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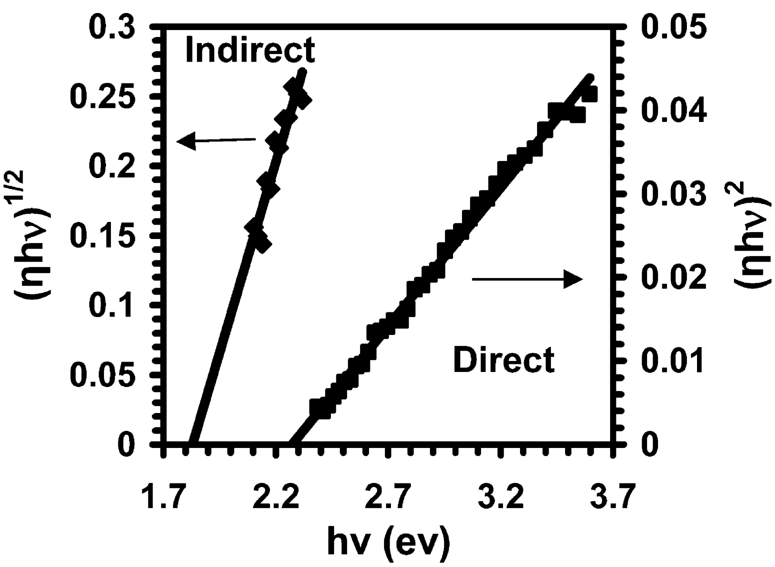

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Photoresponse of p-Type Zinc-Doped Iron(III) Oxide Thin Films

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It is still important to search for semiconductor photocatalysts that can be used in a photoelectrochemical cell to split water to hydrogen and oxygen. To that end, a stable and low-cost semiconductor that is able to absorb a large amount of solar photons while having a low band gap needs to be synthesized. Most stable semiconductors absorb almost exclusively in the ultraviolet radiation range.[1] Iron(III) oxide (Fe_2O_3) is a low-cost semiconductor having high stability that has a band gap of 2.0 to 2.2 eV. It can absorb all UV light and most of the visible light of solar radiation from 295 to 565 nm, which comprises 38% of the photons of sunlight at air mass (AM) 1.5.[2] Even though the band gap of Fe_2O_3 is suitable to allow absorption of about 38% of sunlight, its photoresponse is quite low, mainly due to its high resistivity and consequent recombination of photogenerated carriers. To minimize these limitations, n-type iron(III) oxide has been doped with an iodine dopant[3] and some transition metal dopants,[4] but the effects of zinc metal dopant have not been studied for the formation of p-type iron(III) oxide thin films.

The goal of this work is to synthesize nanocrystalline p-Fe_2O_3 films and dope them with zinc using a spray pyrolytic deposition (SPD) method in order to determine their photoresponse toward photoelectrochemical water splitting.[5] The photoresponse of zinc-doped p-Fe_2O_3 was found to be much higher than those of magnesium-doped p-Fe_2O_3 thin films synthesized in prior work.[6] In this Communication, the effects of dopant concentrations and spray times are examined.

The spray solution for the SPD synthesis of zinc-doped p-Fe_2O_3 was made using iron(III) chloride hexahydrate, $FeCl_3{\cdot}6H_2O$ (Acros Organics), and zinc nitrate hexahydrate, $Zn(NO_3)_2{\cdot}6H_2O$ (Aldrich), in 100% ethanol (Pharmco Products Inc., 200 proof). The concentration of the $FeCl_3{\cdot}6H_2O$ spray solution was kept at 0.11 M, which was found to be the optimum in prior studies.[5]

The concentration of the $Zn(NO_3)_2{\cdot}6H_2O$ was varied from 0.0077 to 0.011 M and the substrate temperature was varied between 663 and 668 K for the SPD of p-Fe_2O_3 thin-film electrodes. Indium-doped conducting tin oxide-coated glass (Swift Glass Co.) was used as the substrate.

One of the major factors influencing the optimization of p-Fe_2O_3 was the zinc dopant concentration. It was observed that photocurrent density increased up to 0.0088 M Zn^{2+} concentration and then started to decline when the dopant concentration was increased further. From 0.0088 to 0.011 M Zn^{2+} solution, there was a slow but steady decline of photocurrent density. This behavior (between 0.0088 and 0.011 M Zn^{2+} solution) was observed when all other parameters were kept constant. For example, slight variations from the optimum substrate temperature of 663 K lowered the photocurrent density in this region.

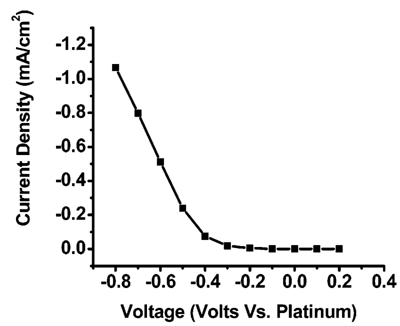

Figure 1. Cathodic current density at p-Fe_2O_3 under illumination with a light intensity of 40 mW/cm^2 from a 150 W xenon arc lamp vs a platinum electrode in a two-electrode configuration. Measurements were done in 0.5 M H_2SO_4 solution. The open-circuit potential was found to be −0.25 V/Pt.

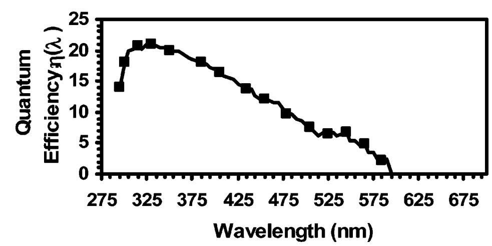

Figure 2. Quantum efficiency, $\eta(\lambda)$, versus the wavelength, λ, of light for zinc-doped p-Fe_2O_3, measured at a potential of +0.0 V/SCE using a Kratos model GM 100 monochromator with a 1.4 mm slit width. The electrolyte solution was 0.5 M H_2SO_4, and the total light intensity was 40 mW/cm^2.

Figure 1 shows the highest current density of 1.1 mA/cm^2 under illumination for optimized zinc-doped p-Fe_2O_3. The increase in photocurrent density with an increase of cathodic bias in Figure 1 indicates the p-type conductivity of Zn-doped Fe_2O_3 films. The photocurrent was measured in a two-electrode system with platinum as the counter electrode. Beyond a cathodic bias of −0.8 V/Pt, the dark current density and the current density under illumination were found to be identical due to degradation of p-Fe_2O_3. Hence, no limiting region was observed. The zinc-doped p-Fe_2O_3 showed a maximum quantum efficiency of 21.1% at 325 nm and the threshold was observed at 590 nm, which corresponds to a band gap of 2.1 eV (Figure 2). However, in an earlier study, a Mg-doped p-Fe_2O_3 electrode showed a maximum quantum efficiency of 3.0% at 380 nm and a threshold was observed at ~515 nm.[6b]

The optimum conditions for the synthesis of Zn-doped p-Fe_2O_3 were found to be a total spray time of 70 s, a spray solution concentration of 0.11 M $FeCl_3{\cdot}6H_2O$ and 0.0088 M $Zn(NO_3)_2{\cdot}6H_2O$ in 100% ethanol, and a substrate temperature of 663 K. The electrolyte solution was 0.5 M H_2SO_4. In this study a 150 W xenon arc lamp (Kratos model LH 150/1) was used with a light intensity of 40.0 mW/cm^2. A "hot" mirror from Edmund Electronics was used to reduce the excess IR and UV radiations (which are not

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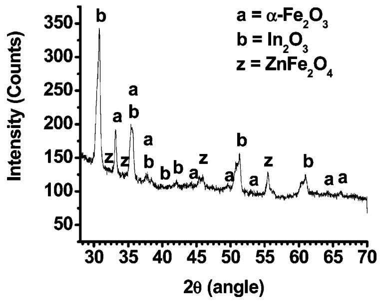

Figure 3. X-ray diffraction (XRD) plots of p-type iron(III) oxide (p-Fe_2O_3) thin film synthesized using 0.11 M Fe^{3+} and 0.0088 M Zn^{2+} solution as a dopant. The peaks in the plots were identified as α-Fe_2O_3 (a), cubic In_2O_3 (b), and zinc(II) iron(III) oxide, $ZnFe_2O_4$ (c).

present in AM 1.5 solar radiation) from the xenon arc lamp. The zinc-doped p-Fe_2O_3 was found to be a direct band gap semiconductor, having a band gap of 2.2 eV, which is in agreement with the known indirect band gap of Fe_2O_3. Thus, zinc converted the indirect band gap Fe_2O_3 to a direct band gap semiconductor due to formation of $ZnFe_2O_4$.[9a]

Mott−Schottky data showed a flatband potential of 0.0 V (vs SCE) at an ac frequency of 2500 Hz. Acceptor density calculated from the slope of the Mott−Schottky plot was found to be 4.4×10^{18} cm^{-3}. However, the acceptor density of magnesium-doped p-Fe_2O_3 was found to be 5×10^{16} cm^{-3}, measured at an ac frequency of 1500 Hz in 0.01 N NaOH.[7] The higher acceptor densities of spray pyrolytically synthesized zinc-doped p-Fe_2O_3 films in this work may be responsible for the significantly higher photocurrent densities because they helped to reduce the resistivity of the film.

The presence of zinc and zinc(II) iron(III) oxides were confirmed by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurements. XPS results showed 4 at. % zinc-doping relative to other elements present on the surface. XRD data, shown in Figure 3, indicate that α-Fe_2O_3 is the only form of iron oxide present in the thin films. Indium oxide from the indium-doped tin oxide substrate was identified. Analysis of XRD confirms that zinc dopant did not exist as solid zinc or zinc oxide. All zinc was identified in the form of $ZnFe_2O_4$.[8] These peaks indicate that spray pyrolytically synthesized p-Fe_2O_3 has mixed structures of α-iron(III) oxide and zinc(II) iron(III) oxide ($ZnFe_2O_4$). Pure Fe_2O_3 lacks adequate conductivity to be an effective semiconductor, whereas the presence of zinc in the form of $ZnFe_2O_4$ was found to show improved magnetic and conductive properties,[9] making it a suitable match for Fe_2O_3 when introduced in optimum ratios. Pure α-state iron(III) oxide was found to be unstable in acidic solution.[10] On the other hand, these Zn-doped iron oxide electrodes showed no obvious signs of deterioration in an acidic solution; however, extended runs to specifically examine the stability of these electrodes were not performed.

It is important to note that this work shows, for the first time, the fabrication of a p-Fe_2O_3 thin-film electrode using spray pyrolytic deposition with optimum zinc doping. The results of this study indicate the possibility of using other dopants or combinations of those dopants to improve the photoresponse of p-Fe_2O_3 for use in conjunction with an n-Fe_2O_3 thin-film electrode to fabricate a p/n-Fe_2O_3 solar cell and use it for efficient photoelectrochemical water splitting.

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Supporting Information Available: Detailed procedures for the synthesis of Zn-doped p-Fe_2O_3 thin films; UV−vis data for the optimized Zn-doped p-Fe_2O_3 sample; Mott−Schottky plot and direct and indirect band gap plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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