observed that granular copper and tubular titanium dioxide are overlapped each other. This indicates that copper successfully loaded on the main catalyst. At 1% content, it can be observed in the form of copper particles, and the aggregation of the entangled coated titanium dioxide nanotubes tubular structure. When the copper increasing to 5%, we can find copper particle size is approximately 70-80nm. From the FESEM diagram, it can be deduced that addition of 3wt% is more suitable than other conditions.
Figure 6. GC analysis for hydrogen yield (a) sodium hydroxide concentration (b) CuO addition.

**GC Analysis**

Figure 6 (a) shows hydrogen yields with different concentrations of sodium hydroxide. The results showed that the hydrogen concentration of the sample prepared at 5M sodium hydroxide concentration reached 2322 μmole/g·cat after 4 hours. The hydrogen concentration decreased to 1876 μmole/g·cat as the sodium hydroxide concentration increased to 7.5M. The results of the sample showed that 5M Titanium dioxide nanotubes present as a stable crystalline particles with higher hydrogen yields.

Figure 6 (b) shows hydrogen yields with different copper additions. In Figure 6 (b), the better performance of the water-splitting sample is 3 wt% CuO, which has about 47082 μmole/g·cat. However, when the addition amount reached 5 wt% CuO, the hydrogen yield became smaller because excessive CuO would cause a shadowing effect resulting in the decrease of the hydrogen production.

**Conclusions**

TiO₂ powders were prepared by the hydrothermal process. Based on above experiment synthesis and characterization, the best sample conditions of hydrogen yield are sodium hydroxide concentration
of 5M and hydrothermal temperature treatment is under 130 °C. It can produce about 2322 μmole/g·cat for hydrogen after 4 hrs. In order to improve the yield, the better loading content of CuO is 3 wt% with the highest hydrogen production at 47082 μmole/ g·cat. It doesn’t cause too many of electron-electron hole recombination and release some electron from long pair on CuO upon proceeding the water-splitting reaction. The two controlling factors (sodium hydroxide concentration and Cu concentration) can enhance the H₂ production efficiency over the TiO₂ nanotubes.

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References


