

A Low Temperature Hydrothermal Synthesis of ZnO Doped SnO₂ Nanoparticles with High Photocatalytic Activity

A. Anaraki Firooz*

Department of Chemistry, Faculty of Science, Shahid Rajaei Teacher Training University, Tehran, I.R.Iran

(* Corresponding author: a.anaraki@srttu.edu
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Abstract

The paper reports the preparation and photocatalytic activity of ZnO doped SnO₂ nanoparticles. These nanoparticles were synthesized by hydrothermal method. The products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Their grain sizes are about 50-100 nm. The characterization results revealed that the synthesized nanoparticles possess just crystal phases of tetragonal rutile phase of SnO₂ with high quantity and good crystallinity. The photocatalytic activity of this material was investigated for congo red removal from aqueous solution under UV light irradiation. It was shown that the use of ZnO doped SnO₂ nanoparticle as a photocatalyst has a better photocatalytic activity for degradation of congo red than SnO₂ or TiO₂ (anatase, particle size: 30 nm) alone. This good performance can be attributed to more charge separation; then the recombination of electrons and holes in ZnO doped SnO₂ nanoparticle is greatly suppressed. This is the reason that the ZnO doped SnO₂ nanoparticles possessed both higher photocatalytic oxidation and reduction activities than those of TiO₂ or SnO₂.

Keywords: Hydrothermal, Nanoparticle, Photocatalyst, SEM, ZnO doped SnO₂.

1. INTRODUCTION

In recent years, heterogeneous photocatalysts have received increasing attention for environmental applications such as air purification, water disinfection, hazardous remediation and water purification [1-3].

However, the high photocatalytic degradation of semiconductors, such as TiO₂, ZnO and SnO₂ has attracted extensive attention of many researchers due to their high photo-sensitivity, low cost and chemical stability [4-9]. In such semiconductors, photogenerated carriers (electrons and holes) could tunnel to a reaction medium and participate in chemical reactions. The high degree of recombination of these carriers greatly decreased their photocatalytic efficiency. Clearly, a wider separation of the electron and the holes increases the efficiency of photocatalyst. Fortunately, utilizing the

multifunctional materials could increase the charge separation and extend the energy range of photooxidation. However, the preparation of these materials is carried out by different methods such as low temperature ion exchange [10], spray pyrolysis [11], thermal evaporation [12] and hydrothermal [13].

SnO₂ is particularly interesting because it has outstanding optical, electrical and mechanical properties, it is a versatile material and widely used as the most attractive material for various potential applications such as photocatalysis, far-infrared detectors, solar cells, optoelectronic devices, catalyst supports, gas sensor, antireflective coatings and transparent electrodes [14, 15]. SnO₂ itself shows very little photocatalytic efficiency due to its large band gap. However, it is known to be a better electron acceptor than

TiO₂ and ZnO due to more positive CB [16]. Hence, it is a good candidate for the doping with other metal oxides to effectively enhance the photocatalytic efficiency by reducing the photogenerated electron-hole pairs recombination.

In this study, we synthesized ZnO doped SnO₂ nanoparticles by a simple hydrothermal method at 120 °C. The products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Also, the photocatalytic activities were evaluated using congo red as a model organic compounds.

2. EXPERIMENTAL

2.1. Hydrothermal preparation

ZnO doped SnO₂ nanoparticles were synthesized by hydrothermal method. In typical experiments, 0.05 g of ZnO (zincite >99.9 Wt% rdh) and 1 g of Na₂SO₄ salt were added to 40 ml of distilled water. Then, 0.25 g of SnCl₂ · 2H₂O (Merck >97 %) was added the above mixture. To acidify the above solid-solution mixture, 1 ml of 4 M HNO₃ solution was used. The mixture was then transferred to a Teflon-lined stainless steel autoclave and placed inside an oil bath at 120 °C for two days. After the reactions, the oil bath cooled naturally at room temperature, the solid products were separated from the liquid phase via centrifugation and washed with deionized water and pure ethanol. Then, the final products were dried in vacuum desiccators at room temperature overnight for material characterization.

We used commercial TiO₂ and SnO₂ for comparison the photocatalytic activity.

2.2. Characterizations of the ZnO doped SnO₂ nanoparticles

The products were characterized using scanning electron microscopy (SEM) of a Holland Philips XL30 microscope. XRD patterns of these products were recorded in ambient air with using a Holland Philips Xpert X-ray powder diffraction (XRD) (CuK α , $\lambda = 1.5406 \text{ \AA}$), at scanning speed of 2°/min from 20° to 80 °(2 θ).

2.3. Evaluation of photocatalytic activity

First, the solution of congo red (C.I. Direct Red 28, M.W = 696.67 g/mol C₃₂H₂₄N₆O₆S₂·2Na) with 5 ppm concentration was prepared in distilled water. The photocatalysis experiments were carried out in beaker containing about 50 ml of congo red aqueous solution and about 0.025 g of ZnO doped SnO₂ nanoparticles as the photocatalyst. The radiation source, a UV lamp (30W, UV-C, $\lambda=253.7 \text{ nm}$, photon provides 4.89 eV, manufactured by Philips, Holland), irradiated perpendicularly to the surface of the solution and the distance equal to 15 Cm was fixed between the UV source and vessel containing reaction mixture. Air was blown into the reaction by an air pump, to maintain the solution saturated with oxygen during the course of the reaction. During irradiation, agitation was maintained by a magnetic stirrer to keep the suspension homogeneous, the suspension was sampled after regular intervals and immediately centrifuged at 3500 rpm for 4 minutes to completely remove catalyst particles. The progress of photocatalytic degradation was monitored by measuring the absorbance of the solution samples with UV-Vis spectrophotometer (Shimadzu UV 2100). Absorption peaks corresponding to Congo red appeared at 497, 347 and 237 nm. By this method, conversion percent of Congo red can be obtained in different intervals.

The concentration of dye in each decolorized sample was determined at $\lambda_{\text{max}} = 497 \text{ nm}$ using a calibration curve. By this method, conversion (X) of Congo red azo dye can be obtained in different intervals based on Eq. (1).

$$X = C/C_0 \quad (1)$$

Where, C₀ is the initial concentration of the dye and C is the concentration of dye at different times.

3. RESULT AND DISCUSSION

Figure. 1(a) shows SEM image of the as-synthesized ZnO doped SnO₂, indicating products consist of nanoparticles

structures. Statistical analyses of different SEM images show that the average diameter of these nanoparticles was in the range of 50 -100 nm. Fig. 1(b) shows the closer-view SEM image of these products. The structure and crystalline state of the powders were characterized by X-ray diffraction. Fig. 2 shows a representative XRD pattern of the ZnO doped SnO₂ nanoparticles.

All the major peaks in the pattern correspond to the rutile structure of SnO₂, which can be indexed on the basis of JCPDS file No. 72-1147.

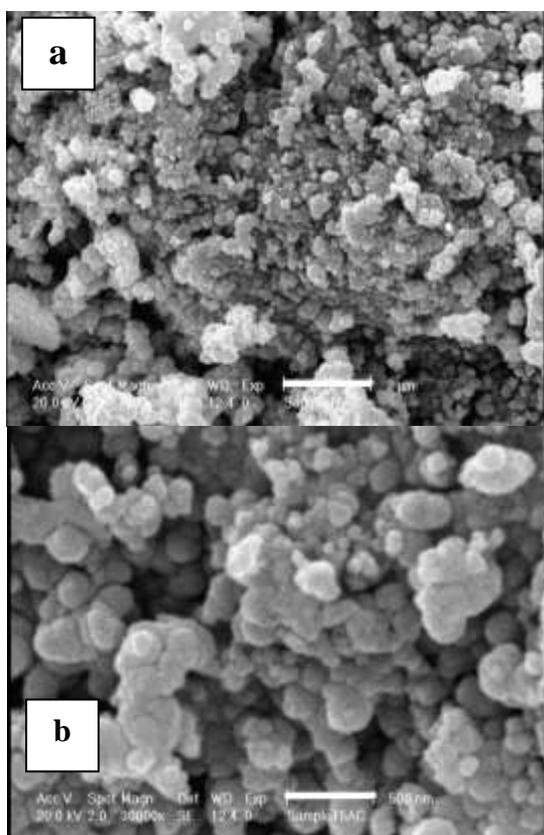


Figure 1. (a) typical of SEM image of the ZnO doped SnO₂ prepared by hydrothermal (b) closer-view SEM image of nanoparticles.

No peaks corresponding to ZnO are observed. Average crystallite sizes of products were calculated using Scherrer's formula: $D = 0.9\lambda / \beta \cos \alpha$ [9], where D is the diameter of the nanoparticles, λ (Cu K α) = 1.5418 Å and β is the full-width at half-maximum of the diffraction lines. The

calculated average crystallite size was about 80 nm.

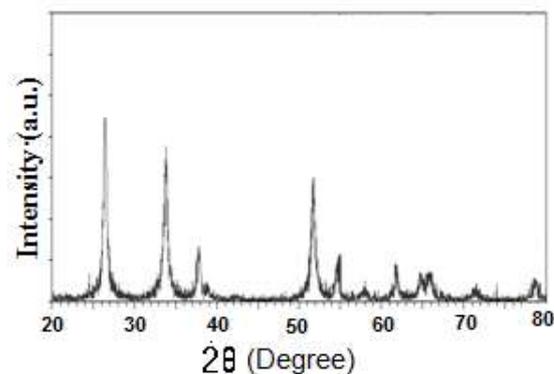


Figure 2. XRD patterns for the ZnO doped SnO₂ nanoparticles

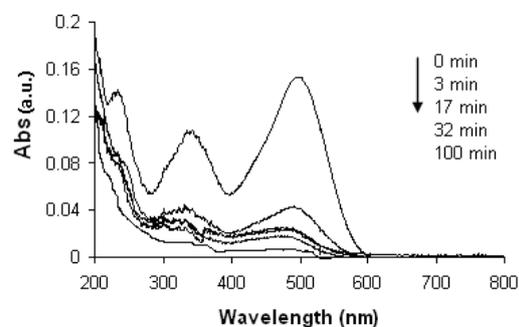


Figure 3. Absorbance spectral changes of congo red solution after different irradiation in the presence of ZnO doped SnO₂.

The time-dependent UV-Vis spectra of congo red during the irradiation are demonstrated in Fig. 3. It can be seen that the maximum absorbance of 497 nm almost disappear after irradiation for 100 min. In the presence of UV light and ZnO doped SnO₂ as photocatalyst, the decolorization of dye molecules increases with irradiation time. After UV light irradiation, not only the main absorbance in visible region decreases dramatically with irradiation time, but also the peak in the UV region reduces, indicating that both the dye chromophoric structure in the vicinity of the azo-linkage and the aromatic rings are destroyed. According to the Eq. (1), the C/C₀ of the ZnO doped SnO₂, commercial SnO₂ and TiO₂ were calculated and were shown in Fig. 4. The results reveal that the decolorization

efficiency increases with doping of ZnO into lattice of SnO₂.

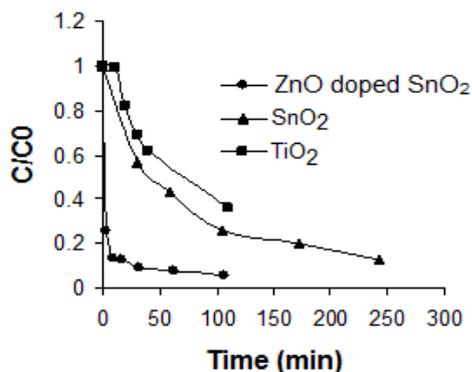


Figure 4. Comparison of the activities of ZnO doped SnO₂, SnO₂ and TiO₂ at $\lambda = 497\text{nm}$, Condition: amount of catalyst = 0.5 g/l.

The enhancement of the decolorization efficiency may be explained in terms of the synergetic effect on the specific adsorption property and efficient electron hole separation at the ZnO-doped SnO₂ photocatalyst interfaces and surfaces.

It means that doping with ZnO may enhance the chance of the separation of electrons and holes (Fig. 5), and their participating in redox reaction with

adsorbed dye molecules on the surface of photocatalyst.

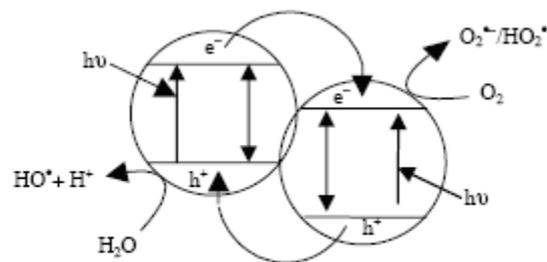


Figure 5. A diagram illustrating the principle of charge separation and photocatalytic activity

4- CONCLUSION

In summary, we synthesized ZnO doped SnO₂ nanoparticles by a simple hydrothermal method at low temperature as a photocatalyst. These nanoparticles exhibited higher photocatalytic efficiency for degradation of congo red than SnO₂ or TiO₂ (anatase, particle size: 30 nm). The enhancement of the decolorization efficiency may be explained due to the enhanced charge separation derived from the coupling of ZnO with SnO₂ because of the potential energy differences between SnO₂ and ZnO.

REFERENCES

1. Yao, B., Peng C., Zhang W., Zhang Q., Niu J., Zhao J. (2015). "A novel Fe(III) porphyrin-conjugated TiO₂ visible-light photocatalyst" *Appl. Catal. B: Env.* 174-175: 77-84.
2. Ren F., Li H., Wang Y., Yang J. (2015). "Enhanced photocatalytic oxidation of propylene over V-doped TiO₂ photocatalyst: Reaction mechanism between V⁵⁺ and single-electron-trapped oxygen vacancy" *Appl. Catal. B: Env.* 176-177: 160-172.
3. Pekárek S., Mikeš J., Krýsa J., (2015). "Comparative study of TiO₂ and ZnO photocatalysts for the enhancement of ozone generation by surface dielectric barrier discharge in air" *Appl. Catal. A: Gen.* 502: 122-128.
4. Naghizadeh-Alamdari S., Habibi-Yangjeh A., Pirhashemi M. (2015). "One-pot ultrasonic-assisted method for preparation of Ag/AgCl sensitized ZnO nanostructures as visible-light-driven photocatalysts" *Solid State Sci.* 40: 111-120.
5. Faisal, M. Ibrahim, AA. . Harraz, FA. Bouzid, H. Al-Assiri, MS. Ismail, AA. (2015) "SnO₂ doped ZnO nanostructures for highly efficient photocatalyst" *J. Molec. Catal. A: Chem.* 397: 19-25.
6. Sabbaghan, M. Anaraki Firooz, A. Jan Ahmadi, V. (2012). "The effect of template on morphology, optical and photocatalytic properties of ZnO nanostructures" *J. Mol. Liq.* 175: 135-140.
7. Abdullah Mirzaie, R. Kamrani, F. Anaraki Firooz, A. Khodadadi, AA. (2012) "Effect of α -Fe₂O₃ addition on the morphological, optical and decolorization properties of ZnO nanostructures" *Mat. Chem. Phys.* 133: 311-316.
8. Anaraki Firooz, A. Mahjoub, AR. Khodadadi, AA. Movahedi, M. (2010) "High photocatalytic activity of Zn₂SnO₄ among various nanostructures of Zn_{2x}Sn_{1-x}O₂ prepared by a hydrothermal method" *Chem. Eng. J.* 165: 735-739.
9. Abdullah Mirzaie, R. Anaraki Firooz, A. Kamrani, F. Khodadadi, AA. (2013) "Highly efficient MoO_{2.5}(OH)_{0.5}-doped ZnO nanoflower for photodecolorization of azo dye" *Solid State Sci.* 26: 9-15.

10. Kovacheva, D. Petrov K. (1998) "Preparation of crystalline ZnSnO_3 from Li_2SnO_3 by low-temperature ion exchange" *Solid State Ionics*, 109: 327-332.
11. Patil, L.A. Pathan, I.G. Suryawanshi, D.N. Bari, A.R. Rane, D.S. (2014) " Spray pyrolyzed ZnSnO_3 nanostructured thin films for hydrogen sensing" *Procedia Mat. Sci.* 6: 1557-1565.
12. Jin, C. Kim, H. An, Lee, S.C. (2012) "Highly sensitive H_2S gas sensors based on CuO-coated ZnSnO_3 nanorods synthesized by thermal evaporation" *Ceram. Inter.* 38: 5973-5978.
13. Balachandran S, Selvam K, Babu B, Swaminathan M. (2013). "The simple hydrothermal synthesis of Ag-ZnO-SnO₂ nanochain and its multiple applications" *Dalton Trans.* 42(46):16365-74.
14. Rashad, M.M. Ismail, A.A. Osama, I. Ibrahim I.A. Kandil, A-HT. (2014) "Photocatalytic decomposition of dyes using ZnO doped SnO₂ nanoparticles prepared by solvothermal method" *Arab. J. Chem.* 7:71-77.
15. Borges, P.D. Scolfaro, L.M.R. Alves, W.L. Dasilvajr, E.F. (2010) "DFT study of the electronic, vibrational, and optical properties of SnO₂" *Theor. Chem. Acc.* 126: 39-44.
16. Wu, S. Cao, H. Yin, S. Liu X. Zhang, X. (2009) "Amino acid-assisted hydrothermal synthesis and photocatalysis of SnO₂ nanocrystals" *J. Phys. Chem. C.* 113:17893- 17898