Effect of Morphology Control on Hematite Nanostructures for Solar Water Splitting
Yen-Jhih Chen and Liang-Yih Chen*

Abstract

Due to the band gap of hematite (α-Fe2O3, Eg = 2.1 eV) in visible light region, it was regarded as a suitable n-type semiconductor material for solar water splitting. Although the theoretical conversion efficiency can be 12.9%, the characteristics of hematite, such as short hole diffusion length (~10 nm), poor charge transport and slow oxygen evolution kinetic rate, cause the generated holes to be trapped in photoanodes for low conversion efficiency. In this study, doping process was used to improve the electrical conductivity. The photocurrent density of Ti doping photoanodes was about 5.5 folds at 1.23 V (vs. RHE) than pristine hematite photoanodes. Besides, water splitting performance could be influenced by morphologies of hematite photoanodes. The nanomaterials with large surface areas could provide high active sites to generate oxygen in the electrode/solution interfaces. Finally, a heterojunction layer was constructed on the surfaces of hematite photoanodes by drop-casting and Co-Pi oxygen evolution catalysts was conducted to decrease turn on voltage and potential of water oxidation.

1. Introduction

Hematite (α-Fe2O3) is a suitable material for solar water splitting because hematite is very stable in water and the band gap (Eg = 2.1 eV) is in visible light region. The theatrical conversion efficiency can achieve 12.9% [1], which is higher than most of metal oxide semiconductors. However the performance of hematite photoanodes is limited by short diffusion length, small charge transport and low oxygen evolution reaction rate, so we dedicated to finding the solution to improve the problems. There are two ways to promote the performance, first is enhancing the electrical conductivity. Improving the crystalline...
of hematite and doping other elements into bulk material, such as Sn [2], Si [3] and Ti [4] also can increase the carrier density in space charge region then enhance the electrical conductivity. Second is lowing turn on voltage and onset potential. Heterojunction layer deposition such as MgFe₂O₄ [5] and ZnFe₂O₄ [6] cause the band bending then the electron-hole pair can be separated effectively. Besides, oxygen evolution catalysis adsorption on the surface of hematite increases water oxidation rate then excited hole can be consumed quickly so the overpotential is reduced [7].

2. Experimental Section

α-Fe₂O₃ nanostructures were grown on FTO substrate by hydrothermal method [8]. The morphology can be adjusted by adding amount of 99% ethanol in the same procedure. Ti doping hematite photoanodes were prepared by dip-coating 10 μL 0.5 vol% TiCl₄ ethanol solution and annealing at 650°C for 2h in N₂. ZnFe₂O₄ layer was deposited on Ti doping hematite by drop-coating zinc acetate dehydrate ethanol solution and 500°C 10 h air sintering. Co-Pi oxygen evolution catalysts were coated on hematite nanostructures anode by photo-assisted electrodeposition [9] at 0.4V bias vs Ag/AgCl under 302 nm 6W UV lamp illumination for 10 min.

3. Results and Discussion

In this study, α-Fe₂O₃ nanostructures grown by hydrothermal method. After 800°C high temperature annealing, the hematite nanostructures became “corals-like” single crystalline and the recombination rate was declined, which is similar as the previous report [10]. In spite of above advantages, glass substrate will be destroyed above 700°C and FTO layer on glass substrate will be cracked to increase electrical resistance apparently [11]. To avoid this problems, herein we decrease annealing temperature to 650°C. The morphology of α-Fe₂O₃ still was “corals-like” and the photocurrent density also enhanced (Fig. 1(a)). Importantly, the series resistance and charge transfer resistance were much lower than that treated via 800°C annealing, as shown in Fig. 1(c). Although α-Fe₂O₃ photoanodes could be regarded as single crystalline, the photocurrent of bare α-Fe₂O₃ photoanode was much lower than theoretical value. In order to enhance the electrical conductivity of α-Fe₂O₃, doping element was a useful strategy to achieve this goal. In Fig. 1(b), the photocurrent density of Ti doped α-Fe₂O₃ (Ti:Fe₂O₃) photoanodes was about 5.5 folds at 1.23 V (vs. RHE) than bare α-Fe₂O₃ photoanodes and the charge transfer resistance was decreased (Fig. 1(c)). Carrier density calculated by Mott-Schottky plot (Fig. 1d) increased from 3.39x10↑16 cm⁻³ to 8.02x10↑18 cm⁻³, which means the electrical conductivity of α-Fe₂O₃ photoanode was improved. The flat-band potential was shifted from 0.55 V to 0.45 V (vs. RHE). In the other hands, we added different volume ethanol (0, 0.5 and 1 mL) to the reactor for controlling the morphologies of α-Fe₂O₃ nanostructures (Fig. 2) and comparing the performance (Fig. 3). When the surface areas were increased, numerous electrolyte/photoanodes interfaces caused the holes to transfer into electrolyte for oxidation apparently and the photocurrent densities were enhanced furthermore.

Due to the short hole diffusion length and poor charge transport, oxygen evolution reaction kinetics was slow, which could be an important factor for causing the accumulation of holes on the surfaces for recombination. Therefore, we dedicated to decrease the overpotential of water oxidation and turn-on voltage for reducing the hole-trapping on the surface. In this study, ZnFe₂O₄ layer was coated on the surfaces of α-Fe₂O₃ photoanode to reduce hole-trapping. According to absorption spectra analysis (Fig. 4(c)), ZnFe₂O₄ layer did not have contribution for light harvesting. Therefore, we can ensure that the electrons and holes were only generated from α-Fe₂O₃ photoanode. Hence, the reason of cathodic shift from 1.0 V to 0.9 V was due to band bending of heterojunction interface causing electron and hole separate easily. After Co-Pi catalyst deposition, the turn-on voltage was negative shift about 0.1 V and conversion efficiency could be achieved to 0.25% (seen in Fig. 4(b)). Finally, we established an
equivalent circuit model [12] to fit the electrochemical impedance spectroscopy (EIS) data (Fig. 5(d)) to explain the holes transport phenomena of $\text{Î}-\text{Fe}_2\text{O}_3$ photoanode. The fitting parameters were listed in Table 1. In the case of only Co-Pi deposition on $\text{Î}-\text{Fe}_2\text{O}_3$ photoanodes, the trapping resistance increased but the charge transfer resistance decreased, which means the holes could be driven to the surface states efficiently (associated with trapping resistance) and the holes were consumed quickly by water oxidation (associated with charge transfer resistance). In addition, when ZnFe$_2$O$_4$ layer was coated on $\text{Î}-\text{Fe}_2\text{O}_3$ photoanodes furthermore, the trapping resistance increased but the charge transfer resistance was similar. It means that the holes were trapped in the surface states but could not be transferred into electrolyte efficiently. However, the charge transfer resistance was still high after Co-Pi deposited on ZnFe$_2$O$_4$/Ti:Fe$_2$O$_3$ photoanodes. It could be considered that ZnFe$_2$O$_4$ layer coating by long time anneal procedure in air causing the electrical conductivity of Ti:Fe$_2$O$_3$ decreased. In the future, we expect that when the anneal process of ZnFe$_2$O$_4$ layer in inert gas environment, it can decrease the conductivity to improve the conversion efficiency.

Fig. 1. (a) Photocurrent density at different annealing temperature; (b) Photocurrent density of bare and Ti doping photoanodes; (c) Nyquist plot of hematite photoanodes at 800$^\circ$C and 650$^\circ$C annealing at 1.23 V v.s RHE and the frequency range was from 10k Hz to 0.1 Hz, all measurements were under 1 sun illumination; (d) Mott-Schottky plot of bare and Ti:Fe$_2$O$_3$ photoanodes in the dark.

Fig. 2. SEM images of $\text{Î}-\text{Fe}_2\text{O}_3$ photoanodes with different volume of ethanol during growth. (a)-(b) without ethanol; (c)-(d) 0.5 mL and (e)-(f) 1mL.

Fig. 3. (a) Photocurrent density and (b) conversion efficiency of different volume of ethanol added during the growth of $\text{Î}-\text{Fe}_2\text{O}_3$ photoanodes under 1 sun illumination.

Fig. 4. (a) Photocurrent density and (b) conversion efficiency of Ti:Fe$_2$O$_3$ photoanodes of different kinds of surface passivation under 1 sun illumination; (c) UV-visible absorption spectra of ZnFe$_2$O$_4$ layer coated $\text{Î}-\text{Fe}_2\text{O}_3$; (d) Nyquist plot of Ti:Fe$_2$O$_3$ photoanodes with different kinds of surface passivation under 1.23 V v.s RHE and 1 sun illumination with the frequency range was 10k-0.1 Hz.
Table 1. Resistance and capacitance obtained from fitting EIS data

<table>
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<tr>
<th>Photoanodes</th>
<th>R_s (Ω)</th>
<th>R_trapping (Ω)</th>
<th>C_bulk (F)</th>
<th>C_Ltrap (Ω)</th>
<th>C_trap (F)</th>
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<tr>
<td>Ti:hematite</td>
<td>40.49</td>
<td>11.56</td>
<td>7.08x10^-6</td>
<td>1793.00</td>
<td>6.07x10^-6</td>
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<td>ZnFe_2O_4/Ti:hematite</td>
<td>53.82</td>
<td>857.10</td>
<td>4.62x10^-7</td>
<td>1679.00</td>
<td>1.47x10^-6</td>
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<td>Co-Pi/ZnFe_2O_4/Ti:hematite</td>
<td>60.48</td>
<td>784.90</td>
<td>3.62x10^-7</td>
<td>2355.00</td>
<td>3.16x10^-6</td>
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<tr>
<td>Co-Pi/Ti:hematite</td>
<td>34.79</td>
<td>1305.00</td>
<td>6.63x10^-6</td>
<td>409.50</td>
<td>3.34x10^-5</td>
</tr>
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</table>

References


Biography

**Liang-Yih Chen** is currently Associated Professor of the Department of Chemical Engineering, National Taiwan University of Science and Technology (NTUST, Taiwan-Tech). His current research interests include the synthesis of semiconductor quantum dots, one-dimensional metal oxide nanomaterial synthesis and sensitized solar cells. **Yen-Jhih Chen** now joined the doctoral program under the supervision of Prof. Liang-Yih Chen from 2011. His research focused on photoelectrochemical water splitting using metal oxide semiconductors and studied the charge transport/transfer mechanism by using electrochemical impedance techniques.