Compared with a-Fe$_2$O$_3$ and ZnxFe$_{3-x}$O$_4$ Thin Films Grown by Chemical Spray Pyrolysis

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Abstract

This work describes hematite (a-Fe$_2$O$_3$) and ZnxFe$_{3-x}$O$_4$ thin films prepared by Chemical Spray Pyrolysis (CSP) method. CSP method allows an optimal control of stoichiometry and impurity incorporation, hematite films modified with Zn$^{2+}$ was also prepared. Moreover, the most attracting characteristics of the hematite are its stability in neutral and basic solutions, abundance and band gap energy (2.0–2.2 eV) which permits it to absorb approximately 40% of the incident solar spectrum on earth. Nevertheless, the performance of hematite electrodes for water oxidation is restricted by their poor charge transport properties. Hematite low conductivity and low charge-carrier mobility. In addition, the photocatalytic activity in the presence of Ultraviolet (UV) and visible light. The most common method to directly convert solar energy into electric energy is Photovoltaic cells is limited by poor conversion efficiency. To overcome these problems, researchers have tried to find suitable methods to produce hydrogen (H$_2$) from photochemical conversion of H$_2$O using sunlight, which can be used in fuel cells for power generation. However, the applications of these materials are limited to the UV portion of sunlight. a-Fe$_2$O$_3$ has an advantage over the other conventional materials like TiO$_2$, ZnO, WO$_3$ etc. in using solar energy for photocatalytic applications due to its lower band gap ~2.2 eV value. As a result of which Fe$_2$O$_3$ is capable of absorbing a large portion of the visible solar spectrum (absorbance edge ~600 nm). Also its good chemical stability in aqueous medium, low cost, abundance and nontoxic nature makes it a promising material for photocatalytic water treatment and water splitting applications [3].

However, the photocatalytic performance of a-Fe$_2$O$_3$ is limited by certain factors such as high recombination rate of electrons and holes, low diffusion lengths of holes (2–4 nm). And poor conductivity, which led to both low efficiencies and a larger requisite over potential for photo-assisted water oxidation [4-8]. Many attempts have been made by researchers to overcome these anomalies of a-Fe$_2$O$_3$ such as lowering the recombination rate by forming nanostructures, enhancement in conductivity by doping with suitable metals and improving the charge transfer ability [9,10].

Photocatalytic ability in materials is one of the most interesting research topics due to its usefulness in various fields such as H$_2$ generation [11-13], artificial photosynthesis [14,15], waste water treatment [16-18], removal of toxic gases from air [19-21].

Fossil fuels have been the most consumed energy by the World during the last 40 years. Indeed, fossil fuels provided approximately 87% of global energy consumption in 2013. Using this kind of energy will continue to provoke the emission of greenhouse gases (e.g. CO$_2$) that pollute and damage our environment. Therefore, optimizing the technology of clean and renewable energies is urgent in order to diminish the use of fossil fuels, and, thus, it will permit the preservation of our environment for the next generations [22-27].

Spintronics is another application field of technology for Iron Oxide, whereas conventional electronic devices ignore the spin property and rely strictly on the transport of the electrical charge of electrons. Spintronics is an emergent nano technology which deals with spin dependent properties of an electron instead of or in addition to its charge dependent properties. Adding the spin degree of freedom to the current technologies will allow for a great number of new opportunities and applications, which would be impossible with conventional electronics. As a result, the field of spintronics has been rapidly expanding in recent years [28-33].

Keywords: Hematite; Zn-doped iron oxide; Photoelectrochemical (PEC); Thin film

Introduction

Photocatalysis has been attracting much research interest because of its wide applications in renewable energy and environmental restoration; however materials limitations have significantly hindered their efficiency. Researchers to find different techniques to use solar energy as an alternative for future energy needs. The objective of our research is to improve the efficiencies of PEC cells by identifying and engineering corrosion-resistant semiconductors that exhibit the optimal conduction and valence band edge alignment for PEC applications [1,2]. There are many materials that are found to show good photocatalytic activity in the presence of Ultraviolet (UV) and visible light. The most common method to directly convert solar energy into electric energy is Photovoltaic (PV), and this process utilizes semiconductors which generate electron–hole pairs upon illumination with visible light, thereby producing electric power in solar cells. However, the utility of photovoltaic cells is limited by poor conversion efficiency. To overcome these problems, researchers have tried to find suitable methods to produce hydrogen (H$_2$) from photocatalysis of H$_2$O using sunlight, which can be used in fuel cells for power generation. However, the applications of these materials are limited to the UV portion of sunlight. a-Fe$_2$O$_3$ has an advantage over the other conventional materials like TiO$_2$, ZnO, WO$_3$ etc. in using solar energy for photocatalytic applications due to its lower band gap ~2.2 eV value. As a result of which Fe$_2$O$_3$ is capable of absorbing a large portion of the visible solar spectrum (absorbance edge ~600 nm). Also its good chemical stability in aqueous medium, low cost, abundance and nontoxic nature makes it a promising material for photocatalytic water treatment and water splitting applications [3].

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Received June 11, 2017; Accepted July 04, 2017; Published July 11, 2017

Citation: Saritaş S, Turgut E, Kundakci M, Gürbulak B, Yildirim M (2017) Compared with a-Fe$_2$O$_3$ and ZnxFe$_{3-x}$O$_4$ Thin Films Grown by Chemical Spray Pyrolysis. Int J Sens Netw Data Commun 6: 152. doi: 10.4172/2090-4886.1000152

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freedom provides new effects, new capabilities and new functionalities. Spintronic devices offer the possibility of enhanced functionality, higher speed, and reduced power consumption. High-volume information-processing and communications devices are at present based on semiconductor devices, whereas information-storage devices rely on multilayers of magnetic metals and insulators. Spin transistors would allow control of the spin current in the same manner that conventional transistors can switch charge currents, which was first spin device proposed for metal-oxide geometry [28-30].

Experimental Details

CSP is one of the solution based coating technique to produce metallic and semiconductor thin or thick films. Apart from the many thin film fabrication methods, this technique is quite simple and comparatively cost effective. Dense, porous or multi-layered films in any composition can be fabricated using this versatile method. Temperature control unit, substrate heater, deposition solution and atomizer are components of the CSP setup. Different type of atomizers such as air blast, ultrasonic or electrostatic can be employed depending on properties of liquid and operating conditions to obtain coatings with desired properties. Atomized droplets of deposition solution spread over the surface of the substrates with respect to the temperature of substrate, volume and momentum of the droplets. The interaction of droplets with substrate surface, aerosol transport, and evaporation of solvent and decomposition of precursor are consecutive or simultaneous processes of this processing technique and these processes are accompanied by decomposition temperature. Therefore, temperature is the main parameter of CSP and significantly affects the microstructural, optical and electrical properties of the resultant thin film. Moreover, air flow rate, nozzle distance and viscosity of deposition solution are the other controllable processing parameter to produce high quality coatings. The salts given in Table 1 were prepared as 0.1 molar solutions in deionized water. The substrate was sprayed with argon gas onto a substrate heated to 320°C at a distance of 30 cm from the nozzle [32].

Results and Discussion

The structural, optical and magnetic properties of a-Fe$_3$O$_4$ and ZnxFe$_{3-x}$O$_4$ compounds have been extensively investigated. XRD, XPS, Raman, FE-SEM and AFM techniques have been used for structural analysis; Absorption technique has been used for optical properties; Hall and Vibrating Sample Magnetometer (VSM) techniques have been used for magnetic properties.

The XRD diffraction pattern of the iron oxide structure growing on the glass substrate is given in Figure 1 and it has been determined that the structure has a tetragonal structure (Table 2). The lattice constants a=b=8.33 Å, c=24.99 Å. Four evident peaks are observed, of which characteristic hematite peak is observed at 2θ = 32.30 degrees. As can be seen from this figure, when compared with the Fe$_2$O$_3$ compound, there has been no drop in severity. It is believed that the atomic oxygen content of the ZnxFe$_{3-x}$O$_4$ compound, the peak of the Raman shift peaks belonging to the hematite phase falls. In addition, the peaks showing the ramping changes of the stretching vibration mode of the ZnxFe$_{3-x}$O$_4$ film is due to the presence of multiple phases due to polycrystalline crystal structure [31].

XPS is used for the analysis of the elemental and chemical state information of the investigated surfaces and can be made approximately 10 nm from the surface. It is able to detect the ions and ligand energies attached to the chemical ligands of the sample studied.

As shown in Figure 4a; Tables 5 and 6 the binding energy of the 2p3/2, 2p1/2 orbitals for the Fe$^{3+}$ (Fe$_2$O$_3$) ion are 711 and 724 eV, respectively. The 1s orbital binding energy of the O$^{2-}$ ion is 531 eV. The peak intensities of the connecting electrons are very close to one another and the number of non-bonding electrons is small, which can be seen as the reason for the insulating properties [37].

We can also say that the conductivity is low because the atomic percentage of the oxygen atom is 65.96% (Table 6) and the oxygen vacancies causing the conductivity are low.

As can be seen in Figure 4b; Tables 5 and 6 the graph showing the binding energies of the Fe$^{3+}$, Zn$^{2+}$ and O$^{2-}$ ions of the ZnxFe$_{3-x}$O$_4$ composition is almost identical to the atomic oxygen content of the Fe$_2$O$_3$ compound. There has been no drop in severity. It is believed that...
It is known that Zn is alloyed with Fe, and as it is known, when an alloy occurs, it often occurs that an element has a defect in the structure of the other element. It can be said that the decrease of Fe in the ZnxFe3-xO4 compound is due to the Zn incorporated in the Fe2O3 compound. This also supports XRD results. For the Fe3+ (Fe2O3) ion, the binding energy of the 2p 3/2, 2p1/2 orbitals is 711.65 eV and 724.3 eV, respectively. The 1s orbital binding energy of the O2− ion is 530 eV. The binding energy for 2p3/2 and 2p1/2 orbitals for Zn2+ ion is 1024.23 and 1047.98 eV, respectively. If we think that the reduction in the amount of binding oxygen can be interpreted as oxygen vacancies in the structure, the cause of the increase in conductance will become apparent.

In Figure 5a, the pure Fe2O3 compound was given a 200 nm scaled FE-SEM image at about 171,000 magnifications taken at 6.6 mm working distance with an inlens detector. As can be seen from this figure, it can be said that the surface/volume ratio in which a stacked leaf-like image exists, it is a widely used material for gas sensor application [29]. Also films surface cover with OH−1 groups.

Figure 5b shows FE-SEM images of the ZnxFe3-xO4 compound at 400,000 magnifications. It is possible to say that the composition is homogeneously dispersed on the surface and that there is a nano porous structure. However, it was found that the decrease of the nanoporous structure in the ZnxFe3-xO4 compound films grown by adding the solution of zinc nitrate solution prepared for the Fe2O3 thin film was confirmed that the Zn element was mixed more into the structure and the pores were closed. This nano porous structure can be used as a suitable substrate for forming many nano rod structures.

Figure 6 shows two-dimensional and three-dimensional (5 × 5 µm) AFM images of Fe2O3 thin film. As it can be seen, there are locally pebbles, and circular-like clusters are arranged regularly. The roughness value is about 28 nm with a maximum height of 51 nm and a maximum depth of 79 nm. The average roughness value Rq\RMS value is 33 nm, which is almost consistent with the linear roughness value.

In Figure 7, the two-dimensional and three-dimensional (5 × 5 µm) AFM images obtained for the ZnxFe3-xO4 film showed that the particles in the structure showed a sharper image. There are pits and hills almost

![Image 63x165 to 275x350](image-url)

**Figure 2:** Plot of (ahu)² (cm⁻¹ eV²) vs. photon energy hυ of Fe2O3 and ZnFe2-xO4 thin films.

![Image 277x274](image-url)

**Figure 3:** Raman scattering intensities are shown as a function of wave-number for Fe2O3 and ZnxFe2-xO4 thin films.

![Image 274x274](image-url)

**Figure 4:** Raman shift and modes of Fe2O3 ve ZnxFe2-xO4 thin films.

![Image 274x274](image-url)

**Figure 5:** FE-SEM images of the ZnxFe3-xO4 compound films grown by Chemical Spray Pyrolysis. In Figure 5a, the pure Fe2O3 compound was given a 200 nm scaled FE-SEM image at about 171,000 magnifications taken at 6.6 mm working distance with an inlens detector. As can be seen from this figure, it can be said that the surface/volume ratio in which a stacked leaf-like image exists, it is a widely used material for gas sensor application [29]. Also films surface cover with OH−1 groups.

![Image 274x274](image-url)

**Figure 6:** Shows two-dimensional and three-dimensional (5 × 5 µm) AFM images of Fe2O3 thin film. As it can be seen, there are locally pebbles, and circular-like clusters are arranged regularly. The roughness value is about 28 nm with a maximum height of 51 nm and a maximum depth of 79 nm. The average roughness value Rq\RMS value is 33 nm, which is almost consistent with the linear roughness value.

In Figure 7, the two-dimensional and three-dimensional (5 × 5 µm) AFM images obtained for the ZnxFe2-xO4 film showed that the particles in the structure showed a sharper image. There are pits and hills almost

**Table 2:** Structural properties obtained from XRD patterns of Fe2O3 thin film.

| 2θ° (hkl) | d (Å) | Crystal System | Chemical Formula | Lattice constant (Å) | Reference Code |
|----------|------|---------------|-----------------|---------------------|----------------|
| 28,14 405 0.071 | a=b=8,33 c=24,99 3.21 | Tetragonal | Fe2O3 | 00-015-0615 |
| 32,30 247 0.437 | a=b=8,33 c=24,99 2.79 | Tetragonal | Fe2O3 | 00-015-0615 |
| 46,02 1112 0.174 | a=b=8,33 c=24,99 1.94 | Tetragonal | Fe2O3 | 00-015-0615 |
| 57,02 2114 0.001 | a=b=8,33 c=24,99 1.60 | Tetragonal | Fe2O3 | 00-015-0615 |

**Table 3:** Structural properties obtained from XRD patterns of ZnFe2-xO4 thin film.

| 2θ° (hkl) | d (Å) | Crystal System | Chemical Formula | Lattice constant (Å) | Reference Code |
|----------|------|---------------|-----------------|---------------------|----------------|
| 27,45 15 0.150 | 3.24 | Hexagonal | Fe2O3 | a=5,560 b=5,560 c=22,550 | 01-076-1821 |
| 29,44 7 0.135 | 3.03 | Hexagonal | Fe2O3 | a=5,560 b=5,560 c=22,550 | 01-076-1821 |
| 31,77 220 0.171 | 2.81 | Cubic | ZnFe2O4 | a=b=c=8,30 | 01-073-1963 |
| 34,50 311 0.001 | 2.59 | Cubic | ZnFe2O4 | a=b=c=8,44 | 01-086-0507 |
| 36,28 222 0.191 | 2.47 | Cubic | ZnFe2O4 | a=b=c=8,30 | 01-073-1963 |
| 45,49 249 0.100 | 1.99 | Hexagonal | ZnFe2O4 | a=12,80 b=12,80 c=57,28 | 00-045-1186 |
| 47,60 331 0.001 | 1.91 | Cubic | ZnFe2O4 | a=b=c=8,30 | 00-016-0653 |
| 47,97 331 0.262 | 1.89 | Cubic | ZnFe2O4 | a=b=c=8,30 | 00-016-0653 |
| 56,57 511 0.148 | 1.62 | Cubic | ZnFe2O4 | a=b=c=8,30 | 00-016-0653 |
| 62,86 440 0.001 | 1.47 | Cubic | ZnFe2O4 | a=b=c=8,35 | 01-073-1963 |
| 66,54 531 0.090 | 1.40 | Cubic | ZnFe2O4 | a=b=c=8,35 | 01-073-1963 |
| 68,02 22-Mar 0.090 | 1.37 | Hexagonal | Fe2O3 | a=5,560 b=5,560 c=22,550 | 01-076-1821 |
Figure 4: XPS analysis of a) Fe$_2$O$_3$ and b) ZnxFe$_{3-x}$O$_4$ thin films.

| Elements | Experimental Ion Bonding Energy (eV) | Literature Ion Bonding energy (eV) |
|----------|--------------------------------------|-----------------------------------|
|          | 2p$_{3/2}$                           | 2p$_{3/2}$                        |
| Fe       | 724.30                               | Fe$^{3+}$ (Fe$_2$O$_3$)           |
| Zn       | 1047.98                              | Zn$^{2+}$ (ZnO)                   |

Table 5: XPS measurement results of the binding energy according to orbitals of Fe$^{3+}$, Zn$^{2+}$ ions.

| Compound | Orbital | Intensity | % Atomic |
|----------|---------|-----------|----------|
| Fe$_2$O$_3$ | O 1s | 12969 | 65.96 |
|          | Fe 2p3/2 | 13470 | 34.04 |
| ZnxFe$_{3-x}$O$_4$ | O 1s | 9847 | 67.39 |
|          | Fe 2p3/2 | 8718 | 27.93 |
|          | Zn 2p3/2 | 13377 | 4.67 |

Table 6: The atomic percentage of the elements in the structure, orbital, peak intensity, bound by ions in the compounds.

Figure 5: FE-SEM images of (a) Fe$_2$O$_3$ and (b) ZnxFe$_{3-x}$O$_4$.

Figure 6: AFM images of the Fe$_2$O$_3$ thin film (Average height is 270.1 nm).

Figure 7: AFM images of the ZnxFe$_{3-x}$O$_4$ thin film (Average height is 266.6 nm).
everywhere resembling craters. The roughness value is about 34 nm, with a maximum height of 90 nm and a maximum depth of 78 nm. The average roughness value \( R_q \) value is 41 nm, which is almost in line with the linear roughness value. The variability of the colors tone indicates that the height difference in the topography is great. It is possible to say that the surface consists mostly of hills and pits.

Figure 8 shows that the sharp morphology of the \( \text{Zn}_{x}\text{Fe}_{3-x}\text{O}_4 \) thin-film AFM image in the three-dimensional (5 \( \times \) 5 \( \mu \text{m} \)) AFM image of \( \text{Zn}\text{Fe}_x\text{xO}_4 \) with a magnification of 5 min resulted in a large structure of sharp-pointed surface area and that the existing morphology stood out as shown in Figure 8. Here, a large surface area appears to be formed and the roughness value is 2.2 nm. It can be considered that such less rough \( \text{Zn}\text{Fe}_x\text{xO}_4 \) thin films are an ideal material for gas sensor application [30].

Results of Hall measurement of p-type \( \text{Fe}_2\text{O}_3 \) thin film are considered, it is expected that the carriers in the valence band of the semiconductor materials may pass to the acceptor levels by thermal excitation and contribute to the conductivity (Figure 9a). In the enlarged film the carrier density is reduced and the resistivity is increased. We can say that the holes in the valence band of the p-type semiconducting material are compensated by the donor type defects and impurities and therefore the density of the hole carrier is lowered (Figure 9b). In this case, the decrease in Hall mobility due to the increased temperature is consistent with the literature (Figure 10a). Phonon scattering of the carriers becomes predominant as temperature increases the vibration amplitude of the cage ions. This may result in an average free path reduction.
As can be seen in Figure 10b it is seen that the p-type ZnxFe_{3-x}O_{4} semiconducting compound exhibits a semiconductor character in the result of the increase in the temperature (50-300 K). Due to the increased temperature the resistivity decreases. In addition, the magnetic field increases the resistivity of the material and shows a positive magneto resistance effect. We can say that the results obtained are in the expected direction and agree with each other.

Figure 10b shows the increase in carrier density due to the increasing temperature of p-type ZnxFe_{3-x}O_{4} thin film. The increase in the number of whole carriers in the valence band with p-type semiconductor-induced thermal excitation can be seen under normal conditions.

Figure 11a and 11b shows the decrease in Hall mobility due to the increased temperature of ZnxFe_{3-x}O_{4} thin film. As a result, the carrier density has increased by two orders of magnitude.

In Figure 12a, the magnetic hysteresis curve of the Fe_{2}O_{3} thin film is observed to be relatively narrow. The saturation magnetic torque value is 4.4 x 10^{-5} emu, which corresponds to a value of 15.78 Oe. In addition, the coercive force is 0.66 Oe and the remanence magnetic moment is 0.74. In these values, it has been determined that Fe_{2}O_{3} has a soft magnetic property. Soft magnetic materials are used in devices that are exposed to alternative magnetic fields and therefore must have low energy losses. They are commonly used in transformers, electric motors, generators, dynamo and switch circuits.

In Figure 12b, the magnetic hysteresis curve of ZnxFe_{3-x}O_{4} thin film seems to be relatively wide. The saturation magnetic moment value is 3.94 x 10^{-5} emu, which corresponds to 1.72 kOe. The coercive force is -2.98 kOe and the remanence magnetic moment is 3.31. It has an emu value of 10^{-5}. When the hysteresis curve is taken into consideration, it can be said that the material exhibits hard magnetism and is difficult to demagnetize. One of the most important application areas of hard magnetic materials is motors. In addition, hard magnets are preferred in wireless drills, screwdrivers, automobile windshield wipers, water sprayers, contact circuits, ventilation systems, recorders, clocks. Other applications that benefit from hard magnets include speakers, headphones, and computer hardware in the audio system.

**Conclusion**

Undoped and modified with Zn^{2+} hematite films were synthesized by the CSP method at 320°C temperature. Raman shifts (216 cm^{-1}, 277 cm^{-1}, 383 cm^{-1}, 584 cm^{-1}, 1272 cm^{-1}) of the stretching vibration mode of Fe_{2}O_{3} films are seen. There are Raman active states of the hematite phase that these peaks are relatively narrow and severe. In the ZnxFe_{3-x}O_{4} compound, the peak of the Raman shift peak belonging to the hematite phase falls. In addition, the peaks showing the ramping changes of the stretching vibration mode of the ZnxFe_{3-x}O_{4} film is due to the presence of multiple phases due to polycrystalline crystal structure and this is consistent with XRD results.

It was demonstrated that the Zn^{2+} doped influenced on the photocatalytic performance of films. The Zn^{2+} doped hematite film exhibited a better photocatalytic performance than undoped hematite film. Hematite has low conductivity and low charge-carrier mobility. In addition, the photoexcited electron–hole pairs have short life time (~10^{-12} s), which makes the hole diffusion length to be also short (2–4 nm). The charge transport properties of hematite can be improved by doping. The better performance of Zn^{2+} doped film was attributed to

![Figure 11: Hall Mobility versus temperature for (a) a-Fe_{2}O_{3} and (b) ZnxFe_{3-x}O_{4}.](image-url)

![Figure 12: M-H curves for (a) Fe_{2}O_{3} and (b) ZnxFe_{3-x}O_{4} thin films.](image-url)
their higher carrier density that improved their conductivity. Because the carrier concentration of ZnFxFe3-xO4 is 7.2 x 10^18 and the carrier concentration of FeO is 4.2 x 10^18. So the carrier concentration of ZnFxFe3-xO4 is nearly 10 times greater. When we consider the magnetization situation, the hardest magnetization property is ZnFxFe3-xO4 film that the magnetic hysteresis curve of ZnFxFe3-xO4 thin film is seen to be relatively wide. The saturation magnetic moment value is 3.94.10^-5 emu, which corresponds to 1.72 kOe, the softest magnetization feature is FeO film that the magnetic hysteresis curve of the FeO thin film is observed to be relatively narrow. The saturation magnetic torque value is 4.41.10^-5 emu, which corresponds to a value of 15.78 Oe. It can be said here that Zn, which has no magnetic property, causes pinning which make defects in the structure difficult to move the domains.

Also when we evaluate the films grown using CSP technique in terms of their applications; FeO, and ZnFxFe3-xO4 films are suitable for spintronic applications. Spintronics is an emergent nano technology which deals with spin dependent properties of an electron instead of or in addition to its charge dependent properties. We can see in the results that the FeO compound can control its magnetic properties by doping with Zn. As a result controlling magnetic properties is very important for spin transistor applications.

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