



1.24 Synthesis and evaluation of the phases SrFe₂O₄ and SrFe₁₂O₁₉ for Hydrogen production from photocathalytic water spliting.

J. A. Jiménez-Miramontes, M. J. Meléndez-Zaragoza, J. M. Salinas-Gutiérrez, A. López-Ortiz, V. Collins-Martínez

Centro de Investigación en Materiales Avanzados, S.C. Chihuahua, Chih. México

* Tel: +52 6144391129; e-mail: virginia.collins@cimav.edu.mx

ABSTRACT

The use of materials whose properties are suitable for hydrogen production by the water splitting via photocatalysis is one of the most promising strategies to solve the current energy demand. These materials must be photoactive under sunlight, inexpensive, ecofriendly and have a band gap that fulfill the water dissociation potential of 1.23 eV. Ferrite systems present adequate optical properties to be used in this type of process, so strontium ferrite was synthesized in two of its most known phases to evaluate its performance in the evolution of hydrogen by water splitting under visible light irradiation. The strontium ferrite in its spinel phase $SrFe_2O_4$ and the hexagonal phase $SrFe_1O_{19}$ have active band gaps in the visible light spectrum of ~ 2 eV. Synthesis of the two phases from nitrates were achieved by using the modified Pechini's method at temperatures of 700-900 °C. The characterization of the materials consisted in the use of different techniques such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and UV-vis spectroscopy. The diffractograms obtained by XRD indicate the presence of pure phases of the strontium ferrite and by applying the Scherrer's equation crystallite sizesof approximately 15 and 30 nm for the spinel and hexagonal phases were obtained, respectively. The two phases have a morphology of sintered irregular polygons with a BET surface area of 18 m²/g for the spinel and 14 m²/g for the hexagonal and present a band gap of 1.77 eV and 1.82 eV, respectively. The photocatalytic evaluation was performed by monitoring the evolution of hydrogen through gas chromatography, showing the best performance for the spinel phase of 730 µmol H₂/gcat.h.

Keywords: Water splitting; Photocatalysis; SrFe₂O₄; SrFe₁₂O₁₉

1. Introduction

There is a considerable need to find environmentally friendly alternative energy sources to supply the high-energy demand covered nowadays by fossil fuels. It is well





known that energy sources coming from oil and its derivatives cause strong consequences on the environment with an alarming increase of CO_2 amounts produced by factories, cars, etc. as well as many other pollutants that are harmful to human health. The remarkable climate change, among many other concerns, is one of the main reasons that aims to find new solutions to this problem.

One of the most promising alternatives is the solar energy. In a year, earth absorbs 3,850,000 EJ (exajoules) of solar radiation in comparison with the 474 EJ consumed. This suggests that an efficient use of this source could provide enough clean and renewable energy to be used indefinitely[1],in order to substitute the aforementioned fossil fuels. Hydrogen production throughout photocatalytic water splitting is a viable technology, since greenhouse gases are not produced, however, this remains as mayor technological challenge.

Photocatalytic water splitting is a chemical reaction produced by the interaction of a semiconductor material with the electromagnetic radiation. This process begins with the material irradiation through a photon with enough energy to promote an electron from its valence band (VB) to the conduction band (CB), thus generating an electron – hole pair (e⁻ -h⁺). The difference between these energetic levels is known as band gap (E_g) and the photon energy must be equal or greater than the E_g value. The electron – hole pair is responsible forthe oxidation or reduction of the chemical species on the semiconductor surface, unless a recombination process that may occur, where the pair returns to its original state, thus releasing energy as light or heat.[2]

In the water splitting process, electrons reduce the water molecule to produce hydrogen, while holes oxidize it to form oxygen. Thus, to achieve the separation, the CB level must be more negative than the redox potential of the H^+/H_2 electrode and the VB level be more positive than the redox potential of the O_2/H_2O electrode. So the band gap of the photocatalyst must be equal or greater than 1.23 eV [1,3]

The search of a photocatalytic semiconductor with an appropriate E_g for water splitting has been an important research topic, where semiconductor materials with high band gap energy (~3.0 eV) are typical to be found [4]. The UV light spectrum comprises near 5% of the solar light, while another 46% corresponds to visible light. Therefore, an efficient and visible light active photocatalyst, must have a band gap energy between 1.1 to 3.0 eV (1100 nm to 400 nm respectively) taking into account the 1.23 eV over potential corresponding to a 237 KJ/mol Gibbs free energy. It is difficult for this reaction to occurthermodynamically by itself, and consequently, band gap values must be between 1.6 and 2.5 eV according to reported results.[1,5]

One of the most promising candidates as photocatalysts are ferrite systems for being environmentally friendly, in addition to generally present a band gap range suitably low to be photocatalytically active under visible light irradiation. Spinel ferrites (MFe₂O₄) have the capacity to absorb more visible light than other similar catalysts because of their stable and unique structural properties. This work, is aimed to study strontium ferrite as a photocatalyst for the production of hydrogen from the splitting of the water molecule. The SrFe₂O₄ spinel phase of strontium ferrite has adequate optical properties, although there





are no relevant studies for this application, even though different phases of this ferrite have been used as catalysts in organic oxidation and degradation processes[5–8].

Strontium ferrite such as spinel (SrFe₂O₄) and hexagonal (SrFe₁₂O₁₉) phases have interesting optical properties such as low band gap energies within the visible spectrum. These systems can be formed at very high temperatures (700-1200°C) with band gaps obtained from 2.1 eV and 1.8 eV for each of the strontium phases.[5,9]

Typical synthesis methods for ferrites include: controlled precipitation, combustion, SSR (solid state reaction), sol-gel, ball milling, hydrothermal and Pechini [10–12]. Each method presents its advantages and disadvantages with respect to one another, for example, the SSR method, although very simple and cheap for this type of preparation, presents the disadvantage of employing very high reaction temperatures and longtimes, which causes low surface area and photocatalytic activity materials [13].

A very suitable method to obtain nanoparticles and thin films, very important features for a good photocatalyst, is the Pechini's procedure [14]proving to be a cheap and easy to perform method, in addition to present good physical, optical and photocatalytic results[12]. The Pechini's method, known as the citrate or modified Pechini's method, is a process to oxidize materials from the mixture of an aqueous solution containing the cations, in stoichiometric proportions, into another solution of an α -hydrocarboxylic acid such as citric acid and polyhydric alcohol such as ethylene glycol often in a 1:1 ratio. This solution is homogenized under constant stirring and then evaporated to obtain a rigid cross-linked polymer, which prevents segregation of the cations.

Citric acid has the ability to chelate the metal ions and homogeneously distributing them, while by the addition of ethylene glycol results in a polystyrifaction, thus forming a polymer network. By heat treatment, this polymer is converted into a homogeneous oxidized powder to obtain the desired material[15].

The main objective in this study is the synthesis of $SrFe_2O_4$ and $SrFe_{12}O_{19}$ nanoparticles by the modified Pechini's method to determine their efficiency in the evolution of hydrogen from a photocatalytic process of the water molecule separation, as well as to correlate the textural and optical properties of the phases with their performance.

2. Materials and Methods

Synthesis process.

In order to obtain different phases of the strontium ferrite, $Fe(NO_3)_3 \cdot 9H_2O$ and $Sr(NO_3)_2$ Sigma-Aldrich® were used as precursors. The synthesis used was the modified Pechini's Method using citric acid as the chelating agent and ethylene glycol for the polymer network (Sigma-Aldrich®). The ratio of Citric acid and metals depends on the valences of these, being 1:3 with Fe³⁺ and 2:1 with Sr²⁺. The molar ratio for AC-EG was





1:1. The calculated amount of ethylene glycol was heated at 70°C under continuous stirring until evaporation was observed. The citric acid dissolved in distilled water is then added, maintaining the same conditions. The required amounts of nitrates were diluted in distilled water to homogenize and then added to the CA-EG gel by raising the temperature to 80°C. Once part of the water and the nitrates are evaporated, a viscous solution is obtained, which is allowed to dry until a polymer resin is produced. This resin is then calcined at different temperatures for each phase to obtain a powder.

Characterization

In order to determinate the calcination temperature, resin thermal decomposition was performed in a thermogravimetric analyzer equipment TA Q500. The characterization of the material consisted of its analysis in a Panalytical XpertPRO X-ray diffractometer with copper radiation (α Cu). For the study of the morphology and particle size an analysis by Field Emission scanning electron microscopy was carried out on aJEM-2200FSmicroscope. The determination of the surface area was by nitrogen physisorptionthrough BET method (Brunauer-Emmett-Teller) in aQuantachrome model NOVA1000equipment. To obtain the absorption spectra and diffuse reflectance of the powders, a Visible Evolution 220 Thermo UV spectrophotometer with integration sphere was used. The same procedure was performed for the two phases.

Photocatalytic activityevaluation

The evaluation of the phases as photocatalysts was performed by measuring the evolution of hydrogen with the gas chromatography technique in a Clarus 500 Perkin Elmer Chromatograph with a TCD (Thermal Conductivity Detector) using nitrogen as the carrier gas. The system used to carry out the separation of the molecule from the water consisted of a reactor equipped with a quartz tube. Inside the reactor a magnetic stirrer is placed, 200 ml of distilled water with a 4% methanol solution as sacrificial agent and 0.2 grams of sample for each evaluation. The reactor is kept under constant stirring for a period of 8 hours by gas sampling every hour. The system is maintained irradiated by a 250 W mercury vapor lamp that emits light in the visible range.

3. Results and Discussion

Thermogravimetric Analysis



XVII International Congress of the Mexican Hydrogen Society, 2017



The obtained material is a mixture of the metal ions of strontium and iron with some organic compounds, so a thermogravimetric analysis is performed to know the suitable temperature to decompose organic compounds present to obtain the expected oxidized phases. Figure 1 shows the thermograms of each phase, with the weight losses ranging between 80-90 % of the initial weight due to the combustion of organics at temperatures around 400-600°C. According to the data of the thermograms and the information reported in the literature, temperatures required to obtain organic-free oxidized phases are very high, in the order of 700-1200 °C. So that for each one of them an optimum temperature was used to achieve the crystallinity, being of 400°C and 700°C for the SrFe₂O₄ in an interval of 2 hours at each temperature for a total time of 4 hours and in the SrFe₁₂O₁₉phase was 900°C for 2 hours, enough time to obtain a crystalline phase.

X-ray diffraction

The diffractograms obtained from each material were indexed using the ICDD database (*International Center for Diffraction Data*) and compared by means of the program MATCH, verifying that the resulting phases were the desired ones. Figure 2 shows the diffractograms compared with the ICDD cards where the peaks obtained are indexed and where it is observed that there is no sign of impurities, indicating that pure phases were obtained. While, in the spinel phase broad peaks are observed, thus suggesting small crystallite sizes. Otherwise, the hexagonal phase, present very intense and sharp peaks, indicating the presence of possibly bigger crystal sizesthan the spinel phase.



Figure 1. Thermograms of each strontium ferrite sample prior to calcination.







Figure 2. Diffractograms of the synthesized phases indexed with ICDD patterns.

Based on the diffractogramsfound from each phase the crystallite size using the Scherrer equationwas calculated by:

$$D = \frac{0.94\lambda}{\beta\cos(\theta)} \tag{1}$$

where λ is the wavelength of the radiation from the copper lamp of the diffractometer (0,154 nm αCu), β is the Full Width at Half Maximum (FHWM) in radians, θ is the angle of the peak with greatest intensity in radians, and D is the crystallite size calculated in nanometers. Table 1 shows the approximate size obtained by equation (2) in each phase, where it can be seen that a crystallite size of the spinel phase is smaller in comparison with the hexagonal phase. From the analysis of Table 1, it can be inferred that the difference in the size of the spinel crystal with respect to the hexagonal was expected, since the temperature used in the latter was considerably higher than that of the spinel, thus favoring crystalgrowth of this phase.





CrystalSize		
Phase	D (nm)	
SrFe ₂ O ₄	15	
SrFe ₁₂ O ₁₉	30	

Table 1. Approximate crystallite size calculated for the strontium ferritephases.

Scanning electron microscopy



Figure 3.FE-SEM micrographs for samples: SrFe₂O₄ a) and b) and SrFe₁₂O₁₉ c) and d).

An analysis of the particle size and shape of each phase was carried out with a field emission scanning electron microscope, where it was very remarkable the evidence of a sintering process associated with the times and high temperatures employed for the crystallization of the samples. These sintering did not allow to observe a defined particle



XVII International Congress of the Mexican Hydrogen Society, 2017



morphology in the spinel and hexagonal phases, suggesting that irregular polygonal forms were obtained.

In Figure 3 c) and d) images of the hexagonal phase are found, where clearly particles with a size greater than those of the spinel phasecan be observed, with an average size of 70 nm. It can also be appreciated the formation of agglomerates of greater sizes reaching nearly 300 nm. As previously mentioned, these results were expected due to the high temperatures used to obtain these phases. Although some particles with nanometric sizes were obtained the sintering effect over these particles may affect the performance of the materials

Surface Area

For the analysis of the surface area, the method BET was used [16]. Table 2 presents the surface area obtained from the adsorption isotherms of each material, whose values are between 4 and 20 m²/g. These relatively small areas can be explained by the high grade of sintering in the sample and this is presumably due to the effect of particle size, since the smaller the size, the greater its surface area.

Phase	A (m²/g)
SrFe ₂ O ₄	18
$SrFe_{12}O_{19}$	14

Table 2.BET surface area of the strontium ferrite synthesized samples.

Figure 4 shows BET isotherms obtained from each material. These isotherms can be classified as type III, since they have low interaction between the adsorbate and adsorbent, where in addition the lack of hysteresis indicates non-porous materials.









Uv-Visible Spectroscopy

An analysis of UV-Vis spectroscopywas performed on the samplesto know in which part of the electromagnetic spectrum absorblight. The diffuse reflectance spectrais employed to determine the band gap of each material by using the Kubelka Munk method. Reflectance *R*, obtained from each phase is substituted in ⁽³⁾ the Kubelka Munk equation [17]:

$$f(R) = \frac{(1-R)2}{2R}$$

where f(R) is multiplied by *hv*, thus obtaining the graphs in figure 5. In the "y" axis is $(f(R)^*hv)^n$ where n is 2 for direct band gap semiconductors and ½ for indirect materials. A band gap of approximately 1.77 eV and 1.74 eV were obtained for the SrFe₂O₄ and SrFe₁₂O₁₉ phases, respectively.



Figure 5. Calculated band gap for the strontium ferrite phases based on the Kubelka Munk method.

Table 3 presents a comparison of the obtained band gap by the synthesis method of this work with respect to values reported in the literature. Here, it can be observed that there is a difference of 0.33 eV for the spinel phase and 0.11 eV for the hexagonal that may be due to the size of the particles obtained, as well as to changes in the structure and defects caused by the synthesis method, as reported by Mohanta and collaborators.





Band Gap				
Phase	Obtained (eV)	Reported (eV)		
SrFe ₂ O ₄	1.77	2.1 [5]		
SrFe ₁₂ O ₁₉	1.74	1.88 [9]		

Table 3.Band gap energies of the strontium ferrite phases compared to those reported in the literature.

Photocatalytic evaluation

Hydrogen evolution within the reactor was measured every hour for a total time of 8 hours resulting in a production of 5837 μ mol H₂/g_{cat}forSrFe₂O₄ and 34 μ mol H₂/g_{cat} forSrFe₁₂O₁₉ (Figure 6). Table 4 presents the photocatalytic performance of the two phases of strontium ferrite for hydrogen generation per mass and surface area of the catalyst, also in production per hour.



Figure 6. Photocatalytic evaluation of the strontium ferrite phases towards the H₂ production.

In this table it is very remarkable the low performance presented by the hexagonal ferrite with respect to the spinel phase. This can be explained by the band gap potential of its conduction band, which although falls within the visible range spectrum, it does not fulfill the potential levels required for the separation of the water molecule[9]. Vijayaraghavan et al. reported that the potential of the conduction band of the spinel phase is above the H₂potential, thus achieving a fundamental requirement for the separation of the water molecule. While the potential of the hexagonal ferrite falls below the level required and





although it is a very small value, it considerably impactsover the photocatalytic performance of this strontium phase[9].

Table 4. Photocatalytic performance of the strontium ferrite phases with respect to the evaluation time and surfacearea.

Phase	μ mol H ₂ /g _{cat} in 8 hrs	µmol H ₂ /m²	µmol H₂/g _{cat} ·h
SrFe ₂ O ₄	5837	324	730
SrFe ₁₂ O ₁₉	34	2	4

Phase	evaluation

Up to date, there are no studies where the performance of these phases has been reported for this application. Therefore, the obtained results in this work are compared with some studies that report the photocatalytic performance towards the hydrogen production of well-known photocatalysts, which were evaluated under similar conditions. A comparison in μ mol H₂/g_{cat} hproduction is shown in table 5, where it is observed that the performance of the spinel phase allows to consider this ferrite system as a potential candidate to be further studied as a water splitting photocatalysts under visible light irradiation.

Table 5. Photocatalysts performance comparison of the strontium ferrite phases obtained in thiswork with some known materials for H_2 production by water splitting.

Photocatalysts Performance Comparison				
Phase	µmol H₂/g∙h	Light source (W)	Reference	
SrFe ₂ O ₄	730	250 Hg	Thiswork	
TiO ₂	68	400 Hg	[18]	
$TiO_2 - ZnO (Ti/Zn = 10)$	203	400 Hg	[18]	
0.1 wt% Pt/TiO ₂ –ZnO	1789	400 Hg	[18]	
Ni–N–TiO ₂	490	400 Hg	[3]	





4. Conclusion

- Strontium ferrite phases were synthesized by the modified Pechini's method, obtaining pure SrFe₂O₄ ySrFe₁₂O₁₉phases.
- The two strontium ferrite synthesized phases are nanocrystalline, with particles sizes of approximately 40 and ~70 nm for the spinel and hexagonal phase, respectively.
- Synthesized materials were nonporous and shown the presence of sintered agglomerates and consequently smaller surface areas than 20 m²/g.
- The SrFe₂O₄ ySrFe₁₂O₁₉ phases present a band gap of 1.77 and 1.74 eV, respectively, which are suitable for the process of water splitting under visible light.
- Performance for the hydrogen generation per hour and catalyst mass of the ferrites was 730 µmol H_2/g_{cat} hfor the spinel phase and 4 µmol H_2/g_{cat} hfor the hexagonal phase.

Acknowledgements

The authors acknowledge M.Sc. Ernesto Guerrero Lestarjette, M. Sc. Karla Campos Venegas, Eng. Wilber Antunez Flores, and Eng. Luis de la Torre Saenz for their contributions to the XRD, SEM, BET, results. Special thanks are given to Laboratorio Nacional de Nanotecnología in Centro de InvestigaciónenMaterialesAvanzados, S. C., for their support in the use of the facilities.

References

- Martin DJ. Investigation into High Efficiency Visible Light Photocatalysts for Water Reduction and Oxidation. Springer T. Switzerland: Springer International Publishing; 2015. doi:10.1007/978-3-319-18488-3.
- [2] Liao C, Huang C, Wu JCS. Hydrogen Production from Semiconductor-based Photocatalysis via Water Splitting. Catalysts 2012;2:490–516. doi:10.3390/catal2040490.
- [3] Selcuk MZ, Boroglu MS, Boz I. Hydrogen production by photocatalytic watersplitting using nitrogen and metal co-doped TiO₂ powder photocatalyst. React Kinet Mech Catal 2012;106:313–24. doi:10.1007/s11144-012-0434-4.
- [4] Acar C, Dincer I, Zamfirescu C. A review on selected heterogeneous photocatalysts for hydrogen production. Int J Energy Res 2014;38:1903–1920. doi:10.1002/er.
- [5] Vijayaraghavan T, Suriyaraj SP, Selvakumar R, Venkateswaran R, Ashok A. Rapid and efficient visible light photocatalytic dye degradation using AFe₂O₄ (A = Ba, Ca and Sr) complex oxides. Mater Sci Eng B 2016;210:43–50. doi:10.1016/j.mseb.2016.04.005.
- [6] Jia T, Yan S, Liu Z. Preparation and Catalytic Properties of SrFe ₂ O ₄ in Selective Oxidation. Adv Mater Res 2012:751–4. doi:10.4028/www.scientific.net/AMR.396-





398.751.

- [7] Pardeshi SK, Pawar RY. SrFe₂O₄ complex oxide an effective and environmentally benign catalyst for selective oxidation of styrene. J Mol Catal A Chem 2011;334:35– 43. doi:10.1016/j.molcata.2010.10.020.
- [8] Mohanta O, Singhbabu YN, Giri SK, Dadhich D, Das NN, Sahu RK. Degradation of Congo red pollutants using microwave derived SrFe ₁₂O₁₉: An efficient magnetic photocatalyst under visible light. J Alloys Compd 2013;564:78–83. doi:10.1016/j.jallcom.2013.02.074.
- [9] Dom R, Borse PH, Cho CR, Lee JS, Yu SM, Yoon JH, et al. Synthesis of $SrFe_{12} O_{19}$ and $Sr_7 Fe_{10}O_{22}$ systems for visible light photocatalytic studies. J Ceram Process Res 2012;13:451–6.
- [10] González G, Carrillo FR, Zamarripa MG, Parga JR, Galván DH. Síntesis de Ferrita de Estroncio a partir de SrCO₃ y Polvo Precursor Magnético. 2010.
- [11] Yourdkhani A, Seyyed Ebrahimi SA, Koohdar HR. Preparation of strontium hexaferrite nano-crystalline powder by carbon monoxide heat treatment and recalcination from conventionally synthesized powder. J Alloys Compd 2009;470:561– 4. doi:10.1016/j.jallcom.2008.03.021.
- [12] Solarte NJ, Ramírez AE, Villaquirán CF, Tirado-Mejía. L, Gaona S. Síntesis de Polvos Cerámicos de Hexaferrita de Estroncio por los Métodos Pechini y Combustión. Rev Lat Met Mat 2015;35:276–84.
- [13] Chen W, Liu H, Li X, Liu S, Gao L, Mao L, et al. Polymerizable complex synthesis of SrTiO₃:(Cr/Ta) photocatalysts to improve photocatalytic water splitting activity under visible light. Appl Catal B Environ 2016;192:145–51. doi:10.1016/j.apcatb.2016.03.057.
- [14] Masoudpanah SM, Seyyed Ebrahimi SA. Structure and magnetic properties of nanocrystalline SrFe₁₂O₁₉ thin films synthesized by the Pechini method. J Magn Magn Mater 2013;343:128–33. doi:10.1016/j.jmmm.2013.05.016.
- [15] Olav T, Sunde L, Grande T, Einarsrud M. Handbook of Sol-Gel Science and Technology. Handb. Sol-Gel Sci. Technol., Switzerland: Springer International Publishing; 2016, p. 1–30. doi:10.1007/978-3-319-19454-7.
- [16] Brunauer S, Emmett PH, Teller E. Adsorption of Gases in Multimolecular Layers. J Am Chem Soc 1938;60:309–19. doi:10.1021/ja01269a023.
- [17] Pike Technologies. Diffuse Reflectance Theory and Applications. Appl Note 2011:2. doi:10.1016/j.soilbio.2011.02.019.
- [18] Xie MY, Su KY, Peng XY, Wu RJ, Chavali M, Chang WC. Hydrogen production by photocatalytic water-splitting on Pt-doped _{TiO2}-ZnO under visible light. J Taiwan Inst Chem Eng 2017;70:161–7. doi:10.1016/j.jtice.2016.10.034.