Advances in Energy and Materials Research https://jaem.qom.ac.ir/

Synthesis, identification and investigation of photocatalytic properties of manganese oxide nanoparticles doped with lanthanide cation

Younes Hanifehpour ✉[1] and **Sang Woo Joo** [2]

1. Corresponding author, Department of Chemistry, Seyed Jamaleddin Asadabadi University, Asadabad, Hamadan, Iran. Email: Hanifehpour@sjau.ac.ir
2. School of Mechanical Engineering, Yeungnam University, Gyeongsan 712-749, Republic of Korea. Email: swjoo1@gmail.com

Article Info

Article type:
Research Article

Article history:
Received 2 Dec 2023
Received in revised form 28 Feb 2024
Accepted 12 Apr 2024
Published online 24 Jun 2024

Keywords: Gadolinium; hydrothermal; manganese oxide; photocatalyst; semiconductor.

ABSTRACT

In this study, nano-structured manganese oxide compounds doped with gadolinium cations were prepared by effective hydrothermal method. Substitution of gadolinium cation instead of manganese in the crystal structure of manganese oxide led to the creation of new materials with different physical and morphological properties. XRD, SEM and DRS absorption spectroscopy techniques were used to identify the synthesized materials. According to the X-ray diffraction patterns, the prepared materials have a spinel manganese oxide crystal structure. The photocatalytic properties of the prepared samples were used and evaluated to remove the methylene blue dye under the photocatalytic and sonophotocatalytic process in aqueous medium. Experiments show that with the increase in the amount of dopant, the percentage of color removal has increased and the highest value obtained for pollutant removal is related to the sample of manganese oxide doped with gadolinium (x=0.08). Also, the role of several factors such as color concentration, catalyst amount and photocatalytic process time were studied. Investigations showed that in the presence of radical and anionic scavenging agents, the color removal percentage shows a significant difference.

Cite this article: Hanifehpour, Y. & Woo Joo, S. (2024). **Error! No text of specified style in document.**, *Advances in Energy and Materials Research*, 1 (2), 1-5. https://doi.org/10.22091/jaem.2025.10911.1012

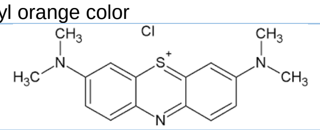
DOI: https://doi.org/10.22091/jaem.2025.10911.1012 Publisher: University of Qom.

1. Introduction

Nowadays, water pollution and energy crisis at the global level have received most of the scientific studies [1]. With the ever-increasing expansion of industries, significant amounts of pollutants such as organic dyes, agricultural toxins, and pharmaceutical compounds enter water resources. One of the processes used in the removal of pollutants resistant to biological oxidation is photocatalytic processes, using semiconductors such as Mn_3O_4 in the presence of ultraviolet and visible light in aqueous HO radical environments. which have high oxidizing power. This HO radical. It destroys organic pollutants and turns them into carbon dioxide and water. Nano photocatalysts are of two types, which include visible light region photocatalysts, which are activated by sunlight, and synthetic UV-activated photocatalysts that can be used at room temperature, and various chemical and biological pollutants in Reduce the weather. Considering that in photocatalysts that are activated by visible light, sunlight can be used to activate the photocatalyst. . Among these types of photocatalysts, we can mention ZnS, ZnO, TiO_2, CdS [2-5]. The application potential of inorganic compounds doped with lanthanide cations has been widely researched in various fields such as thermoelectric devices, fluorescence imaging and material labeling. Biological and light-emitting diodes have been developed with the development of energy levels in the energy gap [6-8]. In addition, the optimization of the energy gap using dopants has been developed to remove pollutants and polluted waters [9-11]. One of the limiting factors of semiconductors is the rapid combination of hole-electron pair and this issue can be improved by replacing cations. These cations act as electron-hole acceptors and increase the charge transport time and reduce the probability of electron-hole pairs. Manganese oxide with spinel structure as a metal oxide composed of two oxidation states has many uses in catalysts. Oxidation of ‚NO‚ CO, benzene and supercapacitor has been found [12-13].

In this research, a simple method for preparing pure mannequin oxide and its doped compounds with gadolinium is introduced and the performance of the manufactured nanomaterials in the removal of methylene blue dye as an example of organic matter has been investigated (Table 1).

Table 1. Features of methyl orange color

Chemical structure	
Color index name	Methylene Blue
Molecular formula	$C_{16}H_{18}N_8SCl$
λ_{max} (nm)	662.5

2. Experimental

Manganese acetate (purity 99%), gadolinium acetate hydrate (purity 99.95%) were purchased from Sigma-Aldrich. Potassium hydroxide were purchased from Merck and used as reaction initiators without any purification. Also, methylene blue dye was purchased from Zhejiang Yide Company.

2.1. Preparation method

In the usual method, we dissolve 4% manganese acetate along with appropriate amounts of hydrated gadolinium acetate and 1 mmol of potassium hydroxide in 40 ml of distilled water and stir for 15 minutes, then it is transferred to a 100 ml teflon reactor container covered with a steel container and for a period of 12 hours at 170 °C in a thermal oven and gradually cooled to room temperature. Then the obtained black product was washed with ethanol and distilled water and dried at room temperature.

2.2. Identification

Detection of crystalline phases was done using a PANalytical X-ray diffractometer using a copper lamp with Å=5406.1Kα. The morphology of the prepared materials was done using a JEOL JSM6700F SEM machine. XPS elemental analysis was done using a device (K-ALPHA, UK) and DRS spectroscopy of samples was obtained with Varian Cary 3.

2.3. Evaluation of photocatalytic performance

The catalytic activity of the synthesized compounds was evaluated against the removal of methyl orange dye as a pollutant. In the usual method, 0.1 g of nanocatalyst was added as a suspension to 100 ml of the intended blue solution with a certain initial concentration, and visible light was emitted by a 40 watt fluorescent lamp. With the help of UV-Vis spectroscopy, the absorbance values of the solution were obtained and the amount of color removal was calculated as a percentage using formula 1.

$$\text{Color removal percentage (\%)} = [1- (C / C0)] \times 100 \qquad (1)$$

To repeat the test, the catalyst was collected and washed several times with distilled water and then dried and used for a new test.

3. Results and Discussion

X-ray powder diffraction in Figure 1 shows that Mn_3O_4 crystals and its compounds doped with gadolinium cation belong to the spinel phase (JCPDS No.18-0803) and no impurity peak can be seen up to 8% concentration of dope in the corresponding pattern [14].

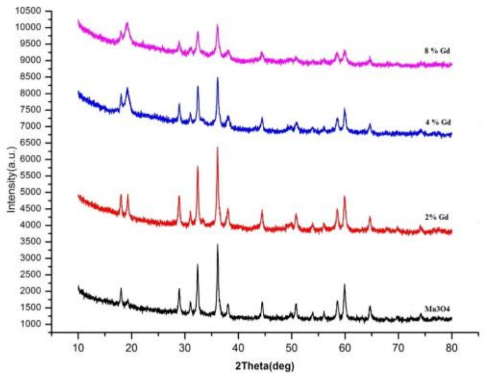


Figure 1. P-XRD pattern of manganese oxide doped with gadolinium cation $Mn_{3-x}GdxO_4$ (x=0 to x=0.08)

Figure 3(a-b) shows the SEM images of nanoparticles synthesized with the chemical formula $Mn_{3-x}Gd_xO_4$ (x=0 to x=0.08). As it can be seen from the pictures, doping Gd ions instead of manganese cations in the crystal lattice does not change the morphology of Mn_3O_4 nanoparticles, and increasing the amount of dopant, the size of the nanoparticles becomes larger. The average diameter of these nanoparticles from the particle distribution diagram (Figure 4) for pure manganese oxide is approximately 10-60 nanometers, and for the example of 8% doped with ytterbium, it is approximately 20-80 nanometers.

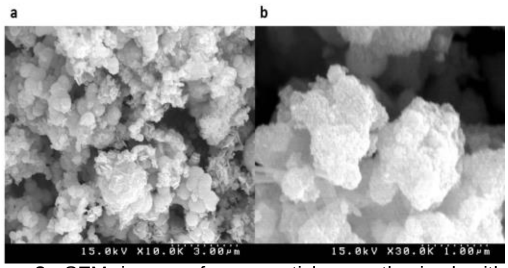


Figure 3. SEM image of nanoparticles synthesized with the chemical formula $Mn_{3-x}Gd_xO_4$ (x=0(a), x=0.08(b))

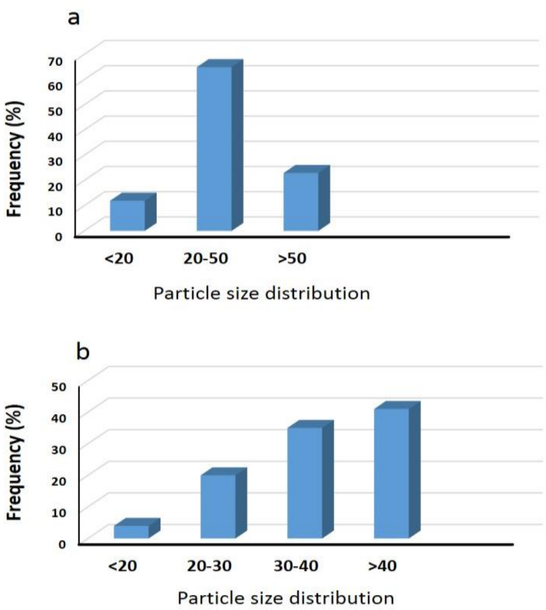


Figure 4. Particle size distribution of pure Mn_3O_4 (a) and 8% Gd-doped Mn_3O_4 (b)

The absorption spectra of the synthesized compounds with the chemical formula $Mn_{3-x}Gd_xO_4$ (x=0 to x=0.08) show a decrease in the energy gap with the increase in the amount of doping, which seems to be unaffected by the change in the size of the nanoparticles [17-19].

To study and compare different processes of sono, photo, and sonophotocatalyst, a series of tests were carried out, which are shown in Figure 5. In case of the photocatalytic process, the color removal rate was 68% under visible light irradiation. This value was recorded as 51% in the sonocatalytic process. In the combined sonophotocatalytic process, the percentage of color removal reached 85%, which is the result of the sample doped with 8% gadolinium. The reason for this can be the production of more reactive oxygen species during the combined sonophotocatalysis process. The results show that with the increase of the dopant factor, the color removal percentage also increases.

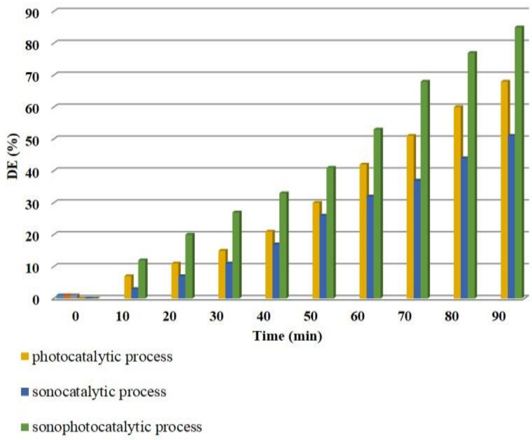


Figure 5. Comparison of different processes in the removal of methylene blue dye considering the following conditions: [Dye] = 20 mg/L, [Catalyst] = 1 g/L.

Through measuring the absorbance of the solution in 10-minute intervals by UV-Vis spectrophotometer, the concentration of methylene blue dye shows a decrease under the sonophotocatalytic process. After 90 minutes, the main peak of the corresponding color was removed and the rank removal percentage was 85% (Figure 6).

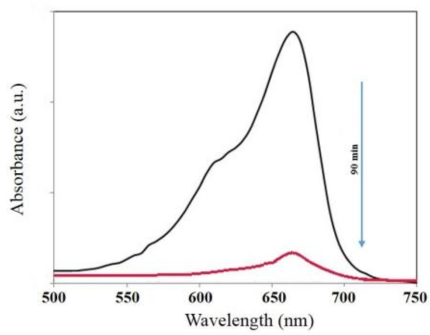


Figure 6. Absorption spectrum of color removal in the presence of manganese oxide doped with gadolinium under sonophotocatalysis process.

The removal percentage of methylene blue color was tested by adding anions such as iodide oxalate and other radical acceptors such as butanol and benzoquinone, the results of which are shown in Figure 7. In the presence of butanol as a hydroxyl radical receptor, the color removal rate shows a decrease of 67%. With the addition of iodide and oxalate ions, this reduction is equal to 29 and 49%. In the presence of the superoxide radical receptor ، benzoquinone, the greatest inhibition of the catalyst performance is observed, which is equal to 15 %.

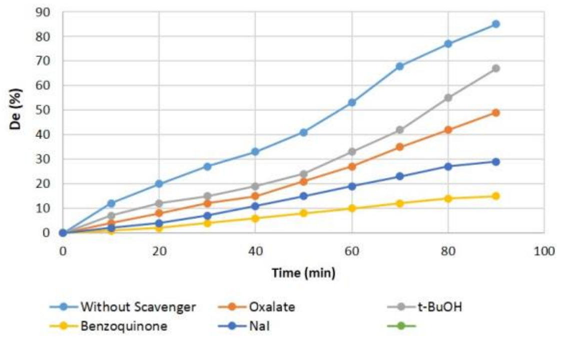


Figure 7. The effects of different inhibitors on the color removal efficiency under the following conditions: [dye] = 20 mg/L, [Catalyst] = 1 g/L, [Scavenger] = 5 mM

Figure 8 shows the stability of the nanocatalyst in reuse in 5 repeated tests, that the performance of the catalyst compared to the first test is accompanied by no degradation of the catalyst and shows a slight decrease.

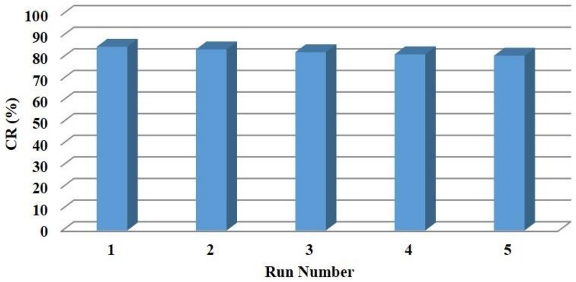


Figure 8- Color removal efficiency after 5 repeated tests

4. Conclusion

Mn_3O_4 nanoparticles and doped compounds were prepared and identified by hydrothermal method with high efficiency and were used to remove methylene blue under photocatalytic processes. The results showed that the activity of the nanocatalyst increases with the increase in the amount of dopant, and the reason for this performance is directly related to the reduction of the band gap in the doped samples. The best performance of the catalyst is related to the 8% doped sample under sonophotocatalyst conditions and with the increase of radical receptors such as anions and benzoquinone. The amount of color removal shows a significant decrease. Based on the results, the above doped compounds can be used as effective catalysts in the removal of organic pollutants.

Conflict of interest

The authors declare no competing interests.

Acknowledgment

This research was funded by Sayyed Jamaleddin Asadabadi University research grant.

References

[1] Nitschke L, Schüssler W. Surface water pollution by herbicides from effluents of waste water treatment plants. Chemosphere. 1998 Jan 1;36(1):35-41. https://doi.org/10.1016/S0045-6535(97)00286-5.

[2]. Roselin LS, Selvin R. Photocatalytic degradation of reactive orange 16 dye in a ZnO coated thin film flow photoreactor. Science of Advanced Materials. 2011 Apr 1;3(2):251-8. https://doi.org/ 10.1166 /sam. 2011.1151

[3] Khataee AR, Aleboyeh H, Aleboyeh A. Crystallite phase-controlled preparation, characterisation and photocatalytic properties of titanium dioxide nanoparticles. Journal of Experimental Nanoscience. 2009 Jun 1;4(2):121-37. https://doi.org/10.1080/17458080902929945

[4] Liu Y, Xi G, Chen S, Zhang X, Zhu Y, Qian Y. New ZnS/organic composite nanoribbons: characterization, thermal stability and photoluminescence. Nanotechnology. 2007 Jun 15;18(28):285605. https://doi.org/10.1088/0957-4484/18/28/285605 .

[5] Khataee A, Khataee A, Fathinia M, Hanifehpour Y, Joo SW. Kinetics and mechanism of enhanced photocatalytic activity under visible light using synthesized Pr x Cd1–x Se nanoparticles. Industrial & Engineering Chemistry Research. 2013 Sep 18;52(37):13357-69. https://doi.org/10.1021/ie402352g

[6] Tachikawa T, Ishigaki T, Li JG, Fujitsuka M, Majima T. Defect-Mediated Photoluminescence Dynamics of Eu3+-Doped TiO2 Nanocrystals Revealed at the Single-Particle or Single-Aggregate Level. Angewandte Chemie International Edition. 2008 Jul 7;47(29):5348-52. https://doi.org/10. 002/anie.200800528

[7] Wang F, Han Y, Lim CS, Lu Y, Wang J, Xu J, Chen H, Zhang C, Hong M, Liu X. Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping. nature. 2010 Feb 25;463(7284):1061-5. https://doi.org/10.1038/nature08777

[8] Sun Y, Chen Y, Tian L, Yu Y, Kong X, Zeng Q, Zhang Y, Zhang H. Morphology-dependent upconversion luminescence of ZnO: Er3+ nanocrystals. Journal of Luminescence. 2008 Jan 1;128(1):15-21. https://doi.org/10.1016/j.jlumin.2007.04.011

[9] Alemi A, Hanifehpour Y, Joo SW, Min BK. Synthesis of novel LnxSb2− xSe3 (Ln: Lu3+, Ho3+, Nd3+) nanomaterials via co-reduction method and investigation of their physical properties. Colloids and Surfaces A: Physicochemical and Engineering

Aspects. 2011 Oct 20;390(1-3):142-8. https://doi.org/10.1016/j.colsurfa.2011.09.018.

[10] Hamnabard N, Hanifehpour Y, Khomami B, Joo SW. Synthesis, characterization and photocatalytic performance of Yb-doped CdTe nanoparticles. Materials Letters. 2015 Apr 15;145:253-7. https://doi.org/10.1016/j.matlet.2015.01.074

[11] Rehman S, Ullah R, Butt A, Gohar ND. Strategies of making TiO2 and ZnO visible light active. Journal of hazardous materials. 2009 Oct 30;170(2-3):560-9. https://doi.org/10. 1016/j.jhazmat. 2009.05.064.

[12] Johns M, Landon P, Alderson T, Hutchings GJ. Decreased methane formation from the hydrogenation of carbon monoxide using zeolite/cobalt–manganese oxide composite catalysts. Chemical Communications. 2001(23):2454-5. https://doi.org/10.1039/B108353H

[13] Einaga H, Futamura S. Catalytic oxidation of benzene with ozone over alumina-supported manganese oxides. Journal of Catalysis. 2004 Oct 25;227(2):304-12. https://doi.org/10. 1016/j.jcat.2004.07.029

[14] Shao C, Guan H, Liu Y, Li X, Yang X. Preparation of Mn2O3 and Mn3O4 nanofibers via an electrospinning technique. Journal of Solid State Chemistry. 2004 Jul 1;177(7):2628-31.https://doi.org/ 10.1016/j.jssc.2004.04.003

[15] Al-Gaashani R, Radiman S, Daud AR, Tabet N, Al-Douri YJ. XPS and optical studies of different morphologies of ZnO nanostructures prepared by microwave methods. Ceramics International. 2013 Apr 1;39(3):2283-92. https://doi.org/10.1016/j.ceramint.2012.08.075

[16] Singh BP, Parchur AK, Ningthoujam RS, Ramakrishna PV, Singh S, Singh P, Rai SB, Maalej R. Enhanced up-conversion and temperature-sensing behaviour of Er 3+ and Yb 3+ co-doped Y 2 Ti 2 O 7 by incorporation of Li+ ions. Physical Chemistry Chemical Physics. 2014;16(41):22665-76. https://doi.org/10.1039/C4CP02949F

[17] Yetim T, Tekin T. Synergistic effect of sonolysis and photocatalysis in the degradation kinetics of effluent solution. Kinetics and Catalysis. 2016 Sep;57:578-85. https://doi.org /10.1134/S0023 158416050190

[18] R Khataee A, Fathinia S, Fathinia M, Hanifehpour Y, W Joo S, Soltani B. Synthesis, characterization and photocatalytic properties of nanostructured Sm-doped CdSe. Current Nanoscience. 2013 Dec 1;9(6):780-6. Without DOI.

[19] Hanifehpour Y, Mirtamizdoust B, Cheney MA, Joo SW. Facile synthesis, characterization and BET study of neodymium-doped spinel Mn 3 O 4 nanomaterial with enhanced photocatalytic activity. Journal of Materials Science: Materials in Electronics. 2017 Aug;28:11654-64. https://doi.org/10.1007/s10854-017-6968-5