Microwave-assisted low temperature fabrication of nanostructured α-Fe₂O₃ electrodes for solar-driven hydrogen generation

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Overview

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  - Photoelectrochemical Water Splitting
  - Desirable Photoelectrode; Selection Criteria
- Experimental Methodology
  - Low Temperature Preparation using Microwaves (Electrodeposition)
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Economical Aspects of Renewable Energy Technologies

- Fossil fuel supply 80% of all energy consumed worldwide
- World energy demand will increase by approx. 45% between 2006 and 2030
- Growing demand of energy
- Depletion of fossil fuel resources
- Global warming and associated climate change
Solar Hydrogen Generation by Photoelectrochemical Water Splitting

Counter electrode

1.23V

H+/H2

H2O/O2

e–

h+

-2.0

-1.0

0

1.0

2.0

3.0

E / RHE

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Criteria for the Selection of Photoelectrodes for PEC

1. Efficiency
2. Stability
3. Low-cost
4. Optimum bandgap
5. Band edge positions (energetics)
6. The bottom of the conduction band and the top of the valence band need to overlap with H2O/H2 and H2O/O2 redox levels respectively in the solution.


Low Temperature Microwave Method

Electrodeposition:
Electrochemical solution consisted of 2 mM FeCl3.6H2O in absolute ethanol and stirred at 60 °C for 2 hours.

The electrochemical deposition of Fe films was performed in a two-electrode configuration. An applied potential of 6.2 V for 50 seconds resulted in a black film of metallic Fe (thickness = 100-150 nm) on the FTO substrates.

Annealing Treatment:
- Conventional annealing in a tube furnace at the heating rate of 20 °C/min
- Microwave-Assisted annealing was performed using a modified microwave oven capable of producing a tuneable continuous power output up to a maximum of 1000 W operating at 2.45 GHz frequency. Electrodeposited films were placed inside a high purity alumina casket to minimise the heat loss. Sic rods were used as secondary susceptors. The top of the casket had a hole at the centre which allowed for the temperature measurement of the film using a thermal imaging camera (FLIR Thermovision A40, FLIR Systems, West Malling, UK) and temperature was recorded using ThermoCAM Researcher software.
The first signs of iron oxide formation in conventional annealing at short times were seen in the sample annealed at 350 °C for 15 minutes. However, similar behaviour was observed for the sample annealed using microwave assisted heating at 200 °C for only 15 minutes, corresponding to a 42% reduction in the annealing temperature for the initiation of the oxidation process.

The highest photocurrent density at 0.55 V vs. VAg/AgCl, before the dark current onset, was 450 μA.cm⁻² for the Si-doped films annealed at 270 °C for 15 minutes using microwave irradiation (and 180 μA.cm⁻² at 0.23 V vs. VAg/AgCl). Conventional annealing at the same temperature resulted in samples with negligible (3 μA.cm⁻²) photoactivity. In contrast, a 450 °C/15 min conventional heat treatment only resulted in a film with 25% lower photocurrent density than that of the microwave annealed sample.
Conclusions

- Hematite films showed improved performance when microwave assisted annealing was used.
- Microwave heating reduced the annealing temperature by ~40%.
- The improved performance by a factor of 2 is attributed to the smaller particle size.
- The rapidity of the microwave assisted method was found to help in retaining the nanostructure of the films at a lower temperature and shorter annealing time.

- The lower processing temperatures employed in the microwave process also opens up the new possibility of fabricating hematite thin films on conducting, flexible, plastic electronic substrates.

- More than 60% of the energy could be saved in lab-scale experiments using this eco-friendly microwave annealing approach compared to conventional procedures for the preparation of hematite films – a trait that can have significant implications for scale-up production.

Suggestions for Future Work

- Investigating the effects of microwave heating on hematite films prepared by other types of fabrication techniques such as CVD, sputtering and chemical bath deposition
- Exploring ferrite and titanate compounds such as FeTiO$_3$ which have great potentials for microwave heating
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