EFFECTS OF Zn-DOPING ON THE PHOTOCATALYTIC ACTIVITY AND MICROSTRUCTURES OF NANOCRYSTALLINE SnO_2 POWDERS

Metin Yurddaskal[1,2], Serdar Yildirim[1,2], Tuncay Dikici[3], Melis Yurddaskal[4], Mustafa Erol[3], Idil Aritman[1,2], Hilmiye Deniz Ertugrul Uygun[1,2] and Erdal Celik[2,5,6]

(*This article first appeared in PPM2017 and was accepted as a non-peer-reviewed manuscript to be published in JOTCSA)*

[1] Dokuz Eylul University, The Graduate School of Natural and Applied Sciences, 35390, Izmir, Turkey
[2] Dokuz Eylul University, Center for Fabrication and Applications of Electronic Materials (EMUM), 35390, Izmir, Turkey
[3] Izmir Katip Celebi University, Department of Materials Science and Engineering, 35620, Izmir, Turkey
[4] Celal Bayar University, Department of Mechanical Engineering, 45140, Manisa, Turkey
[5] Dokuz Eylul University, Department of Metallurgical and Materials Engineering, 35390, Izmir, Turkey
[6] Dokuz Eylul University, Department of Nanoscience and Nanoengineering, 35390, Izmir, Turkey

Abstract: In this study, undoped and Zn-doped SnO_2 nanoparticles in different concentrations were synthesized by flame spray pyrolysis (FSP) technique. The produced particles were post-annealed after FSP process at 600 °C in order to obtain a crystalline structure. The structural analysis of the produced powders was performed by X-Ray Diffraction (XRD) methods. The surface morphology of the nanoparticles was identified using scanning electron microscopy (SEM). In addition, photocatalytic degradation of aqueous methylene blue (MB) solutions were evaluated using undoped and Zn-doped SnO_2 nanoparticles under UV light illumination. Photocatalytic degradation of the MB solutions followed the pseudo-first-order-kinetics and the effect of the Zn doping amount on the photocatalytic reaction was investigated.

Keywords: SnO_2; Zn-doped; nanoparticles; photocatalysis; flame spray pyrolysis.

Cite This: Yurddaskal M, Yıldırım S, Dikici T, Yurddaskal M, Erol M, Arıtman İ, et al. EFFECTS OF Zn-DOPING ON THE PHOTOCATALYTIC ACTIVITY AND MICROSTRUCTURES OF NANOCRYSTALLINE SnO2 POWDERS. Journal of the Turkish Chemical Society, Section A: Chemistry. 2018; 5(sp. is. 1):9–14.

Corresponding Author. E-mail: metin.yurddaskal@deu.edu.tr.

INTRODUCTION

In recent years, environmental pollution has been an important issue (Huang *et al.*, 2012). Semiconducting oxide nanocrystals, which have unique properties, has been intensively studied for photocatalytic applications in the fields of catalytically decomposing and detecting organic compounds that are usually volatile and toxic (Pauluskas *et al.*, 2013).

SnO_2, as an n-type semiconductor with a wide band gap (3.6 eV). SnO_2 materials can be produced by many techniques such as solvothermal synthesis (Jia *et al.*, 2009), chemical precipitation (Shanmugam *et al.*, 2016), hydrothermal (Dave *et al.*, 2010), hydrolysis (Rahman *et al.*, 2011), flame spray pyrolysis (FSP) (Ang *et al.*, 2011). These methods provide to obtain particles with controlled shape, porosity and particle size for wide range of applications such as dye based solar cells, optoelectronic devices, electrode materials, transistors, gas sensors, and catalyst supports (Jia *et al.*, 2009). The versatile capabilities of the flame spray pyrolysis are given ideal characteristics to the method as ideal synthetic method to produce homogeny nanoparticles fast and cost effectively. Instead of wet chemistry the literatures are suggested that doped and undoped metallic nanoparticles production provide homogenous doped material synthesis methodology (Liu *et al.*,2010).

For improving the effective performance of SnO_2, a common way is doping SnO_2 with proper metal elements such as Sb, Fe, Co, Ni, Mn, Zn etc. (Huang *et al.*, 2012). Zn doped SnO_2 has more effective photocatalytic properties and ability to modify it structural performance and preferred by regarding other materials. Doping leads to obtain large surface area and trapping mass centers. These particles have more effective photocatalytic activity (Yildirim *et al.*, 2016).

In this study, Zn doped SnO_2 with different amount of Zn were synthesized by flame spray pyrolysis (FSP) technique to improve the catalytic performance.

EXPERIMENTAL

In this work, undoped and Zn-doped tin oxide (SnO_2) samples were prepared using flame spray pyrolysis (FSP) technique (Tethis, Np 10, Italy). The liquid precursor solution was sprayed into the flame from syringe pump with a ratio of 5 mL/min. The mixture of supporting gas (methane/oxygen) flow rate was kept constant with 5 L/min and oxygen/fuel ratio of 1.5/3. Undoped and different ratio of Zn doped (1, 3, 5, 7 and 9 at.%) SnO_2 nanoparticles with diameters of below 200 nm were obtained with this method.

The phase structure and crystallinity of the samples are studied by 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). The samples were scanned over a range of 20° to 70° with a scanning rate of 2°/min. The morphology and structure of the samples were characterized using by a scanning electron microscope (SEM, Philips XL 30S FEG).

Photocatalytic activity of undoped and Zn-doped SnO_2 nanoparticles were determined by studying photodegradation of methylene blue (MB) dye solution under UV light. MB (Sigma Aldrich) solution with 10^{-5} M concentration was prepared with distilled water and undoped and Zn doped SnO_2 nanoparticles were dispersed in this solution.

The photodegradation of the MB experiments were conducted up to 180 min. The distance between the light source and the suspension beaker was kept as 20 cm. All the absorption experiments of the MB solutions were performed using by a UV-1240 (Shimadzu) spectrophotometer based on the characteristic absorption peak of MB at 664 nm.

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern of the undoped and 1-9 at.% Zn doped SnO_2 nanoparticles produced by FSP technique are shown in Figure 1. It was observed that all peaks of the SnO_2 phases corresponding to 26.6, 33.9, 38.0, 51.8 and 55.0 at 2θ values were assigned to (110), (101), (200), (211) and (220), respectively (JCPDS Card No: 41-1445). These crystal planes were prominently seen in XRD indicating the polycrystalline nature of powder of SnO_2. No other peak for the polycrystalline phases of SnO_2 or any other impurity was seen and no impurities were detected.

SEM analysis was performed to reveal morphological features of the sample. SEM micrographs of polycrystalline SnO_2 nanoparticles are shown in Figure 2. These micrographs show homogeneous, uniform distribution of SnO_2 nanoparticles over a scanned area. It’s clear that the surface morphology of the nanoparticles has an important role in their photocatalytic activity. General view for undoped and 1% Zn doped SnO_2 nanoparticles can be seen in Figure 2a and c, respectively. Additionally, Figure 2b and d represent the detailed structure and morphology of the nanoparticles with 100k magnification. It can be clearly seen that 1% Zn doped SnO_2 nanoparticles have different morphology from undoped SnO_2 nanoparticles. This may affect the photocatalytic activity of the produced nanoparticles.

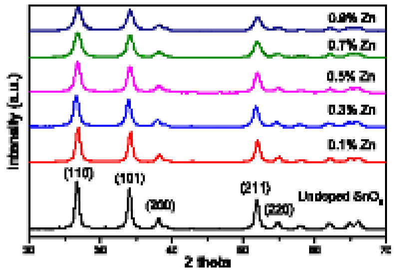

Figure 1: XRD patterns of the undoped and Zn doped SnO_2 nanoparticles produced by FSP.

(a) (b) (c) (d)

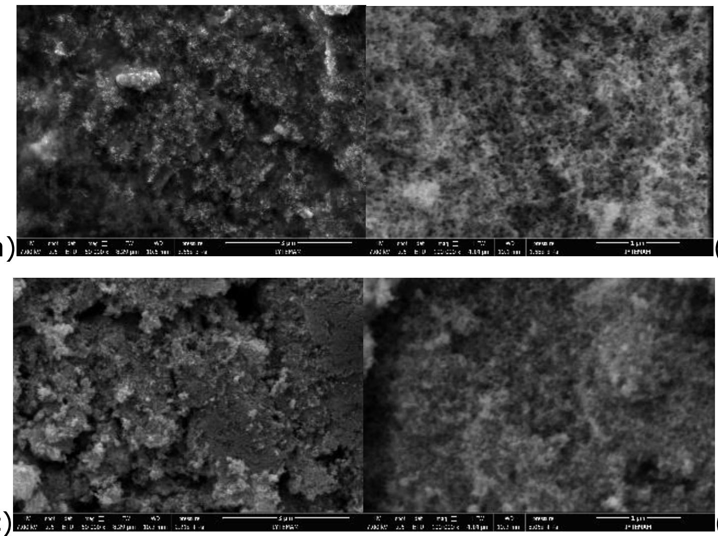

Figure 2: SEM images of the undoped and 9% at. Zn doped SnO_2 nanoparticles with low (a-c) and high magnifications (b-d).

The photocatalytic activities of undoped and Zn doped SnO_2 nanoparticles were investigated by the degradation of MB solution. It was observed that the suspension mixed with 1% Zn doped SnO_2 nanoparticles was decolorized higher than undoped SnO_2. Figure 3 plotted the photocatalytic degradation of MB with irradiation time for 120 min, compared with undoped and 1-9% Zn doped SnO_2. As shown in Figure 3, both undoped and 1% Zn doped SnO_2 nanoparticles decolorized MB effectively, nevertheless 1% Zn doped SnO_2 nanoparticles exhibited the enhanced photocatalytic activity than undoped SnO_2.

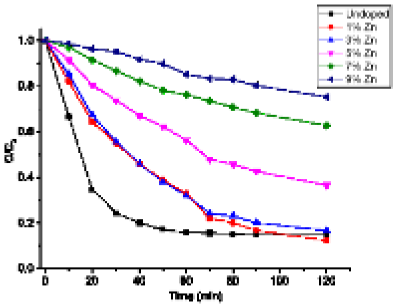

Figure 3: Photocatalytic degradations the undoped and Zn doped SnO_2 nanoparticles produced by FSP.

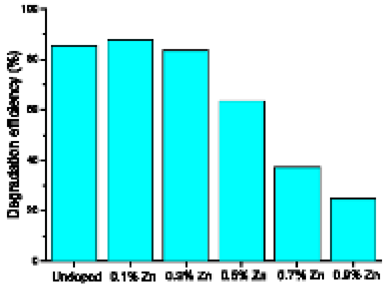

Figure 4: Photocatalytic efficiencies of the undoped and Zn doped SnO_2 nanoparticles produced by FSP.

The degradation efficiency of the photocatalysts was given in Figure 4. The degradation efficiency of the 0.1% Zn doped SnO_2 nanoparticles was 87,6%, whereas that of the undoped SnO_2 nanoparticles was 85.2%. With Zn doping exceeds 1% at., the photocatalytic activity of the SnO_2 nanoparticles began to decrease, which probably is attributed to the increased recombination of photoexcited electrons and holes.

CONCLUSION

In this study, we successfully performed flame spray pyrolysis synthesis of the undoped and Zn doped SnO_2 nanoparticles. The sample 1% Zn doped SnO_2 has the best photocatalyst for degradation of the organic dye, MB. It can be seen that the photocatalytic activity of the SnO_2 nanoparticles increased after Zn doping, and the optimum amount for Zn doped nanoparticles was 1%. With further increasing amount of Zn, photocatalytic performance was gradually decreased. The best dopant concentration exhibiting maximum photocatalytic activity can be explained by space charge creation and rate of charge carrier recombination thanks to Zn doping into SnO_2.

REFERENCES

Ang GT, Toh GH, Bakar MZA, Abdullah AZ, Othman MR. High sensitivity and fast response SnO2 and La-SnO2 catalytic pellet sensors in detecting volatile organic compounds. Process Saf Environ Prot. Institution of Chemical Engineers; 2011;89(3):186–92.

Dave N, Pautler BG, Farvid SS, Radovanovic P V. Synthesis and surface control of colloidal Cr3+-doped SnO2 transparent magnetic semiconductor nanocrystals. Nanotechnology. 2010;21(13):134023.

Huang H, Tian S, Xu J, Xie Z, Zeng D. Needle-like Zn-doped SnO 2 nanorods with enhanced photocatalytic and gas sensing properties.

Jia T, Wang W, Long F, Fu Z, Wang H, Zhang Q. Synthesis , Characterization , and Photocatalytic Activity of Zn-Doped SnO2 Hierarchical Architectures Assembled by Nanocones. 2009;9071–7.

Liu J, Gu F, Hu Y, Li C. Flame Synthesis of Tin Oxide Nanorods: A Continuous and Scalable Approach. J Phys Chem C. 2010;114(13):5867–70.

Paulauskas IE, Modeshia DR, Obaid Y, Basahel SN, Al-ghamdi AA, Sartain FK. Photocatalytic Activity of Doped and Undoped Titanium Dioxide Nanoparticles Synthesised by Flame Spray Pyrolysis. 2013;(1):32–43.

Rahman MM, Jamal A, Khan SB, Faisal M. Highly sensitive ethanol chemical sensor based on Ni-doped SnO2 nanostructure materials. Biosens Bioelectron. Elsevier B.V.; 2011;28(1):127–34.

Shanmugam N, Sathya T, Viruthagiri G, Kalyanasundaram C, Gobi R, Ragupathy S. Photocatalytic degradation of brilliant green using undoped and Zn doped SnO2 nanoparticles under sunlight irradiation. Appl Surf Sci. Elsevier B.V.; 2016;360:283–90.

Yildirim S, Yurddaskal M, Dikici T, Aritman I. Structural and luminescence properties of undoped, Nd 3 þ and Er 3 þ doped TiO 2 nanoparticles synthesized by fl ame spray pyrolysis method. Ceram Int. Elsevier; 2016;42(9):10579–86.