

# Heterostructure Doped Iron Oxide Electrode for Photoassisted Electrolysis of Water

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## Abstract

Ti doped Fe<sub>2</sub>O<sub>3</sub> is a candidate material for use as a solar absorbing material for photoassisted electrolysis of water to generate hydrogen due to its low band gap. Consequently, the low band materials are also prone to rapid rates of photodecomposition and therefore unreliable in long-term applications. To combat this issue, the doped Fe<sub>2</sub>O<sub>3</sub> will be coated with a layer of p type YFeO<sub>3</sub>, a high band gap material, which is more durable against decomposition and will protect the doped Fe<sub>2</sub>O<sub>3</sub> while still allowing the visible spectrum to pass through and be absorbed by the doped Fe<sub>2</sub>O<sub>3</sub> layer. This study investigates the preparation and characterization of thin film doped Fe<sub>2</sub>O<sub>3</sub>/YFeO<sub>3</sub> nanocomposites synthesized using a sol-gel and spin coating method. The nanocomposites were prepared in a 10,000 level clean room from iron acetylacetonate and yttrium nitrate nonahydrate precursor materials. These precursors were mixed accordingly to form 2% and 5mol% Ti-doped Fe<sub>2</sub>O<sub>3</sub> and 2% and 5mol% Sr-doped YFeO<sub>3</sub> upon spin coating onto stainless steel substrates. The samples were fired using a conventional sintering technique to 850°C for densification. Optical microscopy, XRD, Zygo optical interferometry, wavelength dispersion ellipsometry, and ESEM/EDS were used to determine the effect of processing parameters on the synthesis and development of Fe<sub>2</sub>O<sub>3</sub>/YFeO<sub>3</sub> thin film electrodes. Electrical characterization and UV-Vis measurements are currently being performed as part of Stephen Sanford's senior thesis to be submitted to the Materials Science Department at Alfred University in December 2005. The main purpose of this study is to develop a heterostructure electrode resistant against photodecomposition in the application of photoelectrolysis for a clean method of producing hydrogen from an unlimited source. Many of the processing parameters in this study have not been optimized to this point and may require future studies for maximizing the capabilities of the heterostructure electrodes.

## *Introduction*

The drive to develop clean, renewable sources of energy is in high demand with the world's growing dependence on fossil fuels as our primary source of energy. Fossil fuels, when burned to create energy, emit harmful by-products which damage and pollute the environment. Greenhouse gases, such as carbon dioxide, are released contributing to the global warming effect, and sulfur gases are released when burning coal, directly contributing to acid rain. Not only do fossil fuels produce harmful emissions, but obtaining them often destroys large areas of land in mining them.

Fuel cells offer an alternative energy solution that is clean and renewable. To create energy, fuel cells must be supplied with hydrogen and oxygen to carry out the reaction. Oxygen can be easily separated from the surrounding air, but hydrogen must be obtained in other ways. Some of the present methods of producing hydrogen are steam-methane reformation, coal gasification, and electrolysis. These methods still emit some type of pollution in the form of greenhouse gases or sulfur to create hydrogen. Photoelectrolysis is a promising form of creating hydrogen by using solar energy to create enough energy to split water molecules into water and hydrogen.

In 1972, Fujishima and Honda accomplished UV induced electrolysis of water using a TiO<sub>2</sub> semiconducting photoanode combined with a platinum counter electrode soaked in an aqueous electrolyte solution.<sup>(1)</sup> Although the field of photoelectrochemical decomposition of water using sunlight has received substantial attention since then, it has much more potential as a source of generating hydrogen. This method produces hydrogen using a clean source of energy and the most abundant resource on earth. Presently, one of the main drawbacks to implementing this technology is synthesizing electrodes with efficient sunlight absorbing characteristics that are also stable under photoelectrolytic conditions.

To address this issue of rapid decomposition, it has been proposed to develop a nanostructured composite electrode utilizing a large band gap material in combination with a low band gap material. The large band gap material, p type YFeO<sub>3</sub>, will be the outer layer of the electrode, providing corrosion resistance and allowing most of the solar spectrum to pass through to the low band gap material. The low band gap material, n type Fe<sub>2</sub>O<sub>3</sub>, will function as the sunlight absorbing portion of the electrode to drive the photoelectrical reaction.

It is vital to control the microstructure of the nanocomposite to optimize its properties. To obtain this close control of parameters, sol-gel processing and spin coating will be utilized to synthesize the nanostructured composite. This paper outlines materials development, spin coat deposition, and characterization of these nanostructured composites.

## *Experimental Procedure*

An extensive literature search was performed to obtain basic knowledge of possible sol-gel precursor materials available for the synthesis Fe<sub>2</sub>O<sub>3</sub> and YFeO<sub>3</sub> thin films. Two of the most extensive materials found used to create iron oxide sol-gels were Fe(III) acetylacetonate and Fe(III) nitrate nonahydrate. Initial trial solutions created to produce iron oxide thin films were made using an iron nitrate precursor solution. Iron nitrate formed a homogeneous solution when mixed with ethanol but problems were experienced upon spin coating onto substrates. It was decided after multiple trials with

the iron nitrate solutions to use Fe(III) acetylacetonate as the precursor material for the iron oxide. This precursor solution was also used to prepare the precursor solution for the iron ferrite layer.

A 0.08M Fe(III) acetylacetonate stock solution was prepared through a mechanical mixing process via magnetic stirring. The titanium isopropoxide dopant was added as a 0.5M solution to the already mixed iron stock solution to obtain 2 and 5mol% solutions. A 0.08M iron ferrite precursor solution was made in a similar fashion to the iron oxide precursor solution. To create the p type doped solutions of iron ferrite, strontium nitrate was added directly to small portions of the stock solution of iron ferrite. These additions created 2 and 5mol% doped solutions. All of the doped solutions were double syringe filtered after mixing with 300nm filters to remove any particle contaminants. These solutions were then aged for at least a day before being used to spin samples.

A literature search was also performed to gain insight to the spin coating process and determine any typical spin parameters for spinning iron oxide sols<sup>2</sup>. Surface analysis of trial samples showed that at 5000rpm the PV value is better than that obtained at the 3000rpm spin speed and the roughness average is still acceptable at 22nm. This roughness average could be reduced if substrates of a better polish were used for spinning, but the Ra of the substrates are approximately 21nm and peak to valley values are 168nm. Presently, substrates are being polished to achieve a better finish for final samples coated with the doped solutions to obtain more accurate characterization results, specifically in the electrical testing of the samples. Final doped solutions will be applied to the substrates at a spin speed of 5000rpm for both the doped Fe<sub>2</sub>O<sub>3</sub> layer and the doped YFeO<sub>3</sub> layer. Heat treatment of approximately 250°C will be performed on a hot plate after the application of each layer to remove most of the organics from the layer before applying the next.

### *Results and Discussion*

Thermal analysis has not yet been performed on the two sol solutions to determine weight loss and regions of endothermic and exothermic reactions occurring upon firing the solutions. Data obtained from DTA/TGA analysis will be presented in December upon the completion of Sanford's Senior Thesis.

A few techniques were explored to determine the thickness of the deposited films. A prism couple technique was initially explored but not exploited in this study due to constraints of measurement. Another technique which was employed to determine thickness of the films was the use of an ellipsometer. Thickness analysis was performed on stainless steel substrates coated with individual single layers of Fe<sub>2</sub>O<sub>3</sub> and YFeO<sub>3</sub> at speeds of 3000, 5000, and 7000 rpm. The single layer Fe<sub>2</sub>O<sub>3</sub> coated substrates had thicknesses that ranged from 112nm at a spin speed of 7000rpm to 125nm thick at a 3000rpm spin speed. The single layer YFeO<sub>3</sub> coated substrates had thicknesses that ranged from 90nm at a spin speed of 7000rpm to 100nm thick at a 3000rpm spin speed. From this analysis it was determined that a single layer of either material spun onto a substrate at 5000rpm produced an approximate thickness of 100nm for the concentration of the solutions mixed. Plans are in order to observe the cross-section of the layers on ESEM (environmental scanning electron microscope) to attempt to verify the thickness measurements determined from ellipsometer.

ESEM analysis was also performed on preliminary undoped samples of  $\text{Fe}_2\text{O}_3$  and  $\text{YFeO}_3$  to observe the surface morphology of the thin films. High quality images have not yet been obtained with good resolution but current results show approximate grain sizes of 100nm with virtually no defects apparent in the images of single layer fired samples. Electron dispersion spectroscopy (EDS) was performed to verify the composition of the thin films. These results verified the presence of yttrium in the  $\text{YFeO}_3$ , but peaks were small due to nano layers and resolution of the equipment. Most peaks displayed from EDS were obtained from the stainless steel substrate, which showed peaks of Fe, Cr, O, and Si.

X-ray diffraction analysis was performed on the powders produced by firing the Fe-acetylacetonate and the prepared solution of Yttrium nitrate-Fe-acac. Both samples were fired to  $800^\circ\text{C}$  prior to performing XRD and the powders were sieved through a 100 mesh screen to ensure accurate results from the analysis<sup>3</sup>. The XRD analysis confirmed that when fired to this temperature, the Fe-acetylacetonate formed  $\text{Fe}_2\text{O}_3$  in the hematite form and the prepared solution of Yttrium nitrate-Fe-acac formed  $\text{YFeO}_3$  as expected. Future analysis will be performed on the spin coated doped materials using thin film X-ray diffraction to verify the presence of dopants in the thin films and reported in Sanford's thesis submitted in December 2005.

### *Conclusion*

This study has made some progress in the development of a heterostructure electrode using n type  $\text{Fe}_2\text{O}_3$  and p type  $\text{YFeO}_3$ . It proves the possibility of using iron acetylacetonate and yttrium nitrate in conjunction as precursor solutions for sol-gel processing and spin coating to produce thin film nanocomposite electrodes. Optical imaging has shown suitable wettability of the iron acetylacetonate solution onto the stainless steel substrate. Zygo surface analysis has shown that spin coating parameters can be adjusted to achieve a surface roughness of approximately 20nm and this can further be reduced by using better polished substrates. Ellipsometry has been used to determine the thickness of the films with respect to various spin coating speeds. EDS and X-ray diffraction analysis have shown that the composition and crystal structures desired have been obtained.

At this point in the study, a substantial amount of research and analysis is still being performed to determine the feasibility of using this thin film nanocomposite for its intended purpose. New solutions are being prepared to spin coat doped solutions for various final tests. Thin film X-ray diffraction will be performed on the doped samples to verify the presence of the dopants and the preservation of the ideal structure after doping. DTA and TGA analysis will be performed on the stock solutions of iron acetylacetonate and yttrium nitrate-iron acetylacetonate. Electrical testing will be performed on the samples to obtain impedance measurements. UV-VIS spectroscopy measurements are also to be performed on doped samples spin coated onto soda lime silicate glass to determine absorbance spectra for the thin film nanocomposite. A full report of the final results and analysis of the study will be submitted to the Center for Environmental and Energy Research upon completion of Sanford's Senior Thesis in December 2005.

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