

Enhanced PEC water oxidation performance of hematite with low temperature annealing inducing Sn diffusion

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Abstract: High-temperature annealing is well-known method to enhance performance of Hematite in Photoelectrochemical(PEC) system. People insisted that high-temperature increase crystallinity of hematite. However, during annealing process, morphology of hematite is agglomerated and diffusion of Sn from FTO has considerable effect. To protect morphology of nanorod, people encapsulate hematite before annealing, then execute etching process. In this project, induced Sn diffusion and morphology maintained hematite was synthesized at low temperature annealing. In commercialization aspect, low temperature annealing condition, reducing the production process by skipping encapsulating, etching processes can be a strength point.

Keywords: Hematite, PEC cell, Sn diffusion.

1. Introduction

From industrial revolution, consumption of fossil fuel and population were incredibly increasing. Increasing consumption of Fossil fuel causes many problems like air pollution, greenhouse effect and depletion of fossil fuel can cause huge chaos situation. It means development of renewable energy is inevitable challenge. There are several renewable energy sources like biomass, underground heat, wind energy, hydrogen energy and solar energy. That amount overwhelms the sum of energies provided by all these renewable sources. That is why solar to hydrogen research is being performed worldwide, although the efficiency is still low. In water oxidation, there are many candidate materials like TiO_2 , WO_3 , BiVO_4 , Fe_2O_3 . Fe_2O_3 has ideal bandgap and proper band position that is connected to high theoretical photo current value ($\sim 12\text{mA}/\text{cm}^2$). Hematite has advantage in commercialization aspect because Fe is earth abundant element and hematite is relatively stable in aqueous condition. However, Fe_2O_3 has several drawbacks. First, conductivity of hematite is very poor. Diffusion length of hole is very short (2-4nm). Most of generated holes can't reach to surface. Oxygen evolution reaction kinetics at the surface is very poor. Holes reached to surface can't oxidize water directly then recombine.¹ To overcome these drawbacks, doping, heterojunction, co-catalyst, passivation layer, morphology control is recommended. Nanorod structure of hematite is well-known because generated holes easily go to its surface with sufficient thickness. Many people insisted that high-temperature increase crystallinity of hematite. However, during annealing process, morphology of hematite is agglomerated and diffusion of Sn from FTO has considerable effect.² Encapsulated hematite was reported to protect nanorod after high-temperature annealing.³ In this project, induced Sn diffusion and morphology maintained hematite was synthesized at low temperature annealing. Without encapsulating, high-temperature annealing, we maintained nanorod structure and induced Sn diffusion.

2. Experimental (or Theoretical)

FeOOH nanorod was synthesized by hydrothermal method on the fluorine-doped SnO_2 . FTO glass was cleaned by ethanol and acetone. Washed FTO glass was put in to Teflon-lined stainless-steel autoclave. A Teflon-lined stainless-steel autoclave was filled with 20 ml aqueous solution containing 0.15 M of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 1 M sodium nitrate (NaNO_3). After hydrothermal process, the FTO glass was washed by water and ethanol. Bare sample was annealed with air atmosphere at 550°C for 2 h to synthesize hematite. To induce Sn diffusion, FeOOH sample was reduced with H_2 atmosphere. Then the reduced iron sample was annealed with same condition. To confirmed difference between pre hydrogen treatment to

induce Sn diffusion, post hydrogen treatment to make oxygen vacancy, post hydrogen treatment was conducted.



Figure 1. synthesizing procedure of Sn diffused hematite

3. Results and discussion

The morphology of FeOOH, and reduced FeOOH, and hematite was confirmed by SEM images.

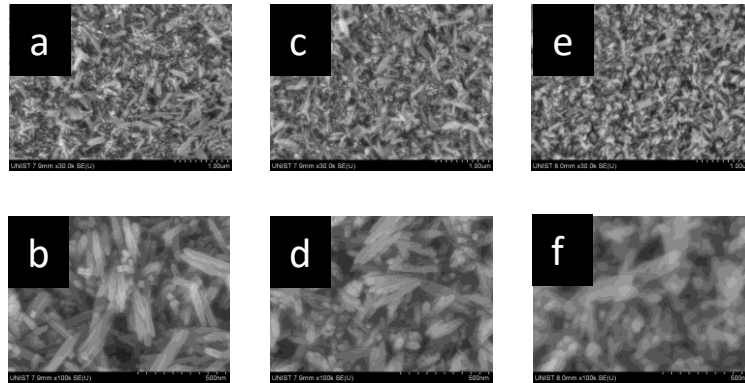


Figure 2. SEM images of FeOOH(a,b), reduced FeOOH(c,d), hematite(e,f)

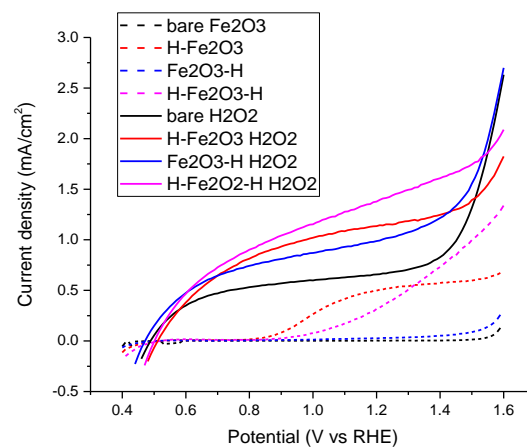


Figure 3. I-V curve of pre, post hydrogen treatment hematite

In creased photocurrent was derived from not only pre-hydrogen treatment but also post-hydrogen treatment. The two kinds of hydrogen treatments are expected to act different role.

4. Conclusions

In summary, Sn diffused hematite via pre-hydrogen treated FeOOH was successfully synthesized. The pre-hydrogen treatment acts different role with post hydrogen treatment for oxygen vacancy and it was confirmed by I-V curve. Additional analyzing tools like SIMS depth-profiling, XPS, TEM would be followed

References

- Huang, Z., et al. (2012). "In situ probe of photocarrier dynamics in water-splitting hematite (α -Fe₂O₃) electrodes." *Energy and Environmental Science* 5(10): 8923-8926.
- Annamalai, A., et al. (2015). "Activation of hematite photoanodes for solar water splitting: Effect of FTO deformation." *Journal of Physical Chemistry C* 119(7): 3810-3817.
- Li, M., et al. (2017). "Morphology and Doping Engineering of Sn-Doped Hematite Nanowire Photoanodes." *Nano Letters* 17(4): 2490-2495.