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# ENHANCED PHOTOCATALYTIC PROPERTIES OF Sn-DOPED ZnO NANOPARTICLES BY FLAME SPRAY PYROLYSIS UNDER UV LIGHT IRRADIATION

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**Abstract:** Zinc oxide (ZnO) is widely used in different areas thanks to its unique photocatalytic, optic and electrical properties. Sn doped ZnO nanoparticles were synthesized through flame spray pyrolysis (FSP) technique. The Sn dopant concentrations were 1, 3, 5, 7 and 9 at. % in produced ZnO nanoparticles. The structural analysis of the produced powders was performed by X-Ray Diffraction (XRD) methods. The surface morphology and particle size distribution of the nanoparticles were identified using scanning electron microscopy (SEM), and dynamic light scattering (DLS) techniques. In addition to this, produced photocatalysts were evaluated for degradation of aqueous methylene blue (MB) solutions under UV light irradiation. Sn-doped nanoparticles have superior photocatalytic activity compared to un-doped ZnO.

**Keywords:** ZnO, Sn-doped, nanoparticles, photocatalysis, flame spray pyrolysis,

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## INTRODUCTION

Doped or non-doped metal oxide nanostructures are preferred in the electronic materials category due to their superior physical, chemical and photocatalytic properties. Studies have demonstrated that broadband semiconductor photocatalysts such as ZnO can reduce various organic contaminants that offer great potential for completely removing toxic chemicals under UV radiation [Sun *et al*., 2011, Wu *et al*., 2011, Jia *et al*., 2011 and Al-Hadeethi *et al*., 2017]. In many photocatalytic reactions, ZnO has been reported to have high photocatalytic activity in the degradation of various organic contaminants in both acidic and basic media. The greatest advantage of ZnO is the absorption of more light quanta than other semiconductors by absorbing a larger portion of the UV spectrum [Postica *et al*., 2017, Kumar *et al*., 2016 and Ismail *et al*., 2016]. The suppression of recombination of photon-electron-hole pairs in semiconductors is necessary to increase the photocatalytic activity. Doping is a very useful way to improve load separation in semiconductor systems [Andolsi *et al*., 2017 and So *et al*., 2017]. In particular, tin (Sn) is considered one of the most important doping elements to improve the photocatalytic activity of ZnO. Among the additive elements, Sn is compatible with the cage structure due to the similarity of ionic radius with zinc. As a result, Sn doping in ZnO is expected to affect the response or sensitivity of these materials for various gases [Aydin *et al*., 2015, Chahmat *et al*., 2014, Zegadi *et al*., 2014 and Li *et al*., 2012]. Different methods have been used in the literature for the synthesis of doped and undoped ZnO or other metal oxides; such as hydrothermal synthesis, sol-gel, solid state synthesis, liquid emulsion method, and magnetron sputtering. Flame spray pyrolysis (FSP) method is preferred method due to low grain size and homogeneous grain distribution compared to other production methods. Moreover, studying at low temperatures makes FSP safer and cheaper than solid state synthesis [Bae *et al*., 2005, Height *et al*., 2006, Salman *et al*., 2017 and Rherari *et al*., 2017]. In this study, Sn doped ZnO nanoparticles were easily produced by FSP. Structural, microstructural and photocatalytic properties of the produced nanoparticles were investigated and compared with the studies done in the literature and the results were evaluated.

## EXPERIMENTAL

Undoped and Sn-doped zinc oxide (ZnO) nanoparticles were produced by flame spray pyrolysis (FSP) equipment (Tethis, Np 10, Italy). The liquid precursor solution was fed into the flame from syringe pump with a feed rate of 5 ml/min. The supporting methane/oxygen flow rate was kept constant with 5 l/min and oxygen/fuel ratio of 1.5/3.

Undoped, 1, 3, 5, 7 and 9 at.% Sn doped ZnO nanoparticles with diameters of below 200 nm were produced using this method.

Phase identification and crystal structures of the samples were performed by means of a Thermo Scientific ARL- Kα X-ray diffractometer (XRD). This instrument works with voltage and current settings of 45 kV and 44 mA, respectively. The Cu-Kα has been used as the radiation source (1.5405 Å). Diffraction patterns were acquired in the range of 20° to 70° with a scanning rate of 2°/min. The surface morphology and microstructure of the samples were characterized by a scanning electron microscope (SEM, Zeiss Carl Ultra Plus).

To simulate the color change due to photocatalytic decomposition (color change of dye component such as methylene blue, MB), an experimental setup was established. $10^{-5}\,M$ MB (Sigma Aldrich) and distilled water solution were prepared. Produced undoped and Sn doped ZnO nanoparticles were dispersed in this solution. The photodegradation of the MB experiments were practiced up to 180 min. The distance between the light source and the suspension beaker was kept as 20 cm. The absorption of the MB solutions was analyzed by a UV-1240 (Shimadzu) spectrophotometer based on the characteristic absorption of MB peak at 664 nm.

## RESULTS AND DISCUSSION

Figure 1 depicts the X-ray diffraction analysis (XRD) of the undoped and 1-9 at.% Sn doped ZnO nanoparticles produced by FSP technique. It was observed that all peaks of the ZnO phases corresponding to 31.8, 34.4, 36.3, 47.6, 56.6, 62.9 and 67.9° at 2θ values were assigned to (100), (002), (101), (102), (110), (103) and (201) of ZnO nanoparticles in accordance with the zincite pattern COD 9004180. These results indicate that the samples were polycrystalline wurtzite structure. No other peak for the cubic phases of ZnO or any other ZnO structures such as $ZnO_2$ or $Zn(OH)_4$ was seen and no characteristic peaks of any impurities were detected.

The surface morphology plays an important role in photocatalytic activity. Figure 2a and c illustrates structures of the nanoparticles in general view for undoped and 1% Sn doped ZnO, respectively. In addition, Figure 2b and d represents the detailed structure and morphology of the nanoparticles with 200k magnification. In contrast to undoped ZnO nanoparticles, 1% Sn doped ZnO nanoparticles have higher surface area. It can be inferred that Sn doping into the ZnO at a certain amount improved the photocatalytic properties due to increasing surface area.

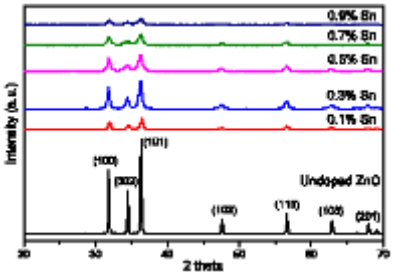


**Figure 1:** XRD patterns of the undoped and Sn doped ZnO nanoparticles produced by FSP.

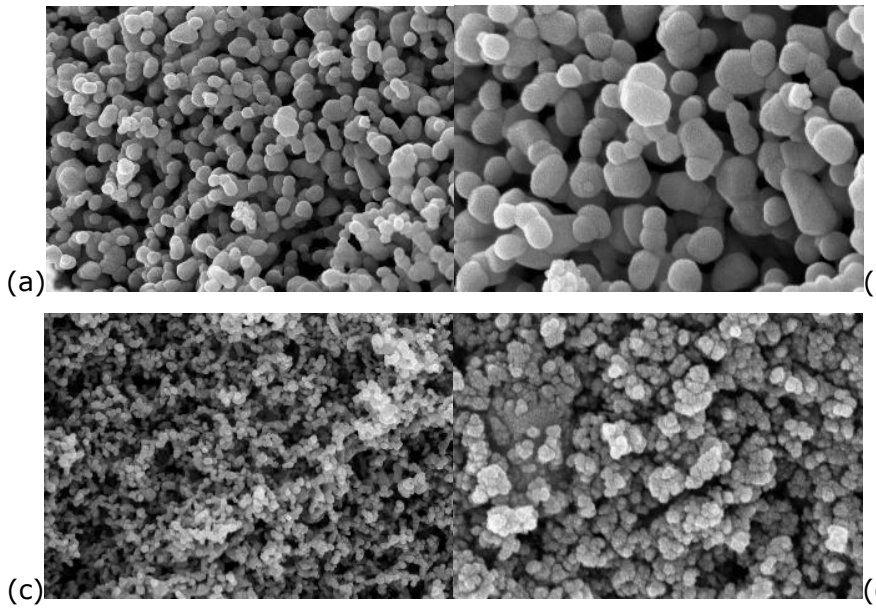


**Figure 2:** SEM images of the undoped and 1% at. Sn doped ZnO nanoparticles with low (a-c) and high magnifications (b-d). (a,c) 1 μm. (b,d) 100 nm.

As mentioned before, the MB dye was used to assess the photocatalytic performance of the undoped and %1-9 Sn doped ZnO nanoparticles. Fig. 3 shows the photocatalytic degradation of MB by the produced nanoparticles. Considering the doping amount into the ZnO nanoparticles, the sample 1% Sn doped ZnO has the best photocatalytic activity. 1% Sn doped ZnO exhibited a very good photoactivity compared to all other samples. At the end of 180 minutes, MB was degraded more than 99% thanks to Sn doping into ZnO. The degradation efficiency of the 0.1% Sn doped ZnO nanoparticles was 99.1%, whereas that of the undoped ZnO nanoparticles was 61.3%.

The degradation efficiency of the photocatalysts was given in Fig. 4. Further observation showed that photocatalytic activity gradually decreased with increasing amount of Sn in the nanoparticles. The 0.1% Sn doped ZnO photocatalyst exhibited the highest

photocatalytic activity for 180 min. The increasing of the photocatalytic performance with 1% Sn doped ZnO can be explained by inhibition of recombination centers (Demirci *et al*., 2017).

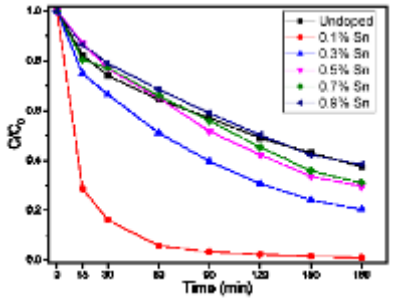


**Figure 3:** Photocatalytic degradations the undoped and Sn doped ZnO nanoparticles produced by FSP.

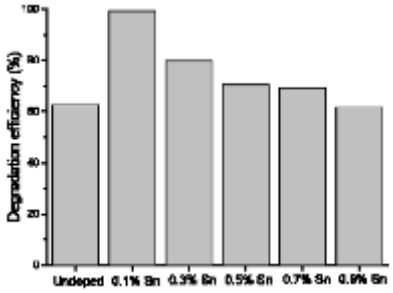


**Figure 4:** Photocatalytic efficiencies of the undoped and Sn doped ZnO nanoparticles produced by FSP.

## CONCLUSION

In summary, undoped and Sn doped ZnO nanoparticles were produced by flame spray pyrolysis method successfully. The sample 1% Sn doped ZnO is the best photocatalyst for degradation of MB. It was observed that the photocatalytic activity of ZnO nanoparticles increased after Sn doping, and the optimal Sn doped content was 1%. With further increasing amount of Sn, photocatalytic performance was gradually decreased. The best dopant concentration exhibiting maximum photocatalytic activity is explained based on space charge creation and rate of charge carrier recombination thanks to Sn doping into ZnO.

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