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Short Communication

The Effect of Different Dopants (Cr, Mn, Fe, Co, Cu and Ni) on Photocatalytic Properties of ZnO Nanostructures

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Abstract

ZnO structures with different dopants (1mol% Cr, Mn, Fe, Co, Cu and Ni) have been synthesized via a simple hydrothermal method using sucrose as a template. These doped ZnO nanostructures characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL). The photocatalytic property of these synthesized materials was studied by a photocatalytic characterization system. The PL results confirmed that these dopants showed a significant effect on photoluminescence properties of ZnO structure. Among the synthesized photocatalysts, Ni doped ZnO showed a significant enhancement of photodecolorization capability (98.6 %) toward Congo red dye in UV irradiation. Also, it showed the highest dye adsorption (80%) at dark conditions. The improvement of decolorization of this photocatalyst might be attributed to enhancement the chance of the separation of electrons and holes, high capacity of dye adsorption and presence of defects in its structure. Preliminary experiment suggested Ni doped ZnO as effective photocatalyst for treating some pollution such as azo dyes.

Keywords: *Photochemistry; Doping; Synthesis of Materials.*

1. INRODUCTION

During the past few decades, wastewater from textile or other dyestuff industries are of great concern in water treatment due to damage to the ecosystem and human health [1-3]. For removing of waste water, photocatalysts have shown great potential for photodegradation of the pollutants by oxidation process [4-7]. Among various photocatalysts, ZnO is more considerable photocatalyst due to low cost, non-toxic nature and high photocatalytic capacity to degrade organic pollutants [8-10]. Photodegration was done through created hydroxyl radical and superoxide radical anions under UV light irradiation. These radicals are very reactive oxidizing agents that can degrade the organic pollutants [11]. However, ZnO semiconductor with having large band gap energy of 3.37eV cannot be excited by visible light [12]. Researchers are trying to solve this problem by doping transition metal ions into the ZnO lattice. It caused to extend the optical response of ZnO from UV to visible region. The doping causes to reduce band gap energy and improve the separating efficiency of photo-induced electrons and holes [13-15].

According to the above discussion, the main objective of this research is to examine decolorization of Congo red dye by synthesized photocatalysts. So, various morphologies of doped ZnO nano-structures as photocatalysts have been successfully synthesized by a simple hydrothermal method using different dopants.

2. EXPERIMENTAL

2.1. Synthesis

All of the chemical reagents used in the experiments were analytic grade without further purification and treatment. All products were prepared using a simple hydrothermal method at low temperature. We used Cr, Mn, Fe, Co, Cu or Ni chloride as dopants with mole ratio of 0.01 than Zinc acetate. In a typical procedure, we dissolved 3 mmol $Zn(CH_3COO)_2 \cdot 2H_2O$ in 50 ml distilled water at room temperature under stirring. Then, we added 3mmol (1.2 g) sucrose ($C_{12}H_{22}O_{11}$) into this solution with vigorous stirring for 30 min. After that time, we added 0.03 mmol of Cr, Mn, Fe, Co, Cu or Ni chloride to the above solution under stirring for 30 min. After that, 6 mmol NaOH powder (molar ratio of NaOH to Zinc acetate 2:1) was added under stirring and then the solution was transferred to an autoclave and kept at 100°C in oven for 2 h. After completion of the reaction time, we filtered the products via centrifugation and washed with double distilled water for several times until free from impurities such as chloride. Finally, we dried the obtained products at room temperature and collect them for physical characterizations.

The samples, after doping with Cr, Mn, Fe, Co, Cu and Ni, will be named Cr/ZnO, Mn/ZnO, Fe/ZnO, Co/ZnO and Ni/ZnO, respectively.

2.2. Characterization

The ZnO nanostructures were analyzed by XRD using the Cu Kα wavelength of 1.5405Å. The morphology of the sample was determined by using a scanning electron microscopy (SEM Holland Philips XL30). The photoluminescence (PL) spectrum was recorded by applying a photoluminescence spectrophotometer (Avantes/Avaspec 2048) at room temperature in the wavelength range of 200-1100 nm.

2.3. Evaluation of Photocatalytic Activity

50 ml of the solution containing 20 ppm (W/V) Congo red (C.I. Direct Red 28, M.W. = 696.67 g/mol $C_{32}H_{24}N_6O_6S_2 \cdot 2Na$) and 50 mg of synthesized phtocatalyst was used for assessment of the photocatalytic activity of the samples. For providing desired UV photon, we installed five UV lamps of 6 W (Philips, Holland) with strongest emission at 254 nm at the height of 15 cm above the reaction vessel and irradiated perpendicularly to the surface of the solution (Fig. 1).

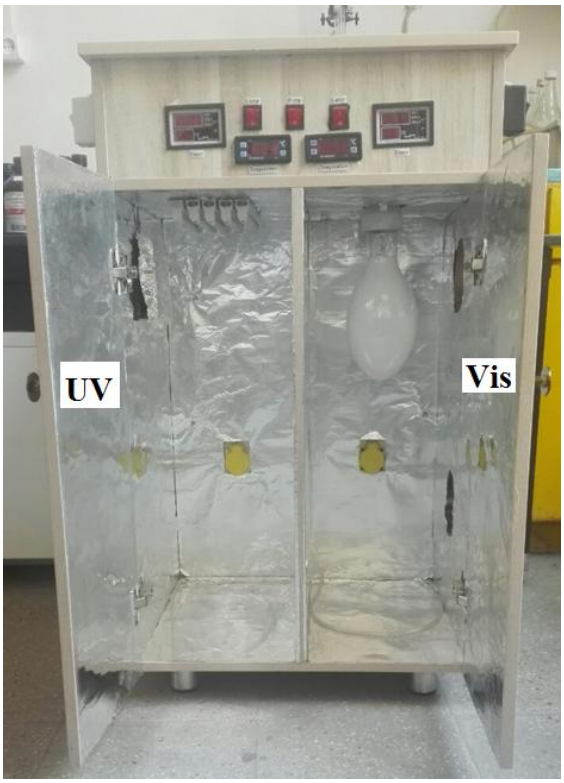


Figure 1. *Photocatalyst setup.*

Air bubbles were blown into the solution by air pump for making the solution saturated with oxygen. Also, magnetic stirrer was used to keep the solution homogenous. At the beginning of each experiment, a solution containing 20 ppm Congo red and 50 mg photocatalyst was stirred for 20 min in dark condition to reach an adsorption/desorption equilibrium for Congo red dye molecules on the surface of photocatalyst. Then we turned on UV lamp. 5 mL of sample was withdrawn at predetermined time intervals, and it was centrifuged for 5 min

immediately to separate catalyst particles. The Congo red concentration of the solution was measured by a UV-visible spectrophotometer. Absorption peak corresponding to Congo red appeared at 497 nm, 347 and 237 nm. The concentration of dye in each decolorized sample was determined at max = 497 nm using a calibration curve. By this method, conversion percent of Congo red azo dye can be obtained in different intervals. The degree of photodecolorization efficiency (X) is given by eq. 1:

$$X=(C- C_o)/C_o \qquad (1)$$

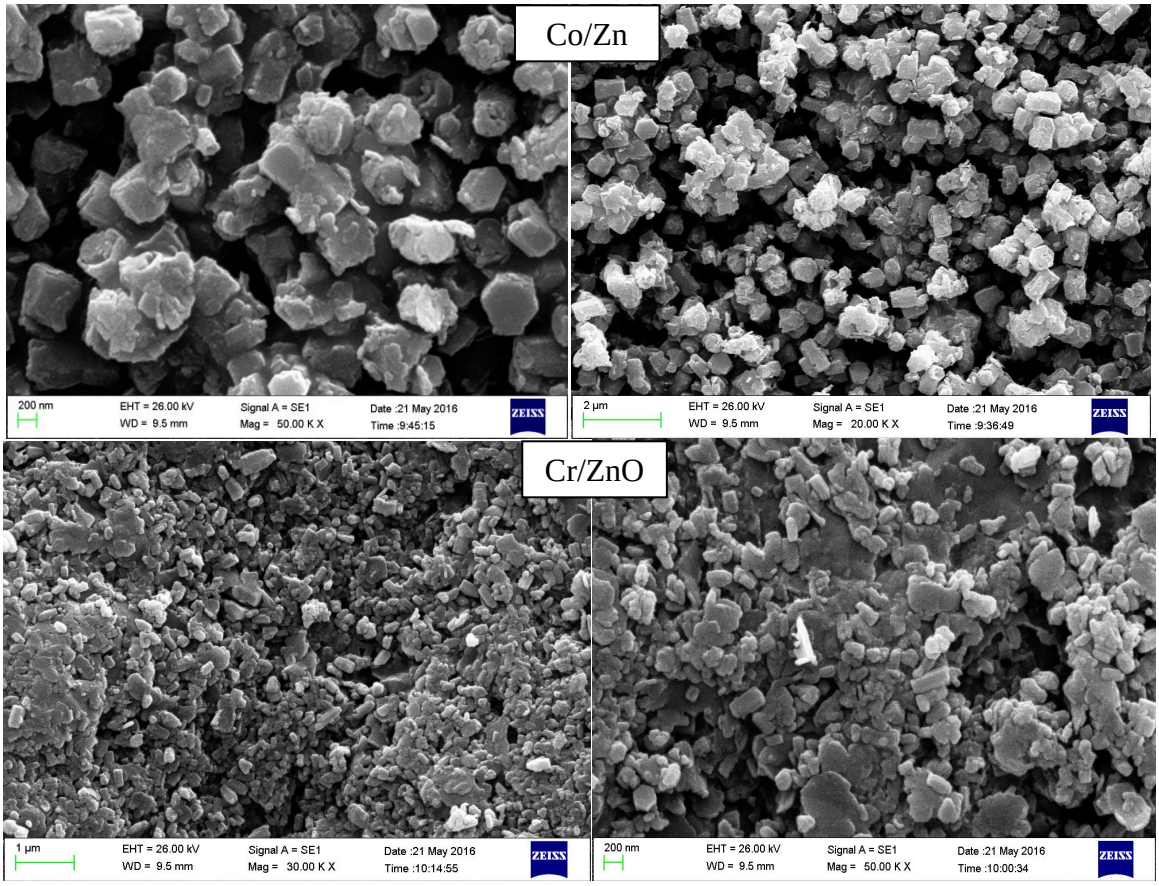
where, C_o is the initial concentration of dye and C is the concentration of dye at different times [16, 17].

3. RESULTS AND DISCUSSION

M/ZnO structures (M= Cr, Mn, Fe, Co, Cu and Ni) were synthesized by hydothermal method at low temperature (100^0C). In this method, sucrose was used as template and then removed by water washing. This method is green with high ability to control nucleation and growth in complex systems and low energy consumption without affecting morphological homogeneity. The obtained products by this method was stable and phase-pure in air that confirmed by results of SEM and XRD. Figs. 2 and 3 show the SEM images of the samples.

As shown in the following Figs. Cu/ZnO, Fe/ZnO and Ni/ZnO are structured as rods with hexagonal plate cross sections. Co/ZnO is formed shorter rods with hexagonal plate cross sections. While, the morphology of Mn/ZnO and Cr/ZnO are nanoparticles and sheet like, respectively [18].

Fig. 4 shows the XRD patterns of undoped ZnO sample. The diffraction peaks of all samples match that of hexagonal wurtzite (JCPDS card No. 36–1451) structure of well crystalline ZnO.



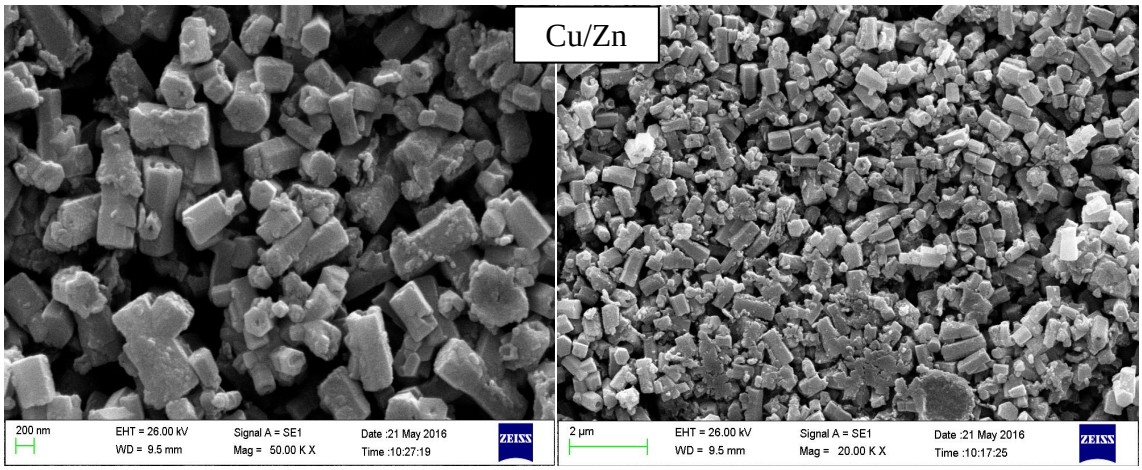


Figure 2*. SEM images of Co, Cr and Cu / ZnO structures; up to down, respectively.*

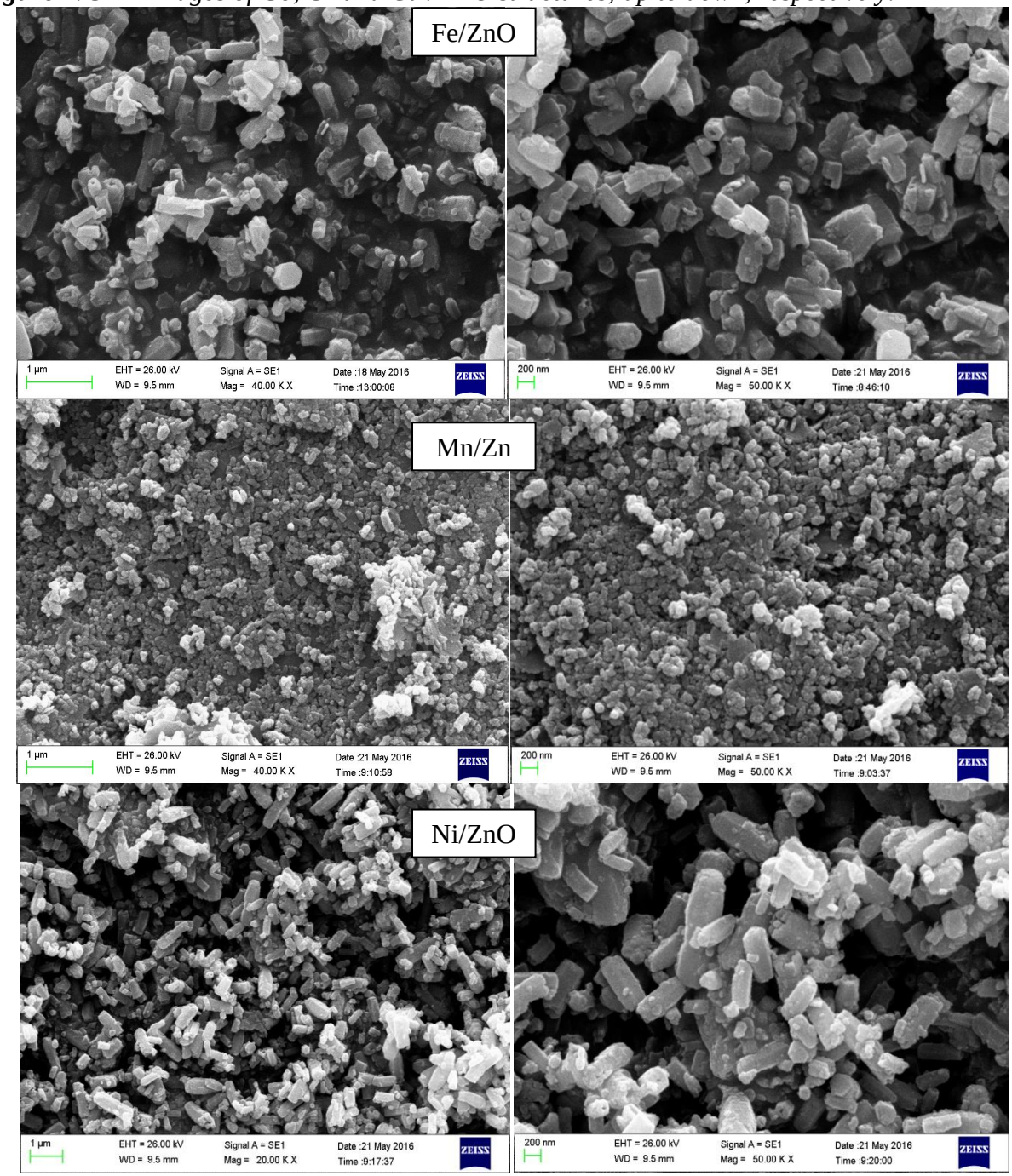


***Figure 3**. SEM images of Fe, Mn and Ni / ZnO structures; up to down, respectively.*

The diffraction patterns of doped ZnO samples were similar except the variation of the peak intensities due to the differences in growth conditions (not shown here). No reflection characteristics related to impurities are observed in the pattern, indicating the successful introduction of Mn, Cr, Fe, Co, Cu or Ni ions in the lattice of the ZnO crystals due to rather similar ionic radii [13, 18].

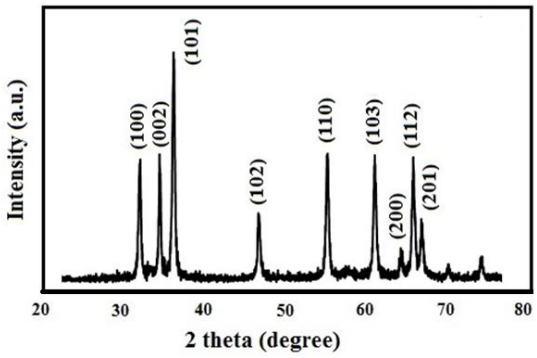


***Figure 4**. XRD pattern of ZnO structure.*

The PL spectrum of the samples was measured at excitation wavelength of 390 nm. As shown in Fig. 5, there is strong peak at around 410 nm in all samples. It can be attributed to the recombination of free excitons through exciton-exciton collision process. In addition, two broad peaks at around 484nm and 625 nm were shown in all samples. The emission at about 484 nm is related to deep level emissions (DLE). This emission in ZnO has been frequently ascribed to several intrinsic and extrinsic defects that are due to electron recombination in the oxygen vacancy with a hole in the valence band [19]. The peaks at 625 nm may be attributed to the more number of defects such as oxygen vacancies due to creation of new recombination centers [20]. The intensity of this peak is different at various doped ZnO structures. Ni/ZnO structures show the highest intensity at 625 nm compared to other doped ZnO nanostructurs. While, Mn/ZnO show the lowest intensity at this λ. These different intensities may be related to greater created defects during the growth course.

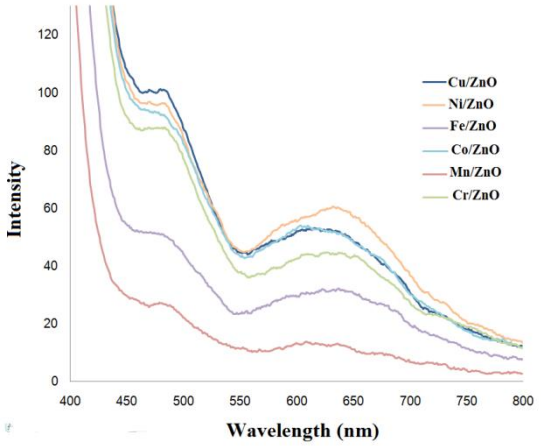


***Figure 5**. PL spectrum of Cr, Mn, Fe, Co, Cu and Ni /ZnO structures.*

We synthesized these materials as photocatalysts for decolorization of Congo red dye. Congo red is a reactive dye formed by the combination of azo-based chromophores with vinyl sulfune as reactive group. The largest chemical class of dyes is azo dyes that used in industries, extensively. The presence of azo group (-N=N-) is responsible for their coloration [21]. So, we employed the photodecolorization of Congo red dye under UV irradiation to measure the decolorization efficiency of doped ZnO nanostructures as photocatalysts. Under UV light and in the presence of photocatalyst, azo bands of Congo red breaks up and the intensity of the visible light chromophore decreases, as a result decolorization occurs.

Fig. 6 shows the adsorption and photocatalytic decolorization behavior of Cr, Mn, Fe, Co, Cu and Ni /ZnO structures as photocatalysts in dark and UV irradiation conditions. When the Congo red solution containing of photocatalyst was applied in dark condition for 20 min, the concentrations of Congo red solution decreased except the solution containing

Cu/ZnO photocatalyst. So, the solution becomes pale at dark condition. This pale is attributed to the adsorption of Congo red dye through two oxygen atoms of the sulfonate group [14]. Among these photocatalysts, Ni/ZnO shows the highest adsorption of Congo red dye molecules (80%). While, Cu/ZnO shows no adsorption of Congo red dye molecules. The capacity of adsorption is different for each photocatalyst, probably due to presence of dopant species on the surface. In addition, Fig. 6 shows that the decolorization of dye molecules increases in the presence of UV light and photocatalysts with irradiation time. As shown in this Fig., the decolorization efficiency of Ni/ZnO photocatalyst is better than the other photocatalysts. So, the presence of Ni species may enhance the chance of the separation of electrons and holes due to the synergetic effect on the specific adsorption surface [13]. In addition, the more target molecules adsorbed on photocatalyst, the faster and more complete decomposition of the molecules [15].

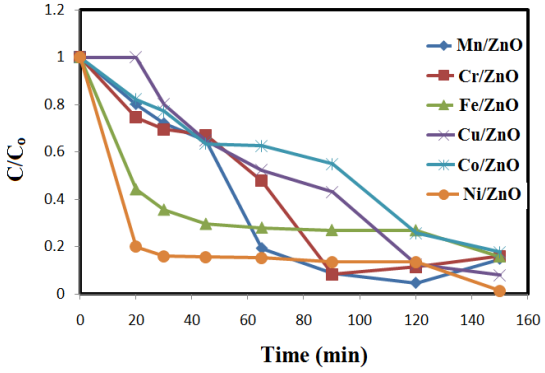


Figure 6*. Adsorption and photocatalytic decolorization behavior of Cr, Mn, Fe, Co, Cu and Ni/ZnO structures as photocatalysts in dark and UV irradiation conditions.*

Also, another key factor that can affect photocatalytic efficiency attribute to the presence of defects in the lattice. The introduction of Ni species in the ZnO lattice increases the lattice defects. This is in good agreement with PL results. So, Ni/ZnO photocatalyst not only shows the highest adsorption, but also shows the highest photodecolorization.

Figure 7 presents Congo red solutions of Co and Ni /ZnO structures after UV irradiation at different times.

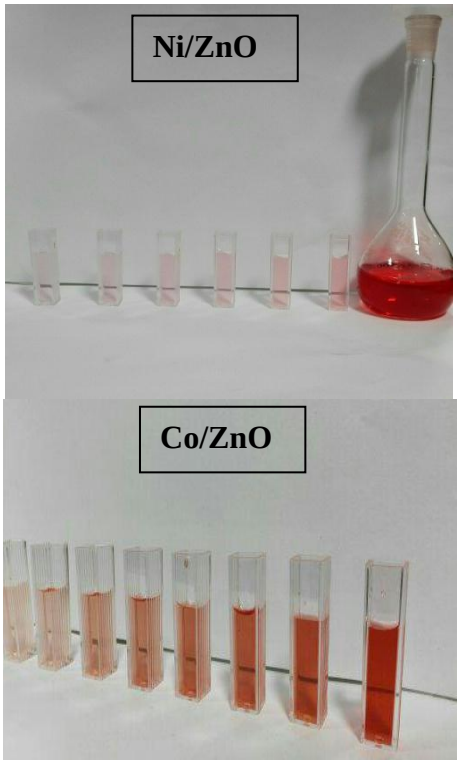


Figure 7*. Congo red solutions of Co and Ni/ZnO structures after UV irradiation at different times.*

4. CONCLUSION

In summary, we synthesized doped ZnO structures as UV light sensitive photocatalysts by a simple hydrothermal method. The results revealed that optical and photocatalytic properties of ZnO structures are strongly affected by different dopants. Ni doped ZnO showed not only the highest adsorption, but also, the highest decolorization under UV irradiation. This may be due to high capacity of molecule adsorption and presence of oxygen vacancies and crystallite defects.

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REFERENCES

1. Paz, A., Carballo, J., Pérez, M. J., Domínguez, J. M., (2017) "Biological treatment of model dyes and textile wastewaters", *Chemosphere*, 181: 168-177.
2. Hassanzadeh, E., Farhadian, M., Razmjou, A., Askari, N., (2017) "An efficient wastewater treatment approach for a real woolen textile industry using a chemical assisted NF membrane process", *Envir. Nanotech. Monitor. Manage.* 8: 92-96.
3. Paździor, K., Wrębiak, J., Klepacz-Smółka, A., Gmurek, M., Bilińska, L., Kos, L., Sójka-Ledakowicz, J., Ledakowicz, S., (2017) "Influence of ozonation and biodegradation on toxicity of industrial textile wastewater, J. *Envir. Manage*, 195:166-173.
4. Reddy Inturi, S. N., Boningari, T., Suidan, M., Smirniotis, P. G., (2016) "Stabilization of Cr in Ti/Si/Cr Ternary Composites by Aerosol Flame Spray-Assisted Synthesis for Visible-Light-Driven Photocatalysis" *Ind. Eng. Chem. Res.*, 55: 4611839-11849.
5. ReddyInturi, S. N., Suidan, M., Smirniotis, P. G., (2016) "Influence of synthesis method on leaching of the Cr-TiO2 catalyst for visible light liquid phase photocatalysis and their stability", *Appl Catal B: Environ*, 180: 351-361.
6. Reddy Inturi, S. N., Boningari, T., Suidan, M., Smirniotis, P. G., (2014) "Visible-light-induced photodegradation of gas phase acetonitrile using aerosol-made transition metal (V, Cr, Fe, Co, Mn, Mo, Ni, Cu, Y, Ce, and Zr) doped TiO_2" *Appl Catal B: Environ*, 144: 333-342.
7. Reddy Inturi, S. N., Boningari, T., Suidan, M., Smirniotis, P. G., (2014) "Flame Aerosol Synthesized Cr Incorporated TiO_2 for Visible Light Photodegradation of Gas Phase Acetonitrile" *J Phys Chem C*, 118 (1): 231-242.
8. Gnanasekaran, L., Hemamalini, R., Saravanan, R., Ravichandran, K., Gracia, F., Agarwal, S., Gupta, V. K., (2017) "Synthesis and characterization of metal oxides (CeO_2, CuO, NiO, Mn_3O_4, SnO_2 and ZnO) nanoparticles as photo catalysts for degradation of textile dyes" *J. Photochem. Photobiol. B: Biol.,* 173: 43-49.
9. Mahdavi, R., Talesh, S.S.A., (2017) "The effect of ultrasonic irradiation on the structure, morphology and photocatalytic performance of ZnO nanoparticles by sol-gel method" *Ultrason. Sonochem*, 39: 504-510.
10. Wang, J., Xia, Y., Dong, Y., Chen, R., Xiang, L., Komarneni, S., (2016) "Defect-rich ZnO nanosheets of high surface area as an efficient visible-light photocatalyst" *Appl. Catal. B: Environ,* 192: 8-16.
11. Hisatomi, T., Kubota, J.,
12. Domen, K., (2014) "Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting" *Chem. Soc. Rev*. 43: 7520-7535.
13. Shahvelayati, A.S., Sabbaghan, M., Bashtani, S.E., (2015) "Imidazolium-based ionic liquids on morphology and optical properties of ZnO nanostructures" *Int. J. Nanosci. Nanotechnol* 11 (2): 123-131.
14. Türkyılmaz, Ş. Ş., Güy, N., Özacar, M., (2017) "Photocatalytic efficiencies of Ni, Mn, Fe and Ag doped ZnO nanostructures synthesized by hydrothermal method: The synergistic/antagonistic effect between ZnO and metals" *J. Photochem. Photobiol. A: Chem.*, 341: 39-50.
15. Abdullah Mirzaie, R., Kamrani, F., Anaraki Firooz, A., Khodadadi, A. A., (2012) "Effect of α-Fe_2O_3 addition on the, optical and decolorization properties of ZnO nanostructures" *Mater. Chem. Phys*.133: 311-316.
16. Abdullah Mirzaie, R., Anaraki Firooz, A., Kamrani, F., Khodadadi, A.A., (2013) "Highly efficient $MoO_{2.5}(OH)_{0.5}$-doped ZnO nanoflower for photodecolorization of azo dye" *Solid State Sci*. 26: 9-15.
17. Banisharif, A., Hakim Elahi, S., Anaraki Firooz, A., Khodadadi, A.A., Mortazavi, Y., (2013) "TiO_2/Fe_3O_4 Nanocomposite Photocatalysts for Enhanced Photo-Decolorization of Congo Red Dye" *Int. J. Nanosci. Nanotechnol*, 9: 193-202.
18. Sabbaghan, M., Anaraki Firooz, A., Jan Ahmadi, V., (2012) "The effect of template on morphology, optical and photocatalytic properties of ZnO nanostructures" *J. Molec. Liq.* 175:135-140.
19. Darvishnejad, M. H., Anaraki Firooz, A., Beheshtian, J., Khodadadi, A. A., (2016) "Highly sensitive and selective ethanol and acetone gas sensors by adding some dopants (Mn, Fe, Co, Ni) onto hexagonal ZnO plates" *RSC Adv.*, 6: 7838–7845.
20. Jin, Y., Cui, Q., Wang, K., Hao, J., Wang, Q., Zhang, J., (2011) "Investigation of photoluminescence in undoped and Ag-doped ZnO flowerlike nanocrystals" *J. Appl. Phys.*, 109: 053521.
21. Karunakaran, C., Jayabharathi, J., Jayamoorthy, K., Vinayagamoorthy, P., (2012) "Inhibition of fluorescence enhancement of benzimidazole derivative on doping ZnO with Cu and Ag" *J. Photochem. Photobiol, A*, 247: 16–23.
22. Mahmoud, M. S., (2016) "decolorization of certain reactive dye from aqueous solution using Baker's Yeast (Saccharomyces cerevisiae) strain, *HBRC j*., 12: 88-98.