Photoassisted electrolysis of water for hydrogen generation with TiO$_2$ aggregate film

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Abstract. In this paper, the nanocrystallite aggregates of TiO$_2$ were synthesized and characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET). The aggregates are of submicron size, formed by nano-sized crystallites and able to offer both a large specific surface area and desirable size comparable to the wavelength of visible light. Therefore, the TiO$_2$ aggregates were also studied as photoelectrode in photoelectrochemical cell for hydrogen generation. The results show that the hydrogen generation rates are 0.47 ml/h*cm$^2$ and 0.27 ml/h*cm$^2$ during the first test with and without illumination, respectively. The current density also presented continually increasing during the light-on period. This was attributed to the photogenerated current, which benefited from the TiO$_2$ aggregates and may significantly enhance the electrolysis rate of water.

1. Introduction

Hydrogen has been becoming more and more attractive due to its high energy density as a possible alternative to the fossil fuel for solving the energy problems in future. Since Fujishima and Honda reported photoelectrochemical water splitting using titanium dioxide (TiO$_2$) photoelectrodes in 1972[1], many studies have been dedicated to the development of photocatalytic materials or photoelectrochemical cells for the conversion of solar energy into hydrogen[2-4]. The TiO$_2$ different in morphology, such as nanotubes, nanowires arrays and nanoparticles, has been widely investigated. Besides these nanostructures, a novel nanocrystallite aggregates was recently synthesized in our group and studied for hydrogen generation. The aggregates are of submicron size, formed by nano-sized crystallites and, therefore, able to offer both a large specific surface area and desirable size comparable to the wavelength of visible light. The aggregates have already been used for a photoelectrode in a dye-sensitized solar cell and achieved very high power conversion efficiencies[5]. The aggregates were employed to generate effective light scattering and thus extend the traveling distance of light within the photoelectrode film. This may result in an enhancement in the light harvesting efficiency of the photoelectrode. In this regard, the TiO$_2$ aggregates were also used as photoelectrode in photoelectrochemical cell for hydrogen generation.

In this paper, the nanocrystallite aggregates of TiO$_2$ were synthesized and characterized by XRD, SEM and BET. Then the hydrogen generation rates and current changes were investigated by using our lab-made electrochemical photocell. The results show that TiO$_2$ aggregate film has the potential application in hydrogen generation.

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2. Experimental Section

2.1 Synthesis of TiO\textsubscript{2} aggregates and preparation of photoelectrode films

The TiO\textsubscript{2} aggregates were fabricated by firstly preparing TiO\textsubscript{2} spheres and then etching the spheres to be of porous structure. Specifically, for the preparation of TiO\textsubscript{2} spheres, a mixture of 1 mL of titanium isopropoxide (TTIP) and 30 mL of ethylene glycol (EG) was added into 400 mL of acetone containing 1 mL of DI-water under vigorous stirring. The reaction resulted in the yield of TiO\textsubscript{2} spheres about several hundred nanometers in diameter. The precipitate of the TiO\textsubscript{2} spheres was collected and then treated with 500 mL of DI-water containing 0.5 mL of acetate acid in a reflux at 120 °C for 1.5 h. Such a treatment leads to the formation of porously structured aggregates through an etching process on the TiO\textsubscript{2} spheres. The product was then washed with ethanol several times, dried at 100 °C, and finally ground into fine powder for use.

The photoelectrode films were prepared on a FTO glass substrate with a screen printing method using a paste of TiO\textsubscript{2} aggregates dispersed in ethanol. The films were annealed at 450 °C for 30 min. The final films were about 10 µm in thickness.

2.2 Characterization of TiO\textsubscript{2} aggregates

The film structure and morphology were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The specific surface area was characterized by Brunauer-Emmett-Teller (BET) technique.

2.3 Photocell for hydrogen generation

Our lab-made electrochemical photocell for hydrogen generation was a two-electrode configuration with two separate compartments connected by a fine glass frit. The anode was made of TiO\textsubscript{2} aggregate film with a geometric area of 0.9 cm\textsuperscript{2} on FTO. The cathode was a platinum wire spiral in a glass burette assembled with a syringe to raise the electrolyte level before start of the experiment. The Pt-stainless rod electrode was inserted through the burette such that all the hydrogen gas evolving at the cathode could be collected in the burette displacing the electrolyte level. The volume of hydrogen gas was measured by directly reading the variation of electrolyte level in the burette. 1 M KOH (Fisher Scientific) solution with 10 vol% ethylene glycol was used as electrolyte. The light source was AM 1.5 illumination.

3. Results and discussion

Figure 1 shows the XRD patterns of films. It shows that the aggregates mainly contain anatase TiO\textsubscript{2} and, in addition, a small fraction of brookite. Figure 2 shows the SEM images of films that consist of TiO\textsubscript{2} aggregates. It can be seen that the TiO\textsubscript{2} aggregates are spherical in shape with submicron dimensions. A very rough surface was observed for these aggregates, as shown in the inset of Figure 2. Through a characterization of the specific surface area using the BET technique, these aggregates were evidenced to be high in porosity, approximately 100 m\textsuperscript{2}/g.

Hydrogen gas was collected using TiO\textsubscript{2} aggregates film at 2.0 V external voltage under AM 1.5 light in 1 M KOH with 10 vol% ethylene glycol. The hydrogen generation rates are 0.47 ml/h*cm\textsuperscript{2} and 0.27 ml/h*cm\textsuperscript{2} during the first test with and without illumination respectively. Figure 3 shows the relationship between the current density and operation time. During the light-on period, the current density presented continually increasing. The current density, however, showed to decrease gradually during the light-off period. This was attributed to the photogenerated current, which benefited from the TiO\textsubscript{2} aggregates being effective in light scattering and may thus significantly enhance the electrolysis rate of water.
4. Conclusions

In summary, we have employed the nanocrystallite aggregates of TiO$_2$ for hydrogen generation primarily. The hydrogen generation rates are 0.47 ml/h*cm$^2$ and 0.27 ml/h*cm$^2$ during the first test with and without illumination respectively at 2.0 V external voltage under AM 1.5 light in 1 M KOH with 10 vol% ethylene glycol. Oxide nanocrystallite aggregates possess both large specific surface area and suitable size comparable to the wavelength of light. The oxide nanocrystallite aggregates are therefore a class of effective light scatterers for hydrogen generation. Future experiments involve increasing the intensity of the incident light, lowering the bias voltage so as to improve the hydrogen generation rate.

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