Water splitting activity evaluation of photocatalytic $CoFe_2O_4$ nanoparticles synthesized by a self-combustion route

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***Abstract*— Self-combustion technique has proven to be an efficient route to synthetize spinel-type nanoparticles. In particular, cobalt ferrite ($CoFe_2O_4$) has been employed in the past for a wide variety of applications and this has been the object of numerous research studies. However, self-combustion (SC) synthesis of $CoFe_2O_4$ has not been reported in the literature towards its evaluation as a visible light photocatalyst for water splitting hydrogen production. Therefore, the present research is aimed to synthesize $CoFe_2O_4$ nanoparticles by the SC route. Characterization of the material consisted in X-Ray diffraction (XRD), Scanning electron microscopy (SEM) and UV-Vis spectroscopy. Evaluation of $CoFe_2O_4$ photocatalytic activity was performed in a laboratory photoreactor under visible light irradiation using a 250 W mercurial lamp. Results indicate that after 8 hours of irradiation 6911.4 µmol H_2/g_{cat} were achieved, which is about 27 times greater than the photocatalytic activity of commercial TiO_2 P-25 under the same experimental conditions.**

Keywords—Self-combustion; $CoFe_2O_4$; Water splitting

I. INTRODUCTION

According to a U.S.-EIA (Energy information administration) report, a continuous increase in world energy consumption of 56% between 2010 and 2040 is predicted, with fossil fuels comprising to about 78%, and the remaining is expected to come from nuclear energy. The massive utilization of fossil fuels is responsible for climate change, greenhouse gas emissions and pollutants (e.g. CO, SOx, NOx, ashes, etc.) [1].

Hydrogen is a clean fuel, which does not produce toxic emissions as well as CO_2, since its only product is water. Hydrogen can be used in transportation systems, fuel cells and combustion engines. Indeed, hydrogen energy yield is approximately 2.75 times greater than hydrocarbon fuels (122 kJ/g). However, there is a general perception that hydrogen can be obtained only by clean technologies, but this is not necessarily true. Nowadays near the 95% of hydrogen production comes from fossil fuels, mainly by natural gas steam reforming. In order to avoid CO_2 generation and high energy consumption, hydraulic, wind and solar together with water splitting technologies, can be good options for hydrogen production, whereas, solar water splitting is the most promising approach, since energy and space limitations are less demanding in comparison with the other ones [2-4].

The research in the field of photocatalytic water splitting initiated using monocrystalline TiO_2 (rutile) as photoanode and a Pt cathode by applying an external current, this photoelectrochemical phenomena is known as the Honda-Fujishima effect. When a TiO_2 anode, n-type semiconductor, is illuminated by light with an energy greater than the TiO_2 band gap, electrons and holes are generated in conduction and valence bands, respectively. The migrating electrons, which will reach the Pt counter electrode reduce the H+ generated from water into H_2. Meanwhile, the holes that were left behind on the TiO_2 surface oxidize water forming O_2. TiO_2 is the most common and widely studied photocatalyst and this is due to its high stability and photocorrosion resistance, which commonly occurs with semiconductor materials. However, its efficiency is very low due to the fact that the process is limited to the high energy radiation (UV) coupled to a band gap energy of ~3.2 eV, which can be only provided from an artificial source and happens to be expensive. For this reason one of the main objectives in this area is to develop efficient photocatalytic materials, which work under visible light irradiation [4-6].

Ferrites with the general formula MFe_2O_4, where (M) represents a metal cation are used in various applications due to its chemical and thermal stability such as electronic devices and circuits, besides their use as absorbers of toxic and harmful substances to health. Spinel ferrites have shown to be effective photocatalysts due to fact that their wide band gap falls under the visible light spectrum and therefore are able to generate hole-electron pairs on the semiconductor surface, apart from their low cost and high corrosion resistance. Its photocatalytic activity is based on their redox potentials, ability to store oxygen on their crystalline lattice, and tendency to form oxygen-vacancy compounds, when synthesized under reducing atmospheres [4, 7].

Different spinel ferrite nanoparticle synthesis have been developed having a common feature that all reagents are mixed in stoichiometric amounts of precursors. Most popular methods are co-precipitation, sol-gel, micro-emulsion, hydrothermal, spray pyrolysis, reverse micelle etc. Complex procedures and

low production rates are common problems of these wet chemical methods. On the other hand, self-combustion method, where the chemical sol-gel and combustion process is combined has shown great potential in the preparation of spinel-type ferrite nanomaterials [8]. This synthesis has been employed for the preparation of MFe_2O_4 type materials using different cations such Li, Ni, Zn, Cd, Mg or their combinations [9-12]. Furthermore, this method have also been employed in obtaining nano-structures, exhibiting photocatalytic properties [13]. However, self-combustion (SC) synthesis of CoFe2O4 has not been reported so far in the literature towards its evaluation as a visible light photocatalyst for water splitting hydrogen production. Therefore, the present research is aimed to synthesize CoFe2O4 nanoparticles by the SC route.

II. Experimental

A. Preparation

Stoichiometric amounts of $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$ and $C_6H_8O_7$ (citric acid) analytical grade reagents were used to prepare three solutions adding minimum quantities of tri-distilled water in order to obtain a final 1:2:2.22 molar ratio mixture. A small amount of NH_4OH was added dropwise to adjust the pH value to about 6, during this procedure the mixture was continuously stirred in a hot plate using a magnetic stirrer. Then, the solution was heated at 80°C and constantly stirred in the hot plate for 1 hour until a very viscous brown solid was obtained. Finally, the material was burnt in a self-propagating combustion manner until complete combustion to form a dark gray loose product, which was pulverized in an agate mortar and later annealed in a muffle at 450°C by 4 hours.

B. Characterization

Characterization of the ferrite was performed by X-ray diffraction (XRD) by using a PANalytical X'Pert PRO diffractometer with X'Celerator model detector, scanning electron microscopy (SEM) with a HITACHI SU3500 and UV-visible spectroscopy on a Cary 5000 Varian/Agilent.

C. Photocatalytic Evaluation

The photocatalytic activity of water splitting was evaluated using a 250 W mercurial lamp and methanol as a sacrificial agent (2% vol). Reaction monitoring was performed by gas chromatography using a Clarus 500 Perkin Elmer GC taking gas samples at regular time intervals using a 1ml syringe through a septum located at the top of the reactor. The system configuration employed was composed of a photoreactor, artificial lighting, and CG analysis with PC data acquisition as shown in Fig. 1.

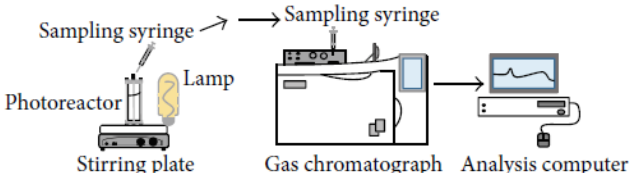


Fig. 1. Schematic experimental evaluation of the material, 0.2 g of $CoFe_2O_4$, H_2O and methanol as sacrificial agent.

A sample under darkness was taken at the beginning of the experiment, then a sample was taken every hour for a total of 8 hour irradiation time.

III. Results and Discussion

A. Characterization

1) X-Ray diffraction: Fig. 2 presents the X-Ray diffraction pattern of the synthesized sample. Data processing of this pattern was performed using the Match! Program from Crystal Impact Inc. using the PDF-2 database. Analysis of the diffraction pattern indicates that the material has crystalline nature and the peaks had coincidence with the spinel phase of cobalt ferrite (IPCC 00-022-1086). Moreover, average crystal size calculation was performed using the Scherrer's equation (1)

$$D = 0.9\lambda/\beta cos\theta \quad (1)$$

Where D is the crystal average size, λ is the X-Ray wavelength, β is the full width at half maximum (FWHM) and θ is the Brag's angle, the FWHM was calculated using OriginPro 8.0 and the estimated crystal size value was about 32 nm. Kanagesan et al. [13] obtained similar sizes in the range 20-40nm for $CoFe_2O_4$ nanoparticles synthesized by the same method.

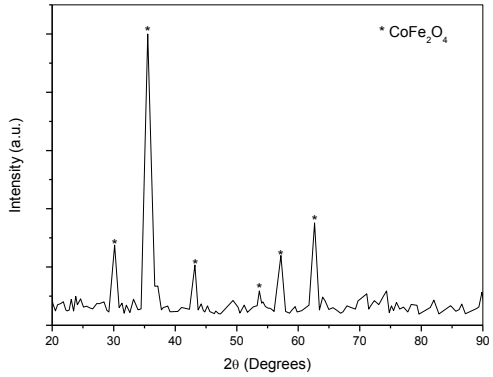


Fig. 2. X-Ray pattern from synthesized sample.

2) Scanning electron microscopy (SEM): Fig. 3 presents a SEM image showing the morphology of the synthesized material where nanoparticles agglomerates can be observed with an approximate size of around < 0.1 µm (100 nm). Also energy dispersive X-Ray spectroscopy (EDS) mapping through SEM was performed in order to observe if the element distribution, and therefore the phase formed was uniform. Trough the image presented in the Fig. 4 it is evident that the composition of the material is fairly uniform, thus suggesting that the unique crystal phase being formed is the $CoFe_2O_4$

spinel and confirming the previous X-ray results presented above.

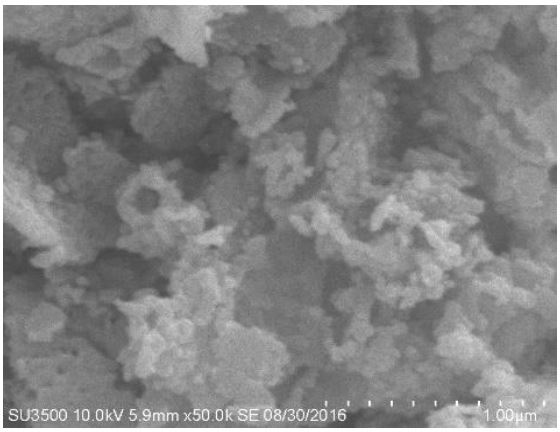


Fig. 3. SEM image of $CoFe_2O_4$ nanoparticle agglomerates.

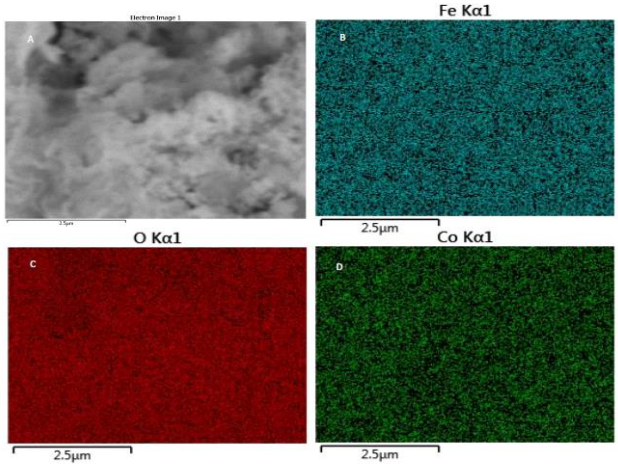


Fig. 4. EDS mapping of $CoFe_2O_4$ synthesized, A) Selected area for the mapping, B), C) and D) element distribution of Fe, O and Co, respectively.

3) UV/Visible spectroscopy: The UV/Vis spectra results are shown in Fig. 5, where a plot of energy vs transformed reflectance by the Kubelka-Munk function is presented. The linear proportion of the diffuse reflectance function cuts the abscissa axis in about a band gap energy value of 1.55 eV.

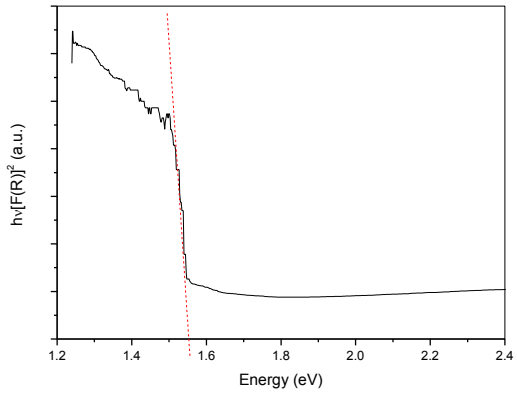


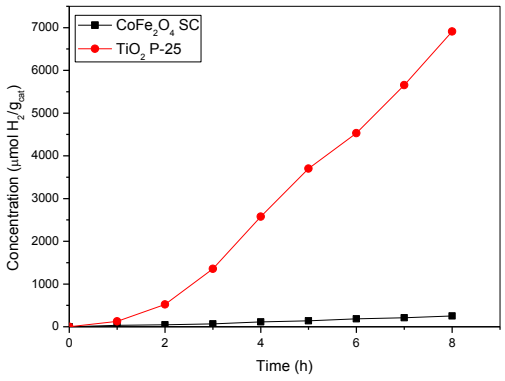
Fig. 5. UV/Visible reflectance spectra for the $CoFe_2O_4$

The obtained value is similar to values reported by Limei et al. (~1.55 eV) [14]. Also, another work by López et al. [4] reported $CoFe_2O_4$ nanoparticles synthesized by ball milling and coprecipitation methods obtaining values of ~1.1 and ~1.4 eV respectively.

B. Photocatalytic Activity

Photocatalytic activity obtained by self-combustion method (SC) is shown in Fig. 6. A comparison was performed respect to the commercial TiO_2 P-25 under the same experimental conditions. Hydrogen produced by $CoFe_2O_4$ by SC was 6911.4 µmol H_2/g_{cat}, while only 253.6 µmol H_2/g_{cat} was generated by TiO_2 P-25 indicating a higher photocatalytic activity of $CoFe_2O_4$ under visible light irradiation. This is expected, because the $CoFe_2O_4$ band gap energy value of 1.55 eV is more suitable to work under visible light, rather than TiO_2, which band gap energy is 3.2 eV and at this value UV light is more adequate for TiO_2 high photocatalytic activity.

Moreover, reported photocatalytic evaluation of $CoFe_2O_4$ towards water splitting hydrogen production performed by López et al. [4] using ball milling (BM) synthesis method showed an important photocatalytic activity. They claim that this activity was due to a significant increase of oxygen vacancies in the solid sample during the ball milling process. They reported a hydrogen production of 3309.42 µmol H_2/g_{cat} under similar conditions. The superior hydrogen production through the SC synthesis technique found in the present investigation compared to previous reported research by Ortega-Lopez et al can be explained by the findings from Feng Gu et al. [15] who suggest that due to a rapid combustion, oxygen vacancies can be generated at a greater degree, and this directly affecting the photocatalytic activity for water splitting, because they serve as electrons traps that prevent the electron-



hole pair recombination [16].

Fig. 6. Comparison of $CoFe_2O_4$ photocatalytic activity with respect to commercial P-25

IV. CONCLUSIONS

Cobalt ferrite nanoparticles were successfully synthetized by the sol-gel self-combustion method reaching a <100nm particle size, a band gap energy of 1.55 eV with a highly pure $CoFe_2O_4$ spinel phase. These features confer to the material the needed properties to work as a photocatalyst for water splitting hydrogen production under visible light. This photocatalytic activity was found to be superior to the one presented by theTiO_2 P-25 under the same experimental conditions. These results can be presumably explained by a high combustion rate, which generate a greater degree of oxygen vacancies on the material thus, directly affecting the photocatalytic activity for water splitting, and these serving as electrons traps that prevent the electron-hole pair recombination.

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