

Application of enzyme-like MnO₂ nanoparticles as cathode materials for Li-ion batteries

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Abstract

In this study, the enzyme-like manganese dioxide nanoparticles with high peroxidase-like activity were synthesized and then characterized. The experimental studies proved the high Li-electroactivity of the as-prepared nanoparticles which makes these nanozymes for applying as cathode materials for Li-ion batteries. To determine the redox peaks of Mn⁴⁺/Mn³⁺ against Li anode, the cyclic voltammetry was used, revealed that the enzyme-like manganese dioxide nanoparticles as cathode materials can receive the Li(I) ions and then give it back to the anode. The charge-discharge tests were performed for several successive operational cycles. The results showed that the capacity of enzyme-like manganese dioxide nanoparticles is as high as 164.9 mAhg⁻¹ at 30 mAg⁻¹ while at 1000 mAg⁻¹ the capacity was found to be about 46 mAhg⁻¹.

Keywords: Li-ion battery; MnO₂ nanoparticles; enzyme-like activity; Li-electroactivity; cathode materials

1. Introduction

Most of the identified enzymes are proteins that are commonly introduced as catalysts of chemical reactions in biological environments (i.e., biocatalysts). The key feature of these biocatalysts is their high catalytic efficiency and substrate specificity which make them suitable for playing a specific role in biochemistry. Among different types of enzymes, peroxidase enzymes, especially horseradish peroxidase (HRP), are attractive enzymes from both industrial and clinical points of view. In the real world, the practical application of peroxidase enzyme in industrial reactions as the biocatalyst is an interesting field. Up to now, several researches on these enzymes have been carried out to provide useful information about the enzyme structure, and its functional groups, reaction pathways, and active sites [1-15]. Regarding the peroxidase enzymes, the enzyme-specific substrate is hydrogen peroxide (HP) while their function is catalyzing the oxidation of a hydrogen-donating substrate (for example, benzidine). More precisely, hydrogen peroxide is the initiator of the peroxidase-mediated reactions [16]. Oxidation of a wide range of organic compounds (substrates) including aromatic amines, phenols, and their mixtures can be initiated in the presence of hydrogen peroxide or other hydroperoxides and HRP as enzymes. Many chromogenic substrates have been defined as secondary substrates of horseradish peroxidase due to its low selectivity to electron-donating compounds. These chromogenic substrates are called chromogenic electron donors because these compounds show a distinct color change when oxidized by hydrogen peroxide in the presence of the peroxidase enzyme. It is noteworthy that

peroxidase and other natural enzymes show some of the following serious disadvantages including: (1) They are sensitive to environmental changes such as pH and temperature changes and are easily denatured. (2) They are digested by protease enzymes. (3) Their preparation and purification are complicated and expensive [16-20]. Fixing these disadvantages is possible through the development of some stable artificial enzymes with high catalytic ability. In this regard, nanotechnology has opened the doors for the development of new enzyme-mimetic materials [21]. In fact, the fast development of nanoscience and material chemistry has increased interest in researching new and innovative synthesis methods to produce new nanomaterials with unique high biocompatibility [22], unique optical properties [23-25], and catalytic activity [26, 27]. In 2007, it was explored that Fe₃O₄ magnetic nanoparticles (NPs) exhibited significant peroxidase-like activity [28]. This research opened the door for a new branch of nanochemistry called “nanozyme chemistry”. Nanozyme chemistry is -consists of design, synthesis, modification, biochemical characterization, structural characterization, and application of nanoscale artificial enzymes as well as evaluation of the mechanism of nanozyme-based systems [3-21]. Among different areas of nanozyme chemistry, the main researches of nanozyme chemistry are regarding sensing and detection aims, for instance, during the last years, a wide variety of nanozyme-based colorimetric sensors have been developed for the detection and quantification of a variety of analytes for instance, tryptophan [29], glutathione (GSH) [30], dopamine [31], tetracycline [32], metal cations

[33], glucose [34], H₂O₂ [35], explosives [36], and cysteine [37] as well as after first report of COVID-19 in 2019 [38, 39], the nanozyme-based sensing methods for COVID-19 detection were also reported [40]. Although the nanozyme field is focused on sensing and detection, recently, Mu et al. utilized heme-based nanozymes as redox materials for Li-O₂ batteries [41]. This investigation can open a new door in nanozyme chemistry regarding nanozyme application in the energy storage field. In this contribution, the manganese dioxide nanozymes with high peroxidase-like activity were synthesized via a very simple and fast method and then characterized for their size, morphology, and crystallinity. The experimental studies proved that MnO₂ nanozymes show simultaneous peroxidase-like activity and Li-electroactivity which makes these nanozymes for applying as lithium-ion batteries cathode materials. The nanozymatic studies revealed a high specific enzyme-like activity. The Michaelis–Menten kinetics studies revealed high catalytic efficiency and substrate affinity of the as-synthesized MnO₂ nanozymes. Besides, the Li-electroactivity studies showed the suitability of MnO₂ nanozymes for the potential application as cathode materials for lithium-ion batteries.

2. Experimental

2.1. Synthesis of MnO₂ nanozymes

The MnO₂ nanoparticles or more precisely MnO₂ nanozymes were synthesized using an one-pot simple, operator-friendly, green, and fast method (the synthesis time was only 5 min). To do this, 450 mg of KMnO₄ was introduced into 45 mL water, followed by the

addition of 0.5 mL hydrogen peroxide (30%) and 1.0 mL hydrazinium hydroxide (20%). Afterward, the synthesis mixture was stirred for about 5.0 min to complete the synthesis of the MnO₂ nanozymes. The nanozymes were then collected by centrifuge, washed with water (5 times), and then dried at ambient conditions.

2.2. Li-electroactivity studies and electrochemical evaluations

Regarding the electrochemical evaluation of the as-synthesized MnO₂ nanozymes, onto a copper foil, MnO₂ nanozymes, Kynar 2801 binder, and Super P carbon black with a mass ratio of 60:20:20 were cast to prepare the positive electrode films. The Li-metal foil was used as the negative electrode. The electrolyte was obtained by dissolving LiPF₆ in a mixed solvent (1:1 v/v) of dimethyl carbonate and ethylene carbonate. Thereafter, the assembled Swagelok-type cell was prepared using positive and negative electrodes and an electrolyte-saturated separator film. This cell was used for galvanostatic cyclic voltammetry at a scan rate of 0.3 mV s⁻¹.

2.3. Nanozymatic studies

The nanozymatic activity assay was performed by the following steps: 40.0 μL of hydrogen peroxide and 500.0 μL of DAB (a final concentration= 0.0028 M) was added into 2.0 mL acetate buffer solution with a constant pH of 4.0 and a molar concentration of 0.4 mol L⁻¹ containing 40.0 μL of 1.0 mg mL⁻¹ MnO₂-nanozymes, followed by 30 min incubation at ambient conditions. Afterward, the absorbance of the resulting colored product was recorded against a reagent blank at 460 nm and the activity of the

nanozymes in nM s^{-1} was estimated by using the absorption coefficient of the oxidation product at 460 nm ($\epsilon=5500 \text{ M}^{-1} \text{ cm}^{-1}$). Besides, the kinetics parameters of the nanozymatic reaction were estimated by the Michaelis-Menten model and its linearization via the Lineweaver-Burk method.

3. Results and discussion

3.1. SEM analysis of MnO_2 nanoparticles

The MnO_2 nanoparticles or more precisely MnO_2 nanozymes were synthesized using a one-pot simple, operator-friendly, green, and fast method (the synthesis time was only 5 min) and then identified via characterization by SEM and TEM imaging methods. The SEM image of the as-synthesized nanoparticles presented in Figure 1, revealed a highly homogenous morphology for the as-mentioned nanomaterials. Besides, according to the SEM results it can be concluded that the as-prepared nanozymes are very small in size and uniform in morphology.

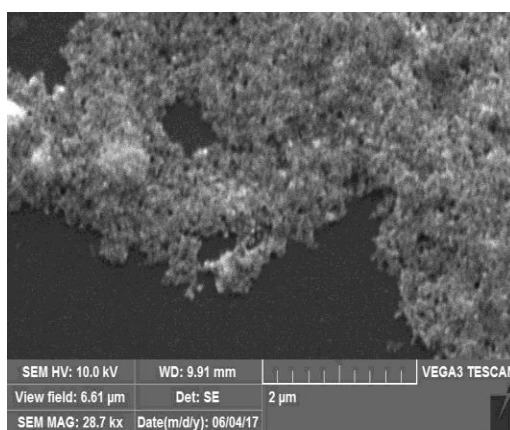


Figure 1. SEM and image of the MnO_2 nanoparticles used as Li-ion cathode materials.

3.2. Investigation of nanozymatic behavior of MnO_2 nanozymes

The enzyme-like behavior of the as-synthesized nanozymes was evaluated by the oxidation of 3,3'-diaminobezedine by hydrogen peroxide in the presence of the peroxidase-like MnO₂ nanoparticles as the biocatalyst as the standard method for nanozyme activity measurements [42-45]. The oxidation process was then probed by recording the UV-Vis spectrum of the colored product (Figure 2), revealing that in the presence of 3,3'-diaminobezedine, the peroxidase-like MnO₂ nanozymes can significantly catalyze the oxidation process of 3,3'-diaminobezedine with hydrogen peroxide to form its corresponding brown-colored indamine polymer which shows a characteristic absorbance at 460 nm. The possible pathway of reaction is represented in Figure 2B, as shown in this figure, during the 3,3'-diaminobezedine oxidation, the peroxidase-like MnO₂ nanozymes interacted with hydrogen peroxide molecules and converted them to active hydroxyl radicals which these active radicals, then, react with 3,3'-diaminobezedine molecules to produce an indamine polymer via an oxidative polymerization process, as previously reported in the literature [46-58].

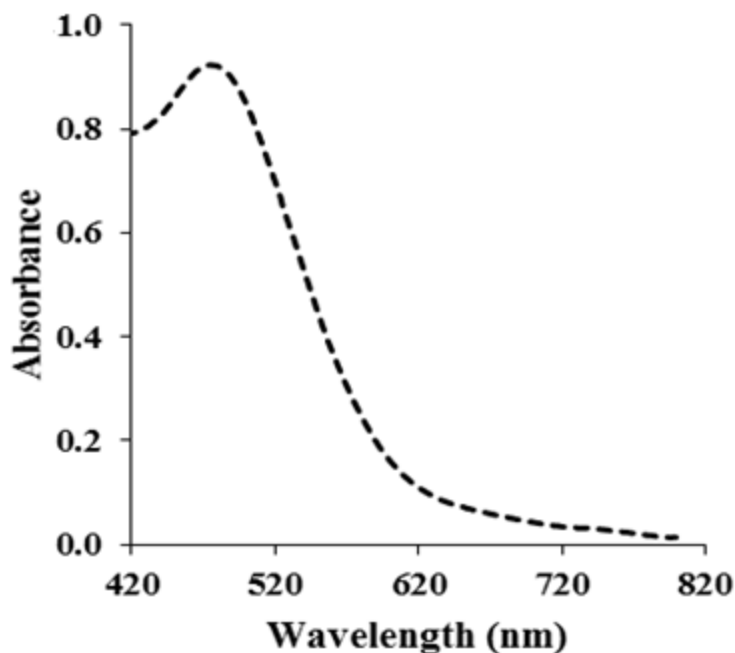


Figure 2. Evaluation of enzyme-like activity of MnO₂ nanozymes via probing the UV-visible of MnO₂ nanozymes-mediated oxidation product of DAB.

3.3. Application of as-prepared enzyme-like MnO₂ nanoparticles as cathode materials for Li-ion batteries

Li-electroactivity measurements for the as-prepared MnO₂ nanozymes were performed by cyclic voltammetry to quantify the oxidation/reduction peaks of Mn⁴⁺→Mn³⁺, against a Li-based anode electrode. In this regard, the cyclic voltammograms of the cathode of Li-ion battery prepared by MnO₂ nanozymes as cathode material were recorded for three successive runs in a potential window of 1.5-4.6 V *vs.* Li electrode at a scan rate of 0.3 mV s⁻¹. The results are shown in Figure 3 where it can be seen that the MnO₂ nanozymes show a reversible redox behavior in the developed system. The oxidation peak was observed at 3.2 V and the reduction peak was found to be positioned at 2.74 V. According to the

results of these experiments, it can be concluded that the electrochemical reactions in the charge/discharge process of the as-prepared nanozymes, when they used as cathode materials for the Li-ion batteries, consisted of lithiation of MnO₂ nanozymes in charging step and de-lithiation of MnO₂ nanozymes in discharging process [59, 60]. The reversible redox behavior of MnO₂ nanozymes in Li-ion batteries pointed out that the MnO₂ nanozymes as cathode materials can receive the Li(I) ions and then give it back to the anode (i.e., lithiation/de-lithiation process can be proceed). Therefore, it is consultable that the MnO₂ nanozymes can respond well to the charge–discharge tests of Li-ion batteries.

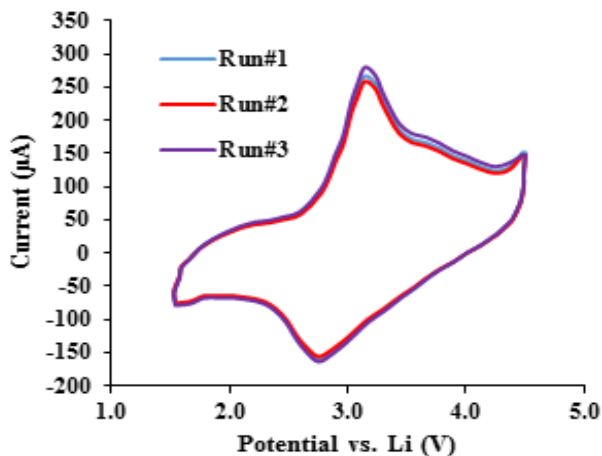


Figure 3. Cyclic voltammograms of the cathode of Li-ion battery prepared by MnO₂ nanozymes as cathode material.

Hence, the charge–discharge tests for the MnO₂ nanozymes cathodes were initially performed at slow charge/discharge rates. Figure 4A shows the 3 cycles of charge-

discharge tests for the as-prepared MnO₂ nanozymes cathodes at 30 mA g⁻¹. As can be seen, the capacity at 30 mA g⁻¹ loss of about 9% at 2 cycles, and then it is stable for the third operational cycle, revealing good stability of the as-prepared MnO₂ nanozymes at slow rates. However, to provide a comprehensive insight into the charge-discharge behavior of the MnO₂ nanozymes cathodes, the charge-discharge tests were carried out at high charge/discharge rates (1000 mA g⁻¹). The charge-discharge performance of the as-prepared MnO₂ nanozymes as cathode of Li-ion batteries at 1000 mA g⁻¹ is shown in Figure 4B, revealing that the capacity of the MnO₂ nanozymes was not changed at high rates and the as-prepared nanozymes show excellent stability at 1000 mA g⁻¹ and can provide stable cycling in both slow and higher rates. It is notable that the charge-discharge tests revealed capacities as high as 164.9 mA h g⁻¹ and 46 mA h g⁻¹ at 30 mA g⁻¹ and 1000 mA g⁻¹, in turn, for the as-prepared MnO₂ nanozymes cathodes. It is observed that the capacity was decreased by increasing the rate which exhibits a diffusion-controlled kinetic process (i.e., controlled by the diffusion of Li⁺), as reported [61]. Besides, as previously reported in the literature, at slow rates, the mechanism of charge storage involves the intercalation which is the proven charge/discharge mechanism of metal oxides. In contrast, at higher rates, ions of lithium (Li(I)) may intercalate not so deep into the MnO₂ nanozymes and provide a surface-closed intercalation at faster charge/discharge rates.

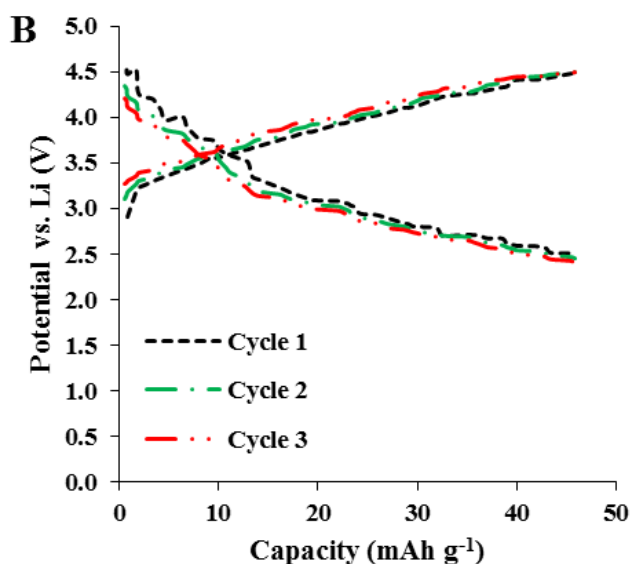
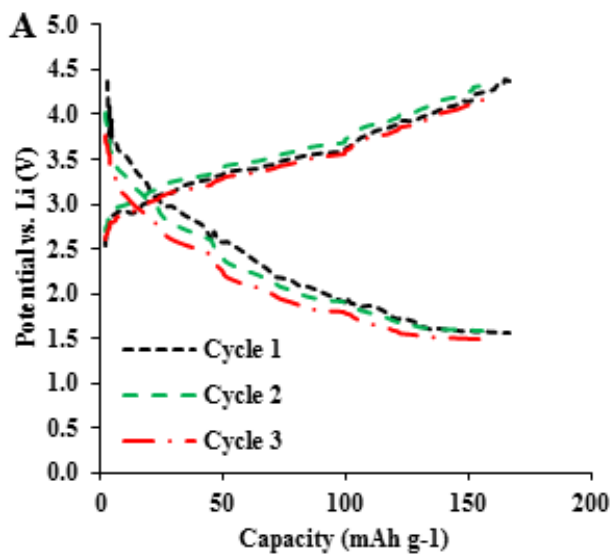


Fig. 4. Charge-discharge performance of as-prepared MnO₂ nanozymes as the cathode of Li-ion batteries at (A) low (30 mA g⁻¹) and (B) high (1000 mA g⁻¹) rates.

4. Conclusions

In this study, the enzyme-like manganese dioxide nanoparticles with high peroxidase-like activity were synthesized and then characterized. The experimental studies proved the high Li-electroactivity of the as-prepared nanoparticles which makes these

nanozymes for applying as cathode materials for Li-ion batteries. To determine the redox peaks of Mn^{4+}/Mn^{3+} against Li anode, the cyclic voltammetry was used, revealed that the enzyme-like manganese dioxide nanoparticles as cathode materials can receive the Li(I) ions and then give it back to the anode. The charge-discharge tests were performed for several successive operational cycles. The results showed that the capacity of enzyme-like manganese dioxide nanoparticles is as high as 164.9 mAhg^{-1} at 30 mAg^{-1} while at 1000 mAg^{-1} the capacity was found to be about 46 mAhg^{-1} .

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Conflict of interest

There is no conflict of interest.

5. References

1. Kraut, J. (1988). How do enzymes work?. *Science*, 242(4878), 533-540.
2. Veitch, N. C. (2004). Horseradish peroxidase: a modern view of a classic enzyme. *Phytochemistry*, 65(3), 249-259.
3. Liang, M., & Yan, X. (2019). Nanozymes: from new concepts, mechanisms, and standards to applications. *Accounts of chemical research*, 52(8), 2190-2200.

4. Wei, H., & Wang, E. (2013). Nanomaterials with enzyme-like characteristics (nanozymes): next-generation artificial enzymes. *Chemical Society Reviews*, 42(14), 6060-6093.
5. Wang, Z., Zhang, R., Yan, X., & Fan, K. (2020). Structure and activity of nanozymes: Inspirations for de novo design of nanozymes. *Materials Today*, 41, 81-119.
6. Zhang, R., Yan, X., & Fan, K. (2021). Nanozymes inspired by natural enzymes. *Accounts of Materials Research*, 2(7), 534-547.
7. Wang, X., Hu, Y., & Wei, H. (2016). Nanozymes in bionanotechnology: from sensing to therapeutics and beyond. *Inorganic Chemistry Frontiers*, 3(1), 41-60.
8. Jiao, L., Yan, H., Wu, Y., Gu, W., Zhu, C., Du, D., & Lin, Y. (2020). When nanozymes meet single-atom catalysis. *Angewandte Chemie*, 132(7), 2585-2596.
9. Liu, B., & Liu, J. (2017). Surface modification of nanozymes. *Nano Research*, 10, 1125-1148.
10. Wang, D., Jana, D., & Zhao, Y. (2020). Metal–organic framework derived nanozymes in biomedicine. *Accounts of chemical research*, 53(7), 1389-1400.
11. Dong, S., Dong, Y., Jia, T., Liu, S., Liu, J., Yang, D., ... & Lin, J. (2020). GSH-depleted nanozymes with hyperthermia-enhanced dual enzyme-mimic activities for tumor nanocatalytic therapy. *Advanced Materials*, 32(42), 2002439.

12. Thakkar, K. N., Mhatre, S. S., & Parikh, R. Y. (2010). Biological synthesis of metallic nanoparticles. *Nanomedicine: nanotechnology, biology and medicine*, 6(2), 257-262.
13. Hajipour, M. J., Fromm, K. M., Ashkarran, A. A., de Aberasturi, D. J., de Larramendi, I. R., Rojo, T., ... & Mahmoudi, M. (2012). Antibacterial properties of nanoparticles. *Trends in biotechnology*, 30(10), 499-511.
14. Hormozi Jangi, S. R. (2023). Synthesis and characterization of magnesium-based metal-organic frameworks and investigating the effect of coordination solvent on their biocompatibility. *Chemical Research and Nanomaterials*, 1(4), 1-9.
15. Hormozi Jangi, S. R. (2023). Biochemical characterization of enzyme-like silver nanoparticles toward nanozyme-catalysed oxidation reactions, *Micromaterials and Interfaces* 1 (1), 2170.
16. Jangi, A. R. H., Jangi, M. R. H., & Jangi, S. R. H. (2020). Detection mechanism and classification of design principles of peroxidase mimic based colorimetric sensors: A brief overview. *Chinese Journal of Chemical Engineering*, 28(6), 1492-1503.
17. Reis, C. L. B., Sousa, E. Y. A. D., Serpa, J. D. F., Oliveira, R. C., & Santos, J. C. S. D. (2019). Design of immobilized enzyme biocatalysts: Drawbacks and opportunities. *Química Nova*, 42, 768-783.

18. Sen, S., Venkata Dasu, V., & Mandal, B. (2007). Developments in directed evolution for improving enzyme functions. *Applied biochemistry and biotechnology*, 143, 212-223.
19. Porstmann, T., & Kiessig, S. T. (1992). Enzyme immunoassay techniques an overview. *Journal of immunological methods*, 150(1-2), 5-21.
20. Hanefeld, U., Gardossi, L., & Magner, E. (2009). Understanding enzyme immobilisation. *Chemical Society Reviews*, 38(2), 453-468.
21. Huang, Y., Ren, J., & Qu, X. (2019). Nanozymes: classification, catalytic mechanisms, activity regulation, and applications. *Chemical reviews*, 119(6), 4357-4412.
22. Hormozi Jangi, S. R. (2023). Synthesis and characterization of magnesium-based metal-organic frameworks and investigating the effect of coordination solvent on their biocompatibility. *Chemical Research and Nanomaterials*, 1(4), 1-9.
23. Dehghani, Z., Akhond, M., Jangi, S. R. H., & Absalan, G. (2024). Highly sensitive enantioselective spectrofluorimetric determination of R-/S-mandelic acid using l-tryptophan-modified amino-functional silica-coated N-doped carbon dots as novel high-throughput chiral nanoprobe. *Talanta*, 266, 124977.
24. Hormozi Jangi, S. R., & Gholamhosseinzadeh, E. (2023). Developing an ultra-reproducible and ultrasensitive label-free nanoassay for L-methionine

quantification in biological samples toward application in homocystinuria diagnosis. *Chemical Papers*, 1-13.

25. Jangi, S. R. H., & Akhond, M. (2021). Ultrasensitive label-free enantioselective quantification of d-/l-leucine enantiomers with a novel detection mechanism using an ultra-small high-quantum yield N-doped CDs prepared by a novel highly fast solvent-free method. *Sensors and Actuators B: Chemical*, 339, 129901.
26. HORMOZI JANGI, S. R., & Akhond, M. (2020). High throughput green reduction of tris (p-nitrophenyl) amine at ambient temperature over homogenous AgNPs as H-transfer catalyst. *Journal of Chemical Sciences*, 132, 1-8.
27. Hormozi Jangi, S. R. (2023). Low-temperature destructive hydrodechlorination of long-chain chlorinated paraffins to diesel and gasoline range hydrocarbons over a novel low-cost reusable ZSM-5@ Al-MCM nanocatalyst: a new approach toward reuse instead of common mineralization. *Chemical Papers*, 1-15.
28. Gao, L., Zhuang, J., Nie, L., Zhang, J., Zhang, Y., Gu, N., ... & Yan, X. (2007). Intrinsic peroxidase-like activity of ferromagnetic nanoparticles. *Nature nanotechnology*, 2(9), 577-583.
29. Xu, S., Zhang, S., Li, Y., & Liu, J. (2023). Facile Synthesis of Iron and Nitrogen Co-Doped Carbon Dot Nanozyme as Highly Efficient Peroxidase Mimics for Visualized Detection of Metabolites. *Molecules*, 28(16), 6064.

30. Jangi, S. R. H., & Akhond, M. (2020). Synthesis and characterization of a novel metal-organic framework called nanosized electroactive quasi-coral-340 (NEQC-340) and its application for constructing a reusable nanozyme-based sensor for selective and sensitive glutathione quantification. *Microchemical Journal*, 158, 105328.
31. Ray, S., Biswas, R., Banerjee, R., & Biswas, P. (2020). A gold nanoparticle-intercalated mesoporous silica-based nanozyme for the selective colorimetric detection of dopamine. *Nanoscale Advances*, 2(2), 734-745.
32. Shen, Y., Wei, Y., Liu, Z., Nie, C., & Ye, Y. (2022). Engineering of 2D artificial nanozyme-based blocking effect-triggered colorimetric sensor for onsite visual assay of residual tetracycline in milk. *Microchimica Acta*, 189(6), 233.
33. Akhond, M., Hormozi Jangi, S. R., Barzegar, S., & Absalan, G. (2020). Introducing a nanozyme-based sensor for selective and sensitive detection of mercury (II) using its inhibiting effect on production of an indamine polymer through a stable n-electron irreversible system. *Chemical Papers*, 74, 1321-1330.
34. Chen, J., Wu, W., Huang, L., Ma, Q., & Dong, S. (2019). Self-indicative gold nanozyme for H₂O₂ and glucose sensing. *Chemistry–A European Journal*, 25(51), 11940-11944.

35. Hormozi Jangi, S. R., & Dehghani, Z. (2023). Spectrophotometric quantification of hydrogen peroxide utilizing silver nanozyme. *Chemical Research and Nanomaterials*, 2(1), 15-23.
36. Hormozi Jangi, S. R., Akhond, M., & Absalan, G. (2020). A field-applicable colorimetric assay for notorious explosive triacetone triperoxide through nanozyme-catalyzed irreversible oxidation of 3, 3'-diaminobenzidine. *Microchimica Acta*, 187, 1-10.
37. Singh, M., Weerathunge, P., Liyanage, P. D., Mayes, E., Ramanathan, R., & Bansal, V. (2017). Competitive inhibition of the enzyme-mimic activity of Gd-based nanorods toward highly specific colorimetric sensing of l-cysteine. *Langmuir*, 33(38), 10006-10015.
38. Hormozi Jangi, S. R. (2023). A Brief Overview on Clinical and Epidemiological Features, Mechanism of Action, and Diagnosis of Novel Global Pandemic Infectious Disease, Covid-19, And its Comparison with Sars, Mers, And H1n1. *World J Clin Med Img*, 2(1), 45-52.
39. Jangi, S. R. H. (2023). Natural Polyphenols of Pomegranate and Black Tea Juices can Combat COVID-19 through their SARS-CoV-2 3C-like Protease-inhibitory Activity. *Qeios*.

40. Hormozi Jangi, S. R. (2023). A Brief Overview of Nanozyme-Based Colorimetric and Fluorometric Sensors for Early Diagnosis of COVID-19. *Trans Med OA*, 1(2), 76-84.
41. Mu, X., Liu, Y., Zhang, X., Wei, H., He, P., & Zhou, H. (2020). Using a Heme-Based Nanozyme as Bifunctional Redox Mediator for Li- O₂ Batteries. *Batteries & Supercaps*, 3(4), 336-340.
42. Hormozi Jangi, S. R. (2023). Time course evaluation of nanozyme-mediated reversible/irreversible oxidation reactions over silver nanoparticles as peroxidase alternatives, *Modern Chemistry & Applications*, 11 (4) 426.
43. Hormozi Jangi, S. R. (2023). Detection mechanism and principles of the multinanozyme systems as the new generation of nanozyme-mediated sensing assays: A critical review. *Petro Chem Indus Intern*, 6(5), 349-357.
44. Hormozi Jangi, S. R. (2023). An Experimental study on the kinetics characteristics and biochemical behaviour of peroxidase mimic core@shell silicone dioxide@gold nanocomposite. *Nano Tech Nano Sci Ind J*, 17(3).
45. Hormozi Jangi, S. R. (2023). Experimental Evaluation of Kinetic Characteristics of SiO₂@ AuNPs Nanocomposite and BSA-stabilized gold Nanoparticles toward Peroxidase-Mediated Reactions. *Adv Nanoscience Nanotec*, 7(1), 01-11.

46. Jangi, S. R. H., Akhond, M., & Absalan, G. (2020). A novel selective and sensitive multinanozyme colorimetric method for glutathione detection by using an indamine polymer. *Analytica Chimica Acta*, 1127, 1-8.
47. Jangi, S. R. H., Davoudli, H. K., Delshad, Y., Jangi, M. R. H., & Jangi, A. R. H. (2020). A novel and reusable multinanozyme system for sensitive and selective quantification of hydrogen peroxide and highly efficient degradation of organic dye. *Surfaces and Interfaces*, 21, 100771.
48. Jangi, S. R. H. (2023). Experimental evaluation of kinetics and biochemical characteristics of MnO₂ nanoparticles as high throughput peroxidase-mimetic nanomaterials. *Micromaterials and Interfaces*, 1(1).
49. Hormozi Jangi, S. R. (2023). Evaluation of Biochemical Behavior and Stability of Gold Nanoparticles with High Intrinsic Peroxidase-Like Activity. *Petro Chem Indus Intern*, 6(4), 234-239.
50. Jangi, S. R. H. (2023). Introducing a High Throughput Nanozymatic Method for Eco-Friendly Nanozyme-Mediated Degradation of Methylene Blue in Real Water Media. *Sustainable Chemical Engineering*, 90-99.
51. Cornish-Bowden, A. (2015). One hundred years of Michaelis–Menten kinetics. *Perspectives in Science*, 4, 3-9.

52. Dowd, J. E., & Riggs, D. S. (1965). A comparison of estimates of Michaelis-Menten kinetic constants from various linear transformations. *Journal of biological Chemistry*, 240(2), 863-869.
53. Chou, T. C., & Talalay, P. (1977). A simple generalized equation for the analysis of multiple inhibitions of Michaelis-Menten kinetic systems. *Journal of Biological Chemistry*, 252(18), 6438-6442.
54. Jangi, S. R. H., Akhond, M., & Dehghani, Z. (2020). High throughput covalent immobilization process for improvement of shelf-life, operational cycles, relative activity in organic media and enzymatic kinetics of urease and its application for urea removal from water samples. *Process Biochemistry*, 90, 102-112.
55. Jangi, S. R. H., & Akhond, M. (2022). Introducing a covalent thiol-based protected immobilized acetylcholinesterase with enhanced enzymatic performances for biosynthesis of esters. *Process Biochemistry*, 120, 138-155.
56. Jangi, S. R. H., & Akhond, M. (2021). High throughput urease immobilization onto a new metal-organic framework called nanosized electroactive quasi-coral-340 (NEQC-340) for water treatment and safe blood cleaning. *Process Biochemistry*, 105, 79-90.
57. Hormozi Jangi, S. R. (2023). A Comparative Study on Kinetics Performances of BSA-gold Nanozymes for Nanozyme-mediated Oxidation of 3,3',5,5'-

Tetramethylbenzidine and 3,3'-Diaminobenzidine. *Biochemistry & Molecular Biology Journal* 9(3), 21.

58. Hormozi Jangi, S. R., & Dehghani, Z. (2023). Kinetics and biochemical characterization of silver nanozymes and investigating impact of storage conditions on their activity and shelf-life. *Chemical Research and Nanomaterials*, 1(4), 25-33.
59. Tan, H., & Wang, S. (2014). Kinetic behavior of manganese dioxide in Li/MnO₂ primary batteries investigated using electrochemical impedance spectroscopy under nonequilibrium state. *Journal of the Electrochemical Society*, 161(12), A1927.
60. Brock, S. L., Duan, N., Tian, Z. R., Giraldo, O., Zhou, H., & Suib, S. L. (1998). A review of porous manganese oxide materials. *Chemistry of Materials*, 10(10), 2619-2628.
61. Chen, Q., Heng, B., Wang, H., Sun, D., Wang, B., Sun, M., ... & Tang, Y. (2015). Controlled facile synthesis of hierarchical CuO@ MnO₂ core-shell nanosheet arrays for high-performance lithium-ion battery. *Journal of Alloys and Compounds*, 641, 80-86.