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Synthesis and Characterization of the Spinel $Znfe_2O_4$ Application to Photodegradation of Organic Pollutant Under Visible Light

Amina Kezzim[1] and Souad Saadi[2]

[1] Laboratory of Physical Chemical Inorganic Materials and Their Applications, Faculty of Sciences, University Blida 1, Algeria.
[2]Laboratory of Applied Chemistry and Materials (LabCAM), University of M'hamed Bougara of Boumerdes, Avenue de l'Indépendance, Boumerdes, 35000. Algeria.

Abstract: *The spinel $ZnFe_2O_4$, prepared by co-precipitation method with NaOH as a precipitating agent, was used for photo-degradation of Safranine O, recalcitrant dey. The textural, optical and electrochemical properties of the as-prepared $ZnFe_2O_4$ were investigated. The X-ray diffraction shows a single spinel cubic phase with a good crystallinity. The specific surface is around of 57.67 m^2/g. The TEM results showed that $ZnFe_2O_4$ nanopowders are mainly composed of irregular particles. Fourier transform infrared spectroscopy (FTIR) demonstrated the presence of Fe–O and Zn–O bonds in the range of 300 cm^{-1} to 700 cm^{-1}. The diffuse reflectance gives a band gap of 1.64 eV, properly matched to the sun spectrum. As application, the photo-degradation of Safranine O was successfully realized yielding a depollution parentage of 36 % within 120 min for an initial concentration of 10 mg L^{-1}. A photocatalytic degradation mechanism occurred through (electron-hole) pairs generation.*

Keywords: *$ZnFe_2O_4$ spinel, co-precipitation photocatalyst, recalcitrant dey, photo degradation*

1. Introduction

Water pollution by dyes, is a serious risk for the environment and human health owing to their toxicity and mutagenic effects causing damage to genetic material and possibly cancer [1, 2]. So eliminate these pollutants is an important and demanding task for the researchers. For this, several techniques have been employed such as filtration, coagulation, and adsorption. However, some of them become unsuitable for the elimination of many dyes. photocatalysis, one of the types of advanced oxidation processes (AOPs), is an eco-friendly alternative technique with high efficiency and non-selective process. The researchers are increasingly attracted to the photocatalysis on semicoconductors to eliminate the recalcitrant and hazardous dyes [3-5], to degrade pharmaceutical products [6] and to produce hydrogen [7, 8]. photocalysis is based on the irradiation of a semiconductor and the generation of free radicals responsible of the oxidation. the main challenge is therefore to develop semiconductor materials with a good cost-effectiveness ratio ensuring a good photocatalytic performance. In this respect, the spinel oxide appeared as attractive due to their low cost [9], chemical stability their optical, electrical, and optoelectronic properties [10]. In this study, our choice is directed toward Spinel ferrite nanomaterial $ZnFe_2O_4$ synthesize by co-precipitation method. The photocatalytic performance of the synthesized Zn_2FeO_4 was examined for the degradation of Safranine O.

2. Materials and Methods

2.1. Synthesis of Catalyst

The photocatalyst ZnFe2O4 was prepared by the co-precipitation method using $Zn(NO_3)_2.6H_2O$ (Merck 98%), Fe(NO3)3.9H2O (Merck 98%) and NaOH (4N) as a precipitating agent. First, zinc nitrate and iron nitrate in their respective stoichiometry were each dissolved in 30 ml of deionized water and then mixed. The solution mixture was stirred continuously during 20min. Then a quantity of NaOH was slowly added until complete precipitation. The obtained precipate was filtered, washed with de-ionized water, and dried at 80 °C for 24 h. Then, the solid was heated at 750 °C for 5h with heating rate of 5 ◦C min− 1.

2.2. Characterisation of $ZnFe_2O_4$

The crystallinity of the obtained spinel was analyzed by X-ray difraction (XRD) using a BRÜKER D5005 difractometer equipped with Cu-Kα anticathode (λ=1.54059 Å). The morphology and microstructure of the spinel have been studied by scanning electron microscopy (SEM) on Quanta TM 250. The ATR-FTIR spectrum was recorded between 400 and 4000 cm−1 using a JASKO FT/IR-4100 spectrometer. The difuse reflectance spectrum was plotted with a UV–Visible spectrophotometer (Specord 200 Plus).

2.3. Photocatalysis

Safranine O (SO) dye (C16H18ClN3S, molecular weight = 350,85 g.mol-1) was used as a model polluant to evaluate the photocatalytic activity of the ZnFe2O4. The photo-catalytic efficiency was calculated through the degradation of SO under visible-light irradiation using a tungsten lamp (200 W). The experiments were carried out in a 500-mL Pyrex reactor and the temperature was regulated at 25 °C by a thermostated bath. 40 mg of catalyst powder were dispersed in 200 mL of the SO solution with 20 mg/L of concentration. Before irradiation, the suspension was stirred in the dark for 60 min to reach the adsorption/desorption equilibrium between ZnFe2O4 and SO. During irradiation and at regular time intervals, 5 mL of suspension were drawn and centrifuged to remove the catalyst powders. The remaining SO concentration was determined with UV–vis spectro photometer (Shimadzu UV-1800) at λmax = 519 nm and the degradation rate was calculated from the following relation:

$$\text{Degradation } \% = [1 - (Ct / C0)] \times 100$$

Where Ct is the concentration of SO at time t and C0 is the initial concentration.

3. Results and Discussion

The X-ray diffraction pattern of the synthesized powder is illustrated in Fig. 1. Rietveld refinement was operated in order to investigate the purity of the obtained powder using Highscore Software. All peaks are indexed in a cubic spinel structure with lattice constant of 8.43856 Å in agreement with JCPDS card N° 00-022-012 of space group Fd-3m. The average crystallite size (D= 20.222 nm) is evaluated from the broadening (β, radian) of the intense XRD peak:

$$D = 0.94\,\lambda(\beta \cos\theta)^{-1}$$

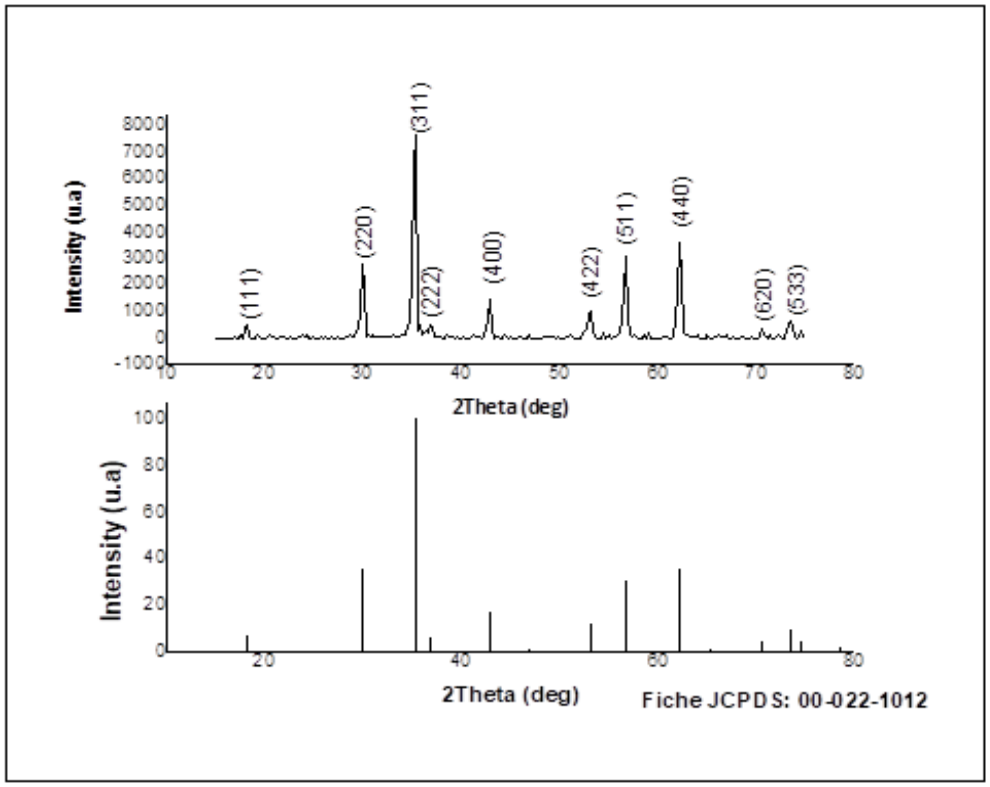

Fig. 1: X-ray diffraction pattern of $ZnFe_2O_4$ prepared by co-precipitation method.

The morphology of the material was studied by scanning electron microscopy SEM (Fig. 2). The SEM image shows the presence of agglomerates of dense grains with an average nanoparticle size less than 10 µm.

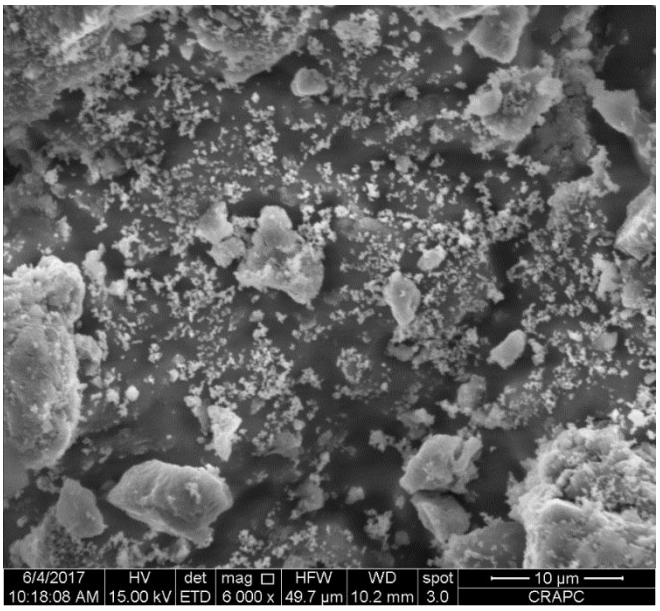

Fig. 2: SEM image of $ZnFe_2O_4$

Fig. 3 shows the FTIR spectra of ZnFe2O4 spinel powder recorded at room temperature between 450 and 3000 cm–1. The characteristic of metal-oxygen (M-O) bond vibrations of the spinel structure are observed

between 500 and 800 cm-1. ZnFe2O4 presents three absorption bands at 498 cm-1, 536 cm-1 and 825 cm-1 which are characteristic of Zn-O, Fe-O and Zn-O-Fe bond vibrations, respectively the bands observed at 1044 cm–1 and 1354 cm–1were attributed to the bending vibration of M-OH. while the band at 1620 cm-1 is due to water when the oxide is handled in air.

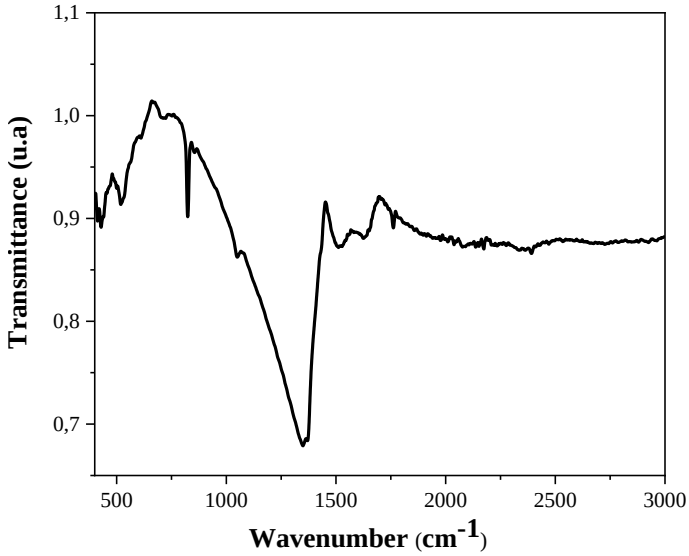

Fig. 3: FTIR spectrum of $ZnFe_2O_4$.

The knowledge of the optical gap (Eg) is crucial for the photocatalytic applications; it is determined from the plot (αhν)2 as function of the incident photon (hν) where n takes the value 1/2 or 2, respectively, for indirect and direct optical transitions, a being the optical absorption coefficient. The variation of (αhν)2 with the photon energy (hν) gives a direct gap at 1.64 eV.

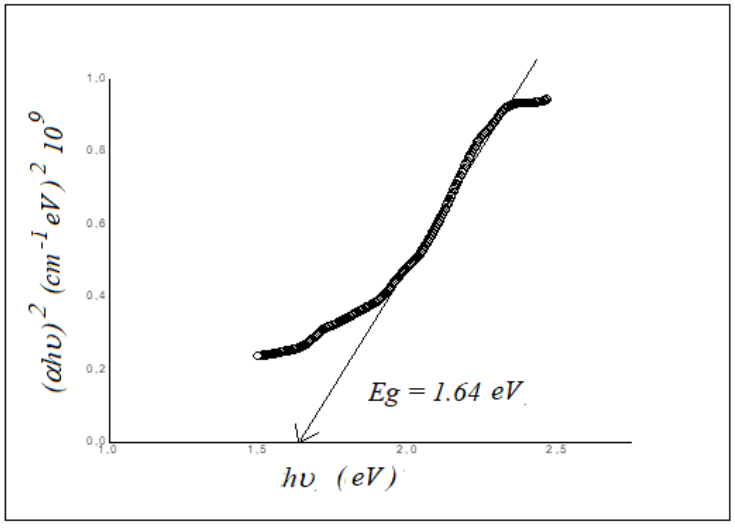

Fig. 4: The direct band gap transition of $ZnFe_2O_4$

The variation of the decimal logarithm of the conductivity (σ) as a function of (1000/T) is illustrated in Fig. 5. The figure shows that the conductivity (σ) increases with increasing temperature indicating a semiconducting character. The evolution obeys an Arrhenius type law with activation energy (Ea) of 0.98 eV.

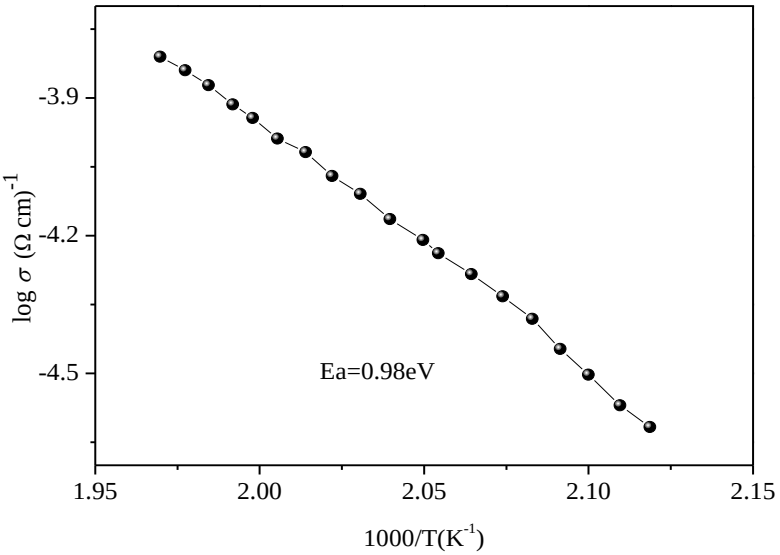

Fig. 5: The thermal variation of the electrical conductivity of $ZnFe_2O_4$

The photocatalytic efficiency of the nanocomposite was examined by the removal of SO under visible light at room temperature. Fig. 6 illustrates the evolution of SO concentration as a function of time with and without the catalyst. The photocatalytic decolorization of SO solution in the absence of catalyst is limited and not exceeding 3%. In contrast, in the presence of $ZnFe_2O_4$ the reduction of 36 % is obtained after 3h irradiation time. On the other hand The photodegradation activity increases with the increase of the catalyst mass concentration up to 0.04g L-1 (Fig. 7). After that, the photoactivity decreases, which can be associated with the turbidity of the solution and light scattering.

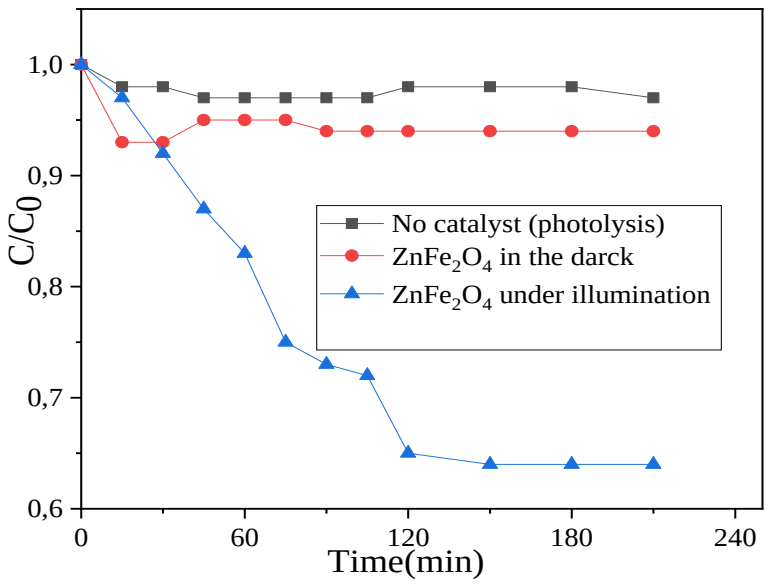

Fig. 6: Photodegradation of SO with $ZnFe_2O_4$ (initial SO concentration: 10 mgL^{-1}, pH ~7).

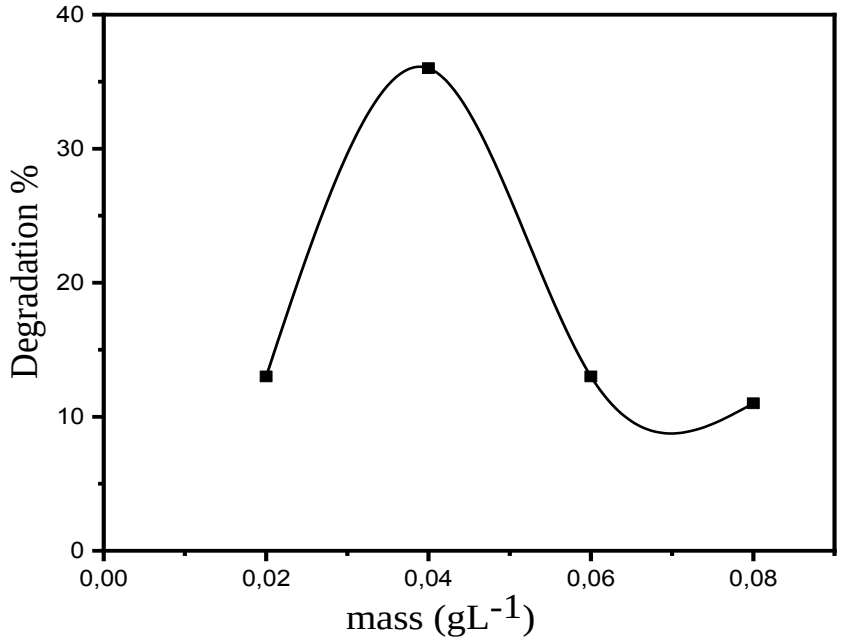

Fig. 7. Disappearance of SO at different catalyst loads. (Initial SO concentration: 10 mgL^{-1}, pH ~7).

4. Conclusion

The elimination of the SO under visible light was studied by using $ZnFe_2O_4$. The catalyst was synthesized by co-precipitation method and characterized by XRD, SEM and FTIR techniques. The XRD analysis confirmed the formation of a pure cubic spinel with nanocrystallites (~ 20 nm). An optical gap of 1.64 eV was obtained with a direct allowed transition. The semi conductivity of $ZnFe_2O_4$was demonstrated by thermal variation of the conductivity which follows an Arrhenius type law with an activation energy of 0.98 eV. The experimental results with the optimal conditions (initial concentration = 10 mg/L, pH free, dose of catalyst: 40mg/mL, T ~ 25 °C) showed that less 3% of the initial amount was reduced in the absence of photocatalyst and 36 % is obtained in presence of photocatalyst after 3h irradiation time.

5. References

[1] C. M. C.C. Brambilla, A. L. H. Garcia, F. R. Silva, S. R. Taffarel, I. Grivicich, J. N. Picada, A. Scotti, D. Dalberto, M. Mišík, S. Knasmuller, J. Silva, '' Amido Black 10B a widely used azo dye causes DNA damage in pro- and eukaryotic indicator cells'', Chemosphere vol 217, pp 430-436, February 2019.

https://doi.org/10.1016/j.chemosphere.2018.11.026

[2] M. M. Motlagha , S.A. Hassanzadeh-Tabrizib,n and A. Saffar-Teluri, '' Influence of Mn2O3 content on the textural and catalytic properties of Mn2O3/Al2O3/SiO2 nanocatalyst'', Ceramics International vol 40, pp 16177-16181, July 2014.

https://doi.org/10.1016/j.ceramint.2014.07.049

[3] F.Z Akika, M. Benamira, H. Lahmar, A. Tibera, R. Chabi, I. Avramova, Ş. Suzer and M. Trari, '' Structural and optical properties of Cu-substitution of NiAl2O4 and their photocatalytic activity towards Congo red under solar light irradiation'' Journal of Photochemistry & Photobiology A: Chemistry vol 364, pp 542-550, June 2018.

https://doi.org/10.1016/j.jphotochem.2018.06.049

[4] S. G. Hosseini , H. Sharifnezhad and M. Fathollahi, '' Quantitative and Qualitative Characterization of Pure Copper Chromite Nanocomposites for Photodegradation of p-Nitrophenol in Aqueous Medium'', Journal of Electronic Materials, vol 48, 4207-4216, April 2019.

https://doi.org/10.1007/s11664-019-07192-9

[5] S. A. Jadhav, S. B. Somvanshi, M. V. Khedkar, S. R. Patade and K. M. Jadhav, '' Magneto structural and photocatalytic behavior of mixed Ni–Zn nano spinel ferrites: visible light enabled active photodegradation of rhodamine B'', Journal of Materials Science: Materials in Electronics May 2020.

https://doi.org/10.1007/s10854-020-03684-1

[6] A. Kezzim, A. Boudjemaa, A. Belhadi and M. Trari ''Photo-catalytic degradation of ibuprofen over the new semiconducting catalyst a-(Cu,Fe)2O3 prepared by hydrothermal route'', Res Chem Intermed,dec 2016

https://doi.org/10.1007/s11164-016-2837-8

[7] S. Saadi, A. Bouguelia and M. Trari, ''Phototocatalytic hydrogen evolution over $CuCrO_2$'', Solar Energy, vol 80, pp 272-280, 2006.

https://doi.org/10.1016/j.solener.2005.02.018

[8] S. Saadi, A. Bouguelia, A. Derbal and M. Trari, '' Hydrogen Photoproduction over new catalyst CuLaO2'', Journal of Photochemistry ans Photobiology A : Chemistry, vol 187, pp 97-104, 2007.

https://doi.org/10.1016/j.jphotochem.2006.09.017

[9] K. Cherifi, G. Rekhila, S. Omeiri, Y. Bessekhouad and M. Trari, '' Physical and photoelectrochemical properties of the spinel $ZnCr_2O_4$ prepared by sol gel: Application to Orange II degradation under solar light'', Journal of Photochemistry ans PhotobiologyA : Chemistry, Vol 368, pp 290-295, 2019.

https://doi.org/10.1016/j.jphotochem.2018.10.003

[10] Xiuhua Wei and Donghua Chen, '' Synthesis and characterization of nanosized zinc aluminate spinel by sol–gel technique'', Materials Letters, vol60, pp 823–827, 2006.

https://doi.org/10.1016/j.matlet.2005.10.024