Propriedades estruturais e fotocatalíticas do composto $Zn_{1-x-y}Pr_xAl_yO$ obtido por co-precipitação

Structural and photocatalytic properties of compound $Zn_{1-x-y}Pr_xAl_yO$ obtained by co-precipitation

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RESUMO

O óxido de zinco vem se destacando no ambiente científico devido suas propriedades únicas que o possibilita ser aplicado em diversas áreas da ciência e tecnologia. Uma característica fundamental desse semicondutor é sua versatilidade em aplicações optoeletrônicas e por ser um material esperançoso para a remediação ambiental. A variação dos parâmetros de síntese e a adição de um ou mais cátions na estrutura são algumas das alternativas usadas para tornar o ZnO o material semicondutor mais eficiente em suas aplicações. Neste trabalho, sintetizamos pelo método de co-precipitação e caracterizamos o sistema $Zn_{1-x-y}Pr_xAl_yO$*, [x, y] = (0,00, 0,00); (0,03, 0,01); (0,03, 0,03) para utilizar na descoloração fotocatalítica de laranja de metila. Variações nos parâmetros estruturais estão ligadas aos cátions* Zn^{2+} *com a substituição de* Pr^{3+} *e* Al^{3+}*, bem como o distúrbio atômico na estrutura. De acordo com os espectros Raman, o pico característico* E_2*(high) da vibração de oxigênio na estrutura do cristal de ZnO passa por uma pequena mudança, sugerindo a presença de defeitos de oxigênio na estrutura sintetizada. Os testes fotocatalíticos demonstraram que o dopante contribuiu para o aumento da descoloração do corante de laranja metila, atingindo valores entre 53,7 e 90,0% da remoção do poluente. Os testes de inibidores sugerem que as espécies reativas responsáveis pela fotodegradação/descoloração do corante alaranjado de metila seguem a seguinte ordem* $\bullet O_2^- > \bullet OH > e^- > h^+$.

Palavras-chave:*ZnO; Co-dopagem; Alaranjado de metila;distúrbio estrutural; Fotocatálise.*

ABSTRACT

Zinc oxide has been standing out in the scientific environment due to its unique properties that enables it to be applied in various areas of science and technology. A fundamental feature of this semiconductor is its versatility in optoelectronic applications and because it is a hopeful material for environmental remediation. The variation of synthesis parameters and the addition of one or more cations to the structure are some of the alternatives used to make ZnO the semiconductor material more efficient in its applications. In this work, we synthesize by the co-pre-care method and characterize the $Zn_{1-x-y}Pr_xAl_yO$, [x, y] = (0.00, 0.00) system; (0.03, 0.01); (0.03, 0.03) To use in methyl orange photocatalytic discoloration. Variations in structural parameters are linked to the Zn^{2+} cations with the replacement of Pr^{3+} and Al^{3+}, as well as the atomic disorder in the structure. According to the Raman spectra, the characteristic peak E_2(high) of oxygen vibration in the ZnO crystal structure goes through a small change, suggesting the presence of oxygen defects in the synthesized structure. The photocatalytic tests showed that dopant contributed to increased discoloration of the methyl orange dye, reaching values between 53.7 and 90.0% of pollutant removal. Inhibitor tests suggest that the reactive species responsible for the photodegradation/discoloration of methyl orange dye follow the following order $\bullet O_2^- > \bullet OH > e^- > h^+$

Keywords: ZnO;Co-doping; Orange methyl; structural disorder; Photocatalysis.

INTRODUCTION

Zinc oxide (ZnO) has aroused great interest in the scientific community due to its versatility, which led to a wide range of applications in various areas such as: antibacterial, gas sensors, opto-electronics, photovoltaic cells and photocatalysis[1,2].ZnO is characterized by the Wurtzite hexagonal structure with $P6_{3MC}$ space group. It stands out because its morphology, structure, optical, electrical and photocatalytic property can be easily enhanced through changes in the synthesis process or the addition of one or more dopant atoms[3].The popularity of zinc oxide compounds in environmental remediation by photocatalysis increased due to their ability to degrade various types of dyes and drugs[4]. However, the reported disadvantages of zinc oxide in environmental remediation include electronic recombination, cluster formation and low surface area[5]. In this scenario, there are several methods to improve the photocatalytic properties of zinc oxide. Some of them include the use of different synthesis techniques, insertion of dopant cations, composite formation, using clay as support material and employing green synthesis[6].

Motivated by this, the present work aims to analyse the effect of Zn^{+2} replacement by Pr^{3+} and Al^{3+} cations on the structural, morphological, and optical properties of the $Zn_{1-x-y}Pr_xAl_yO$, [x, y] = (0,00, 0,00); (0,03, 0,01); (0,03, 0,03)synthesized by the co-precepation method.

MATERIALS AND METHODS

The compound$Zn_{1-x-y}Pr_xAl_yO$, [x, y] = (0,00, 0,00); (0,03, 0,01); (0,03, 0,03)It was synthesized by the co-preecipitation method[1]. In the synthesis process, reagents were used Zn (NO_3) 2.6 (H_2O) (96% purity), $Pr(NO_3)3$(99,9% purity) e $Al(NO_3)3$(99,9% purity). The raw materials were heavy and added in 50 ml of distilled water to obtain 0.02 mol L^{-1}. After stirring for 1 h, the sodium hydroxide solution (5m) was gradually added until the solution reaches pH 9. The solutions were agitated by 1h, to a white precipitate. These precipitates were washed five times with distilled water and three times with alcohol, then dry at 100 ° C for 24 h. Finally, they were thermally treated at 240 ° C for 2 h. The samples were identified asZPA00 (For ZnO not doped), ZPA31 (for the compound$Zn_{0,96}Pr_{0,03}Al_{0.01}O$) and ZPA33 (for the$Zn_{0,94}Pr_{0,03}Al_{0,03}O$).For structural characterization, an X-ray diffractometer was used, with Cu-Kα radiation (λ = 1.5406 å) and a Raman spectrometer.

The photocatalytic discoloration of methyl orange was performed using a borocilicates reactor, connected to a thermostatic bath to maintain constant temperature (24°C ± 1°C). The degradation rate was obtained by the equation[5]:

$$Degradationrate = \frac{C_0 - C_t}{C_0}\ (100)(1)$$

where C_0 is the dye and C_t equilibrium concentration corresponds to concentration after the radiation time. Spectral variations resulting from dye degradation were monitored using the UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

Single -phase training analysis using DRX and Raman measures.

Figure 2 is shown the XRD patterns for system $Zn_{1-x-y}Pr_xAl_yO$ synthesized by the co-precipitation and calcined method at 240°C by 2h. As shown, the XRD patterns of all samples are similar, without apparent segregation of extra phases (Figure 1 (A))suggesting that the synthesis conditions used to obtain oxide co-doped with $Pr^{3+}$and Al^{3+} were effective.

suggesting that the synthesis conditions used to obtain oxide of CO-DOPADO with $Pr^{3+}$and Al^{3+} were effective. The formation of the Wurtzite structure for the synthesized system was confirmed by the JCPDS Crystallographic database reference code No. 36-1451[7].Figure 1b illustrates the region referring to crystallographic planes (100), (002) and (101). Dislocations to angles less of 2θ suggest the complete replacement of Zn^{2+} cations by Pr^{3+} and Al^{3+} in the ZnO structure, leading to significant modifications in the structural parameters.

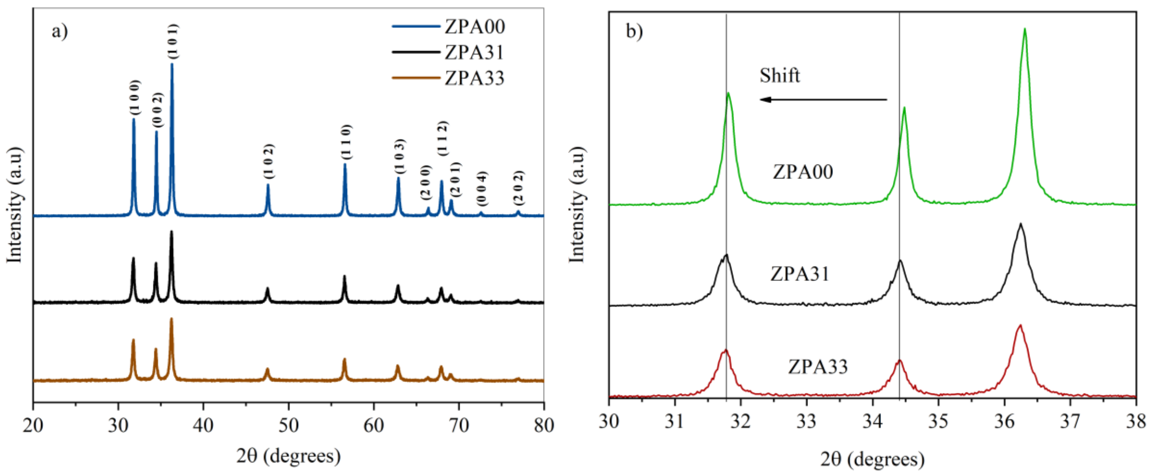

Figure1.a)XRD patterns for the $Zn_{1-x-y}Pr_xAl_yO$ system and b) Shifts to smaller angles after $Pr^{3+}$and Al^{3+} inclusion in the hexagonal structure.

Figure 2 displays the Raman spectra to the $Zn_{1-x-y}Pr_xAl_yO$system. It has been confirmed that all samples have similar characteristics, indicating ZnO single -phase formation, which is consistent with XRD results. In addition, the decrease in E_2(high) mode, which is associated with the crystallinity of the compound, proves the reduction in the size of the crystallitus, resulting from the replacement of Zn^{2+} ions by P^{3+} and Al^{3+} ions in the ZnO structure.

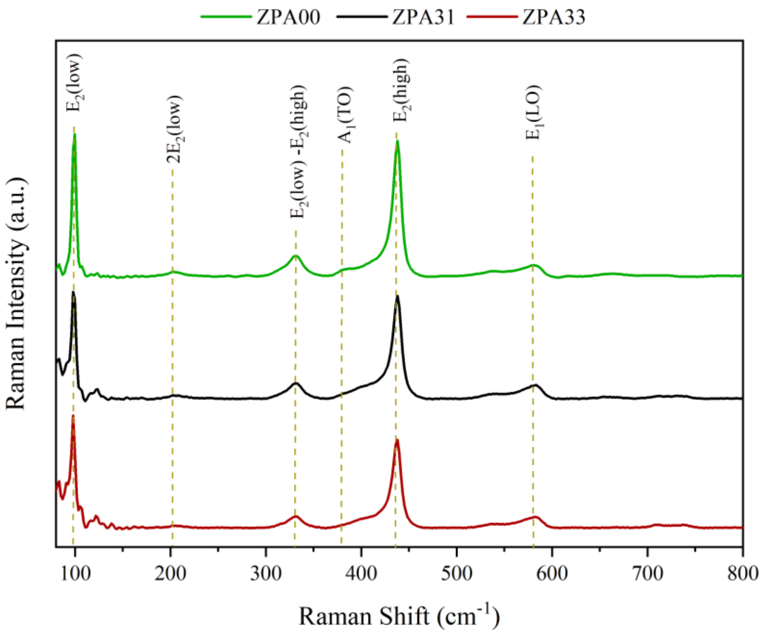

Figura 2. Raman spectra for the $Zn_{1-x-y}Pr_xAl_yO$system. The small shifts are linked with the dopant cations addition (Pr^{3+}/Al^{3+}) into the hexagonal structure.

Analysis of the photocatalytic properties of the $Zn_{1-x-y}Pr_xAl_yO$ system synthesized by the co - precipitationmethod.

Experiments to test photocatalytic efficacy of synthesized semiconductors were performed using the methyl orange dye (MO), as well as photocatalytic degradation percentages as a model pollutant under UV irradiation. Figure 3 (a) shows the variation C/C_0 versus irradiation time, monitoring the maximum dye absorption band at 464 nm, and Figure 3 (b) characterizes photodegradation percentages for each in nanophotocatalysts compared to thephotolysis for a maximum time of 150 minutes. Nanocatalyst ZPA33 promoted 90% degradation of methyl orange dye.

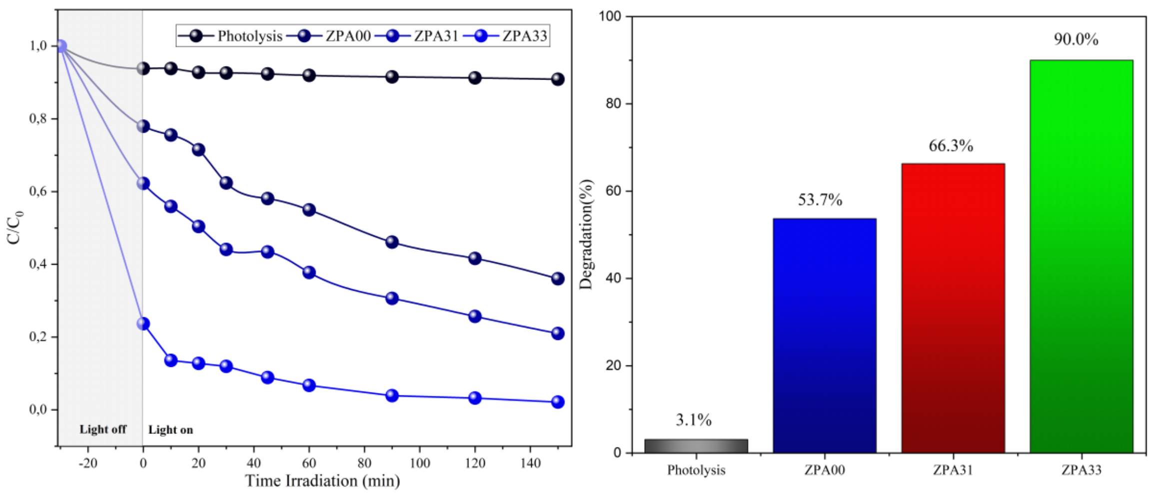

Figure 3 a) shows the relative absorption of the nanophotocatalysts and b) shows the relative percentage of photodegradation for the synthesized nanoparticles.

CONCLUSIONS

In the present work there was the synthesis of single-phase photocatalytic nanostructures proven by the measures of DRX and Raman with minor changes attributed to interstitial addition of cations $Pr^{+3}$and Al^{+3} that have lightly larger ionic rays than Zn^{+2}, in the hexagonal structure Wurtzite.

Regarding the photocatalytic activity of nanocatalysts in 240^0C (ZPA31 and ZPA33), they have a relative percentage of 66.3% and 90%, respectively, in the presence of orange of methyl in ultraviolet light, which makes them a good alternative for remediation of this pollutant.

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Bibliographic references

[1] A.S. Soares, F.P. Araujo, R. França, J.A. Osajima, Y. Guerra, S. Castro-Lopes, E.C. Silva-Filho, F.E. Santos, L.C. Almeida, B.C. Viana, R.R. Peña-Garcia, Effect of pH on the growth and ibuprofen photocatalytic response of Zn1 − xCoxO compound synthesized by the co-precipitation method, J. Mater. Res. 38 (2023) 2439–2452. https://doi.org/10.1557/s43578-023-00980-4.

[2] M. Rocha, F.P. Araujo, S. Castro-Lopes, I.S. de Lima, E.C. Silva-Filho, J.A. Osajima, C.S. Oliveira, B.C. Viana, L.C. Almeida, Y. Guerra, R. Peña-Garcia, Synthesis of Fe–Pr co-doped ZnO nanoparticles: Structural, optical and antibacterial properties, Ceram. Int. 49 (2023) 2282–2295. https://doi.org/10.1016/j.ceramint.2022.09.196.

[3] N.A. Raship, S.N.M. Tawil, N. Nayan, K. Ismail, Effect of Al Concentration on Structural, Optical and Electrical Properties of (Gd, Al) Co-Doped ZnO and Its n-ZnO/p-Si (1 0 0) Heterojunction Structures Prepared via Co-Sputtering Method, Materials (Basel). 16 (2023) 2392. https://doi.org/10.3390/ma16062392.

[4] S. Majumder, S. Chatterjee, P. Basnet, J. Mukherjee, ZnO based nanomaterials for photocatalytic degradation of aqueous pharmaceutical waste solutions – A contemporary review, Environ. Nanotechnology, Monit. Manag. 14 (2020) 100386. https://doi.org/10.1016/j.enmm.2020.100386.

[5] Manikanika, L. Chopra, Photocatalytic activity of zinc oxide for dye and drug degradation: A review, Mater. Today Proc. 52 (2022) 1653–1656. https://doi.org/10.1016/j.matpr.2021.11.283.

[6] A.T. Le, T.D.H. Le, K.-Y. Cheong, S.-Y. Pung, Immobilization of zinc oxide-based photocatalysts for organic pollutant degradation: A review, J. Environ. Chem. Eng. 10 (2022) 108505. https://doi.org/10.1016/j.jece.2022.108505.

[7] F.P. de Adriano Santana Soares, Samuel Jônatas de Castro Lopes, B.C.V. Araújo, Francisco Eroni Paz dos Santos, Yuset Guerra Dávila, N. and R.R.P. Garcia, Effect of pH on structural, optical and photocatalytic properties of Co-doped ZnO nanostructures, in: 2022: p. 2022.