Study of ZnO$_{1-x}$S$_x$ synthesis by non-alcoxide sol-gel method employed in the photocatalytic degradation of a persistent organic pollutant in water

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Abstract. Non-Alcoxide Sol-Gel method was used as synthesis route to obtain the ZnO$_{1-x}$S$_x$ compounds at calcination temperatures of 250 °C, 300 °C and 400 °C, doped with Sulfur at mole fractions of $x = 0.05, 0.50, 0.80$. The samples obtained were characterized structural and optically by both X-ray diffraction (XRD) and diffuse reflectance spectrophotometry. The XRD analysis showed the formation of the Wurtzite type structure proper of ZnO up to Sulfur mole fraction of $x = 0.50$. It was observed that this phase disappears at a mole fraction of $x = 0.80$ and converts to Cubic Zinc blende type structure proper of Zinc Sulfide. Furthermore, it was observed that increasing calcination temperature higher crystallinity was achieved for all set of samples. The Rietveld refinement method was used to obtain lattice parameters for Wurtzite structure as well as cell volume and the ratio c/a. These parameters show slight incremental changes in relation to S doped ZnO crystalline structure. On the other hand, it was determined optically, that increasing the dopant concentration to a mole fraction $x = 0.50$, a maximum reduction of the band gap from 3.29 eV to 2.70 eV was reached, while increasing the calcination temperature shows a general tendency to band gap reduction. Photocatalytic activity of Sulfur doped and pure ZnO powders were tested for degradation of $p,p'$-DDT under visible light, measuring the $p,p'$-DDT time-dependent concentration by gas chromatography-$\mu$ECD coupling. The results revealed that the sulfur modified ZnO material showed an improved photocatalytic activity towards $p,p'$-DDT under visible light illumination respect to pure ZnO.

Keywords: ZnO, Photocatalysis, POPs, Non-Alcoxide Sol-Gel, Visible light.

1. Introduction
The development of industrial and agricultural sectors has been characterized by the emission of toxic substances such as the Persistent organic pollutants (POPs), these represent a global concern because can accumulate in environment and organisms where biomaximize by their lipophilicity character [1-2] and present resistance to degradation [3]. $p,p'$-DDT is a pesticide, categorized as POP and Class B II toxicant by WHO [4-6]. $p,p'$-DDT can be absorbed in soils and leach into groundwater [7]. This

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pesticide can be transferred to humans by drinking water and foods like fruits. As a strategy to remediation of POP contamination, have been proposed process like Fenton reaction [8]. One of the actually most studied methods, is the semiconductor mediated photocatalysis [9], where photon assisted generated catalytically active species are formed on a semiconductor surface. This kind of process has shown to be capable to convert difficult biodegradable and highly toxic organic molecules in carbon dioxide and water, in a mechanism known as mineralization. Actually the most studied and applied semiconductor for such aim is Titanium Dioxide widely employed in degradation of miscellaneous organic molecules such as Nitrogen Organic, Azo Dyes, VOC’s, and pesticides as reviewed by [10], however due to be a wide band gap material, its indispensable the use of UV lamps for complete such degradations. Zinc Oxide is another important semiconductor that can be used with this purpose, and in comparison with TiO$_2$ presents higher light absorption of the solar spectrum [11], but also present a similar wide gap energy value. In order to reduce gap size and improve its photocatalytic activity, has been proposed introduce dopant atoms, like metallic species: Mg [12], Fe [13], Al [14], Ag [15], Co [16], Cu [17], among others. Also, non-metal species have been studied like: Nitrogen [18] [19], Carbon [19] [20] and Sulfur [20]. The material ZnO$_{1-x}$ S$_x$ is of interest due to the same valence state of sulfur in relation with oxygen in ZnO structure, it has been obtained by physical and chemical methods like Pulsed Laser Deposition [21], Reactive Sputtering [22], Chemical Spray Pyrolysis [23], Manual Mechanochemical Synthesis [24] and High Energy Milling synthesis [25]. Zinc Oxide has been evaluated for photocatalytic degradation of various Dyes and molecules, however there is not such works related to POP’s of the Stockholm Convention and WHO lists. The Sulfur modified ZnO has been applied in degradation of Resorcinol [24] and the organic Congored dye [26]. In the present work, were synthesized and characterized sulfur doped ZnO powder obtained by Non-Alcoide Sol-Gel method, in three doping levels: diluted, intermediate and saturated, related to sulfur mole fraction $x = 0.05, 0.50$ and 0.80 respectively and three different calcination temperatures: 250°C, 300°C and 400°C. Also, we report some results of the improved photocatalytic degradation of the POP $p, p'$-DDT with S doped Zinc Oxide in comparison with pure Zinc Oxide.

2. Experimental
For S-doped ZnO preparation by Non-Alcoide Sol-Gel method, were prepared Zinc Chloride/Thiourea aqueous solutions with molarities (M) of 1.18/0.06, 0.57/0.57 and 0.22/0.86, to obtain doping Sulfur mole fraction of $x = 0.05, 0.50$ and 0.80 respectively. Reactions were performed under fast stirring for 2 hours at 90°C and pH raised to 10. The semisolid product was filtered, dried at 160°C, rinsed and finally calcinated at 250°C. Finally, pure ZnO was obtained following the same procedure, omitting the Thiourea addition. All the procedure was repeated for calcination temperatures of 300°C and 400°C for each value of mentioned mole fraction ($x$). All obtained powders were characterized using X-ray Diffraction (XRD) Cu K$\alpha$ radiation in the range 5°- 90°, UV-Vis Diffuse Reflectance Spectrometry with integrating Sphere (wavelength range 200-800 nm). Photocatalytic performance of the synthesized sulfur doped at $x = 0.50$ mole fraction and pure ZnO, both obtained at 400°C were studied by the degradation of $p, p'$-DDT under visible light. Photocatalytic essays were performed in an open Pyrex vessel, which was filled with aqueous fortified solution with 200 ppb of $p, p'$-DDT and a suspension concentration of 1g/L of sulfur doped and pure ZnO respectively. The radiation source was a Newport Solar LED simulator with an illumination power of 110mW/cm$^2$, the samples were irradiated vertically to the solution surface at 20°C. Suspensions were stirred in the dark for 30 minutes. Then during the course of irradiation of samples, aliquots were collected between 5 minute intervals, these were centrifuged for 5 minutes and the supernatant extracted with a chromatographic grade Hexane:Dichloromethane (1:1) mixture. Extracts were concentrated and reconstituted with Hexane and analyzed by an Agilent 7890A gas chromatograph, coupled to a micro-electron capture detector ($\mu$ECD).

The chromatographic conditions for $p, p'$-DDT determination was as follows: Injector temperature of 250 °C, Splitless injection mode, capillary column Agilent HP-5 (30m x 0.32 mm x 0.25 um). Oven Initial temperature: 100°C, with an increase of 5°C per minute until reaching 300°C for 5 minutes. The detector was set at a temperature of 290 °C, using Nitrogen as make up gas.
3. Results and discussion
UV-Vis Reflectance spectra of all Sulfur doped and pure ZnO samples, obtained at proposed mole fraction and different calcination temperatures, were analyzed in order to determine the optical gap by applying the Kubelka-Munk (K-M) method [27]

\[ F(R) = \frac{(1 - R)^2}{2R} = \frac{\alpha(h\nu)}{S} \] (1)

where \( R \) is the reflectance; \( F(R) \) the K-M function, \( \alpha \) is the absorption coefficient and \( S \) the dispersion coefficient. Since \( F(R) \) is directly proportional to \( \alpha(h\nu) \), and the last is defined by Tauc equation as

\[ F(R) \approx \alpha(h\nu) = A(h\nu - E_g)^{1/2} \] (2)

In this relation \( h\nu \) is the incident photon energy and \( E_g \) is the optical gap energy for a direct band transition semiconductor as in this case is Zinc Oxide. Figure 1 shows the Tauc graph for samples at different sulfur mole fraction doping at 250°C. Similar Tauc Graph were obtained for 300°C and 400°C respectively. It was observed that as the sulfur concentration in the material increases, was perceived change in the samples color.

For pure Zinc Oxide samples, it was observed a characteristic white color, at mole fraction \( x = 0.05 \) it turned slightly yellow and for \( x = 0.50 \) and \( x = 0.80 \) the yellow color intensifies, until reaching an Ocher tonality (Figure 2). We can observed optical gap variation as function of sulfur concentration in the material. For values of \( x = 0.05 \) a slight variation is observed with respect to pure ZnO \( (x = 0.00) \), for doping levels of \( x = 0.50 \) the lowest values were obtained in comparison to the other doping levels of doping, with smallest value of 2.70 eV, value associated with monochromatic light with a wavelength of approximately 440 nm, which corresponds to the blue band of the visible spectrum. For level of

![Fig.1 Tauc Graph and Band gap energies for Sulfur doped and pure ZnO samples calcinated at 250°C](image)
$x = 0.80$, a tendency to increase is observed, related to the formation of the Zinc Sulfide phase, where highest optical gap value obtained was 3.41 eV. Figure 3 summarizes the behavior of optical gap values as a function of dopant concentration $x$ (for each sample group). This tendency is related to the following phenomena:

![Fig.2 Color change in Sulfur doped and pure ZnO in function of mole fraction level: a) $x = 0.00$; b) $x = 0.05$; c) $x = 0.50$; d) $x = 0.80$.](image)

i) The sulfur atom has the same valence electrons as oxygen (6 electrons), since it is located in the same group in the periodic table, however, taking into account the electronic configurations of oxygen [He] $2s^22p^4$ and Sulfur [Ne] $3s^23p^4$, valence electrons of Sulfur are located in layer $n = 3$ generating an upward displacement of the valence band of ZnO, which is mostly populated by the $2p$ states of oxygen and then by doping by the $3p$ states of sulfur. ii) The charge of the sulfur anion is the same as the anion oxide: $-2$, facilitating the inclusion of the impurity as a substituent. Computational calculations have shown that the replacement of oxygen is energetically more stable, since the interstitial inclusion or substituent of the cation have higher formation energies, since they generate more distortions in the structural parameters of the crystal lattice [28]. iii) A higher concentration of Sulfur atoms tends to the formation of the Zinc Sulfide phase, which has an optical gap higher than Zinc oxide (~ 3.60 eV [29]). The displacement of the conduction band is due to the change of the crystal structure of the wurtzite phase from ZnO to the cubic FCC phase of ZnS, added to the fact that the conduction band of the latter is mainly formed by hybridized states Zn-4s and S-3p [30, 31] which are located at a higher energy level in relation to the Zinc oxide conduction band that is mainly formed by O-2s states [28].

![Fig.3 Band gap values in function of sulfur mole fraction doping level in ZnO structures](image)
The behavior of optical gap as a function of the calcination temperature was analyzed for samples with $x = 0.00$ and $x = 0.05$, it is observed a slightly change of optical gap, both samples shows similar pattern in relation to temperature. At higher sulfur mole fraction, greater the fall in the value of the optical gap with temperature increment, this observation is related to particles agglomeration and the increment of crystallite size. From these results it is important to emphasize that the lowest optical gap obtained was for the sample doped with a sulfur mole fraction of $x = 0.50$ and calcinated at 400°C.

![Diffractograms of samples obtained at 250°C at Sulfur mole fraction of $x = 0.00$ (black line), $x = 0.05$ (red line), $x = 0.50$ (green line) and $x = 0.80$ (blue line)](image)

**Fig. 4** Diffractograms of samples obtained at 250°C at Sulfur mole fraction of $x = 0.00$ (black line), $x = 0.05$ (red line), $x = 0.50$ (green line) and $x = 0.80$ (blue line)

Figure 4 shows the XRD patterns of Sulfur doped and pure ZnO synthesized by Non-Alcoxide sol gel method with different mole fraction at 250°C calcination temperature. All peaks of prepared sulfur doped and pure ZnO samples assigned to Zinc Oxide under standard card COD2013-96-900-8878. These peaks of crystallographic planes (100), (002), (101), (102), (110), (103), (112) y (201) proper of hexagonal ZnO indicate that wurtzite type structure was obtained from this temperature up to 400°C. It can be seen that at this temperature, excess precursors peaks appears on the diffractograms base line. It was confirmed that at sulfur mole fraction of $x = 0.50$ the wurtzite structure maintains, indicating the substitution of oxygen atoms by sulfur ones, but at $x = 0.80$ there is a conversion of the material to cubic Zinc blende type structure proper of Zinc Sulfide Phase with characteristic peaks of planes (111), (220) and (311). Presence of NaCl peaks was evidenced too in this doping level. Also, it was observed that increasing temperature, increase the crystallinity of materials (figure 5) and peaks of impurities in the base lines tend to disappear. Rietveld refinement was applied to all samples, table 1 summarize all the lattice parameters obtained that were contrasted with theoretical reported by [32] for Wurtzite structure Zinc Oxide and [33] for Cubic structure Zinc Sulfide. We observed that with increment in sulfur content in material, appears a directly proportional slightly increment of lattice parameters of the wurtzite type
Fig. 5 Increment of crystallinity in function of sulfur mole fraction doping at calcination temperatures employed: 250°C, 300°C and 400°C for doped ZnO x = 0.05 (red lines) and pure ZnO (black lines).

| Phase-Temperature | a (Å)     | b (Å)     | c (Å)     | c/a       | V (Å³) |
|-------------------|-----------|-----------|-----------|-----------|--------|
| ZnO 250°C         | 3.255352  | 3.255352  | 5.213240  | 1.601437  | 47.84  |
| ZnO 300°C         | 3.250009  | 3.250009  | 5.206077  | 1.601865  | 47.62  |
| ZnO 400°C         | 3.250009  | 3.250009  | 5.205502  | 1.601688  | 47.62  |
| ZnO_{0.05}S_{0.95} 250°C | 3.256448  | 3.256448  | 5.215333  | 1.601540  | 47.90  |
| ZnO_{0.05}S_{0.95} 300°C | 3.252818  | 3.252818  | 5.211368  | 1.602109  | 47.75  |
| ZnO_{0.05}S_{0.95} 400°C | 3.253000  | 3.253000  | 5.212608  | 1.602400  | 47.76  |
| ZnO_{0.50}S_{0.50} 250°C | 3.265901  | 3.265901  | 5.225690  | 1.600076  | 48.27  |
| ZnO_{0.50}S_{0.50} 300°C | 3.263001  | 3.263001  | 5.218052  | 1.599157  | 48.11  |
| ZnO_{0.20}S_{0.80} 250°C | 5.194526  | 5.194526  | 5.194526  | 1.59932   | 48.07  |
| ZnO_{0.20}S_{0.80} 300°C | 5.748047  | 5.748047  | 5.748047  | 1.6151    | 155.63 |
| ZnO_{0.20}S_{0.80} 400°C | 5.189363  | 5.189363  | 5.189363  | -         | 155.80 |

Table 1 Lattice parameters for sulfur doped and pure ZnO samples obtained at calcination temperatures of 250°C, 300°C and 400°C with different mole fraction doping worked levels.
ZnO, indicating the increment of unitary cell volume and as other evidence of substitution of Oxygen by Sulfur in the ZnO lattice.

The photocatalytic essays were made using the material ZnO$_{0.50}$S$_{0.50}$ and pure ZnO both obtained at 400°C.

The degradation percentage (R%) is defined as:

$$R\% = \left( \frac{C_0 - C}{C_0} \right) \times 100$$

The reaction kinetics of the photocatalytic degradation of $p, p'$-DDT in the presence of pure ZnO and doped with sulfur can be explained by a pseudo first-order model, Langmuir-Hinshelwood (LH) type [34]. The equation, of the LH model, showing the relation of $[p, p'-DDT]$ and the time t, is given by the lineal relation:

$$ln\left( \frac{[p, p'-DDT]_0}{[p, p'-DDT]} \right) = k_{obs} \cdot t$$

Plot of the linear relationship of relation (4), is shown in figure 6. The $R^2$ value for the linear regression exhibits the tendency of the reaction, which follows the pseudo-first-order linear pattern. It should be noted that with the doped semiconductor a removal percentage of 100% is reached around 25 minutes, while for pure ZnO the contaminant is not completely degraded (See figure 7). When comparing the values of the velocity constant ($k_{obs}$), values for ZnO and ZnO$_{0.50}$S$_{0.50}$ were 0.0230 min$^{-1}$ and 0.1287 min$^{-1}$ respectively, the pattern indicates that the reaction rate increases with the use of the semiconductor doped, this due to the reduction of the optical gap.

Figure 7 shows the removal percentage of the pollutant as a function of time. It can be seen that the percentage is always lower for pure zinc oxide in the time range studied, due the ability to absorb photons in the visible range is low, the surface of the material tends to become saturated with the molecules of
$p$, $p'$-DDT, thus hindering the process of photocatalytic degradation. It can be seen that with doped material the percentage of removal reaches 100% around 25 minutes, however, in contrast to the pure ZnO, removal efficiency is greater. That is, the doped specie has more capacity to absorb photons of the visible range, thus generating on the surface of the material, the production of $e^-$ and $h^+$, increasing the concentration of hydroxyl radicals that end up attacking the $p$, $p'$-DDT molecules.

![Fig.7](image.png)

Fig.7 Removal percentage of $p$, $p'$-DDT removal as a function of time, using ZnO and ZnO$_{0.50}$S$_{0.50}$

4. Conclusions
In the present study we demonstrated the synthesis of Sulfur doped and pure Zinc Oxide by Non-Alcoxide Sol-Gel method for dopant mole fraction of $x = 0.05$, 0.5 and 0.8. The crystalline structure of the resulting compound characterized by X-ray diffraction (XRD), shows the wurtzite structural phase for pure ZnO, maintaining this structure up to the sulfur concentration of 0.5 molar fraction, indicating that sulfur randomly substitutes oxygen up to this concentration, introducing an increase in the lattice parameters. For sulfur mole fraction 0.8, material showed a phase change to cubic zinc blende Zinc sulfide. Also, was verified that with the increase of the calcination temperature an increase in the crystalline quality was observed. The spectral UV-Visible optical characterization shows a decrease in the gap of forbidden energy up to the sulfur mole fraction of 0.5 to a value of 2.70 eV, indicating the influence of the substitution of sulfur by oxygen in the optical behavior. The change of crystalline phase for the concentration of 0.8 of sulfur, shows an increase in the forbidden energy gap according to the new structure of cubic Zinc Sulfide with maximum increase of 3.41 eV. Finally, it was demonstrated the enhancement of photocatalytic degradation of $p$, $p'$-DDT was given for the material obtained with sulfur mole fraction of 0.5 and calcination temperature of 400 °C, with a 100% removal efficiency in 25 minutes under visible light, respect pure ZnO obtained with same temperature.

References
[1] UNEP. United Nations Environment Programme. Stockholm convention on persistent organic pollutants (POPs). Available: http://www.pops.int, 2007
[2] Buccini J. 2003. The development of a global treaty on persistent organic pollutants (POPs). The hand book of environmental chemistry series (Springer-Verlag, Berlin) 2003.
[3] UNEP. United Nations Environment Programme. Regionally based assessment of persistent toxic substances. Global report 2003. Chatelaine, Switzerland: UNEP Chemicals; 2003. [Available: http://www.chem.unep.ch/pts/ accessed 2 June 2013].

[4] U.S. Environmental Protection Agency. In Environmental Fate and Effects Division, Pesticide Environmental Fate One Line Summary: DDT (p, p’). Washington, DC.; Augustijn-Beckers, 1989.

[5] Gray, N. F., 2008. Drinking water quality: Problems and solutions. (United Kingdom, Cambridge University Press) pp158-165.

[6] World Health Organization (WHO). In Environmental health Criteria, DDT and its Derivatives in Environmental Effects. World Health Organization, Geneva, 1989, 83–85.

[7] Senthilnathan, J. and Philip, L. 2010. Water, Air, and Soil Pollution 210 143.

[8] Dalla Villa, R., Nogueira Pupo, R.F., 2006. Science of the Total Environment 371 11-18.

[9] Lee, K.M., Lai, C.W., Ngai, K.S., Juan, J.C. 2015. Recent Developments of Zinc Oxide Based Photocatalyst in Water Treatment Technology: A Review, Water Research

[10] Chin Boon Ong, Law Yong Ng, Abdul Wahab Mohammad. 2018 Renewable and Sustainable Energy Reviews. 81 536.

[11] Qiu R, Zhang D, Mo Y, Song L, Brewer E, Huang X. 2008 J Hazard Mater 156 80

[12] Mahmood MA, Baruah S, Dutta 2011 J. Mater Chem Phys 130 531

[13] Ba-Abbad MM, Kadhum AAH, Mohamad AB, Takriff MS. 2013 Chemosphere 91 1604.

[14] Balaprakash V, gowrisankar P, rajkumar R, Sudha S. 2018. Sādhanā 43:86

[15] Shinde SS, Bhosale CH, Rajpure KY. 2012 J Photochem Photobiol A: Chem. 199 170.

[16] Kale G, Arbuj S, Kawade U, Rane S, Ambekara J, Kale B. 2018 Mater. Chem. Phys. 163.

[17] L.C. Chen, Y.J. Tu, Y.S. W, R.S. Kan, C.M. Huang. 2008 J. Photochem. Photobiol. A: Chem. 199 170.

[18] Weilai Y, Jinfeng Z, Tianyou P. 2016 Applied Catalysis B: Environmental 181 220.

[19] Soref A, Moos HW 1964 J Appl Phys 35 2152.

[20] Hart J, Kurnia F. 2015 Chem Phys Chem 16 2397

[21] Opoku F, Poornani P, Govender K. 2017 New J. Chem. 41 8140

[22] Wyckoff, R. W. G. 1963 Crystal Structures 1 85.

[23] Skinner, B. J. 1961 American Mineralogist 46 1399.

[24] Hermann JM. 2010. Journal of Photochemistry and Photobiology A: Chemistry. 216 85.