Annals of R.S.C.B., ISSN:1583-6258, Vol. 25, Issue 5, 2021, Pages. 2962 – 2969
Received 15 April 2021; Accepted 05 May 2021.

Preparation, Characterization and Surface Area Properties of Manganese Oxide Nanoparticles

Rasha S. Sahib and Juman A. Naser*
Department of Chemistry, College of Education for Pure Science- Ibn Al-Haitham, University of Baghdad, Baghdad (Iraq)
juman.a.n@ihcoedu.uobaghdad.edu.iq

ABSTRACT

The precipitation method was used to prepare manganese oxide nanoparticles (MnO_2NPs) successfully. Infrared spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), X-ray dispersion spectroscopy and (EDS) X-ray Diffraction (XRD) were used to characterize the microstructure, morphology and particle size of particles that produced by this method. The N_2 adsorption-desorption isotherms, pore structure and specific surface area of MnONPs were measured by using Langmuir, Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) academic models. The results show that the sample has a tetragonal crystal structure with an average particle size of about 35 nm as determined by SEM and verified by XRD. So, the specific surface area is 57.449 m^2g^{-1}, pore volumes are 0.2454 cm^3g^{-1} and average pore diameter is 6.95 nm.

Keywords; Manganese Oxide;Nanoparticles; Precipitation method; Specific surface, Pore volume; Pore diameter.

Introduction

Nanomaterials, described as materials with a length scale of less than 100 nanometer, are gaining popularity due to their fundamental science significance as well as the possible applications derived from their fascinating magnetic, electrical and catalytic properties [1-3].

Manganese oxide nanoparticles can be prepare using both top-down and bottom-up methods. The top-down method is not commonly used due to high preparation costs and structural defects on manufactured nanoparticles [4]. Most researchers favor the bottom-up method because particles of uniform size and morphology can be collected [5]. Sol gel [6], Hydrothermal [7], thermal reflux [8], redox [9], chemical precipitation [10] and green synthesis [11] are examples of wet chemical methods used to produce manganese oxide nanoparticles.Despite the fact that these techniques are commonly used, none of them are are perfect.

Manganese oxide, such as MnO, MnO_2 and Mn_3O_4 have been used in sensors, catalysis, rechargeable batteries, supercapacitors and wastewater treatment [12]. For their high theoretical capacity, environmental friendliness, low cost and unique properties, MnO and MnO_2 nanomaterials have piqued interest as anode materials in lithium-ion batteries [13]. Thus, manganese oxide nanoparticles are one of the most appealing inorganic materials because of their physical and chemical properties, as well as their wide range of applications in molecular adsorption [14], ion exchange [15], catalysis [16], energy storage [17] and biosensors [18].

In this work, MnO_2 nanoparticles were prepared and characterized using a variety of techniques, including Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray dispersion spectroscopy (EDS), X-ray diffraction (XRD). Additionally, Langmuir, Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Holland (BJH) models have been applied to detrmine thespecific surface area and pore structure of prepared nanoparticles by N_2 adsorption-desorption technique.

Annals of R.S.C.B., ISSN:1583-6258, Vol. 25, Issue 5, 2021, Pages. 2962 – 2969
Received 15 April 2021; Accepted 05 May 2021.

Experimental

Chemicals

The chemical materials that usesd; manganese sulfate $MnSO_4.H_2O$ and sodium hydroxide NaOH were purchased from Sigma-Aldrich.

Instruments

Electronic balance Sartorius (CPA 22), Hotplate magnetic stirrerLabTech (LMS-1003), FT-IR spectrophotometerShimadzu (IRAffinity 1800), Scanning electron microscope TESCAN (S8000), X-ray diffraction spectrophotometerShimadzu (XRD-6000) and Surface area analyzer BELSORP MINI II (ISO9277).

Preparing of MnO_2NPs

The precipitation method was used to prepare manganese oxide nanoparticles (MnO_2NPs). An aqueous solution of manganese sulfate $MnSO_4.H_2O$ 0.02M (500 mL) was heated to 70 ºC, then anaqueous solution of sodium hydroxide NaOH 0.08M (500 mL) was added drop by drop with keeping the temperature constant. The mixture was stirred continuously until it reached room temperature, after that it was collected and washed several times with distilled water. Finally, the resulted product was calcinated in the furnace for 3 h and at 500 ºC.

Results and discussion

FT-IRspectroscopy

Fourier-transform infrared spectroscopy (FT-IR) is one of the most relevant and commonly used analytical methods for determining the existence of unique functional groups in nanomaterials [19]. Figure 1 confirms the prepration of MnO_2NPs, it is observed that there are several distinct peaks at 597 cm^{-1}, 524 cm^{-1}, 493 cm^{-1} and 960 cm^{-1} attributed to Mn-O vibrations [20]. Moreover, the absence of any peak in the region (4000-3000) cm^{-1} indicates that the nanoparticles are free of any trace of water molecules, which may be due to solvent residues or air moisture.

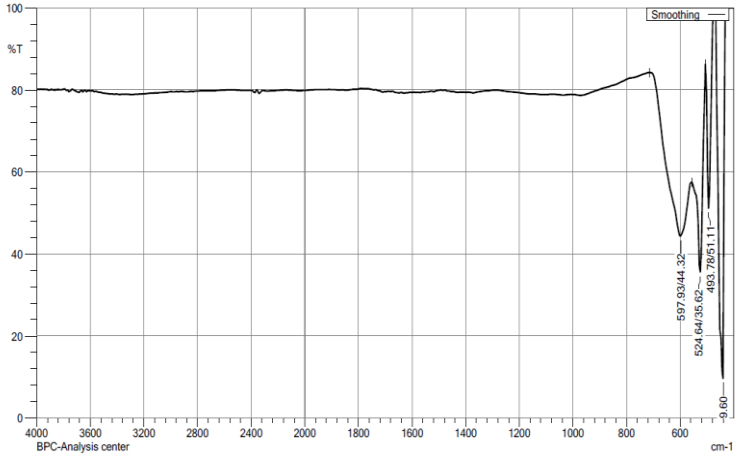

Figure 1: FT-IR spectra of prepared MnO_2NPs.

Annals of R.S.C.B., ISSN:1583-6258, Vol. 25, Issue 5, 2021, Pages. 2962 – 2969
Received 15 April 2021; Accepted 05 May 2021.

SEM microscopy

Figure 2 shows microscopic photographs of MnO_2NPs taken with a scanning electron microscope, which allowed for a better understanding of particles morphology and size.It was discovered that it had tetragonal crystalline shape and a strong attractive force. Furthermore, nanoparticle diameters ranged from (30–40) nm. The microstructure photographs are indicated nanoflowers structure of prepared nanoparticles [21], which reflects their owned a large specific surface area.

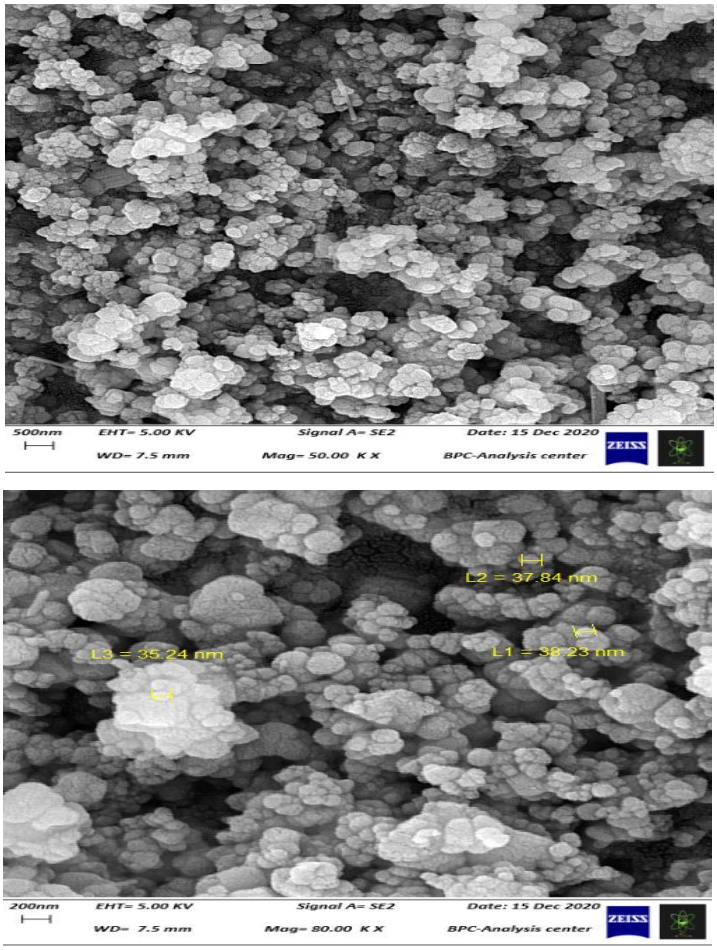

Figure 2: SEM photographs of prepared MnO_2NPs.

EDS spectroscopy

X-ray dispersive spectroscopy verified the presence of manganese in prepared MnO_2NPs (EDS), Figure 3. The percentage of elemental composition of MnO_2NPs were 38.00% Mn and 62.00% O. The maximum intensity of the nanoparticles for Mn with high purity was 2.2keV, 5.9keV and 6.2keV, confirming the reduction of manganese ion to zero valences. Other researchers have recorded a maximum intensity peak of 6.0 keV for Mn [22].

Annals of R.S.C.B., ISSN:1583-6258, Vol. 25, Issue 5, 2021, Pages. 2962 – 2969
Received 15 April 2021; Accepted 05 May 2021.

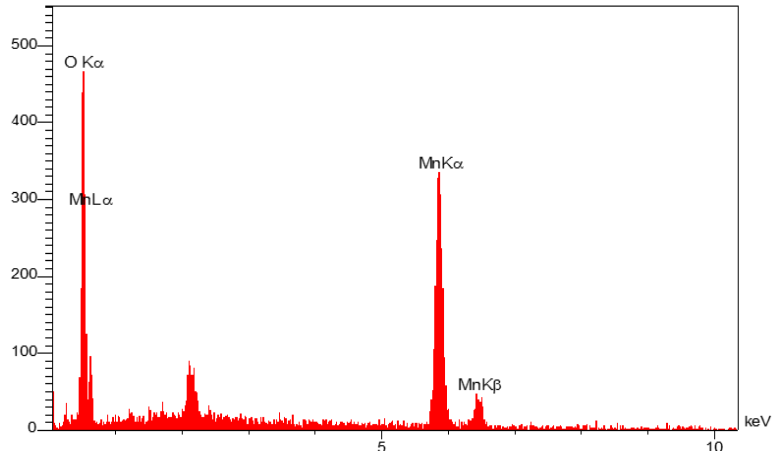

Figure 3: EDS spectrum of prepared MnO_2NPs.

XRDspectroscopy

X-ray diffraction spectroscopy technique was used to analyze the crystalline structure of the prepared MnO_2NPs, Figure 4. The diffraction peaks at 2θ of prepared nanoparticles were 12.94°, 18.34°, 28.78°, 37.66°, 42.14°, 49.90°, 56.44°, 60.26°, 69.74°, 71.34° and 73.72° which correspond to crystal planes of (110), (200), (310), (211), (301), (411), (600), (521), (541), (222) and (730), respectively. That suggests the tetragonal crystalline structural of MnO_2 nanoparticles were successfully prepared, which agrees well with JCPDS card number (44-0141) [23]. Using Deby Scherrer's equation, the average crystallite size of the particles was 32 nm [24].

$$L = \frac{0.94\,\lambda}{\beta \cos\theta} \quad \ldots\ldots\ldots\ldots (1)$$

where D is the particle size in nanometer, λ is the used x-ray wavelength in nanometer, β is the full widith at half maximum beam (FWHM) and is the Bragg angle.

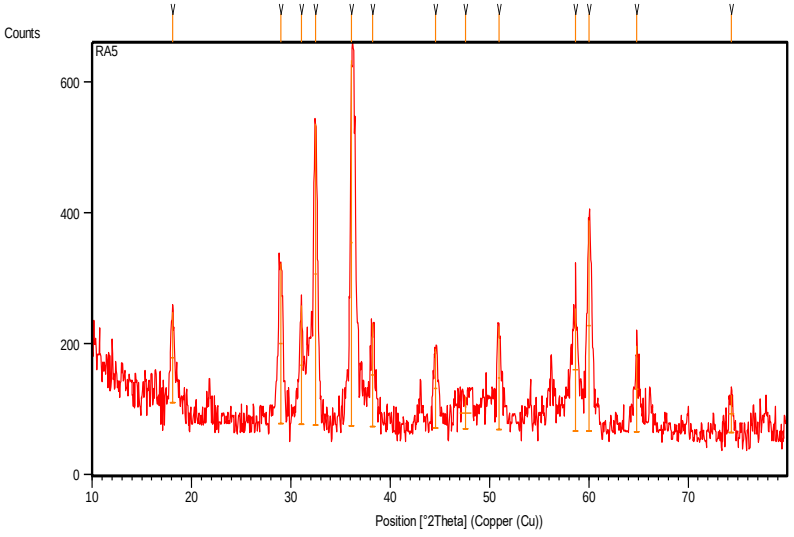

Figure 4: XRD spectrum of the prepared MnO_2NPs.

Annals of R.S.C.B., ISSN:1583-6258, Vol. 25, Issue 5, 2021, Pages. 2962 – 2969
Received 15 April 2021; Accepted 05 May 2021.

Surface area properties

One of the major factors influencing adsorption is the surface area and porous surface of the adsorbed. To determine the surface area and pore size of the prepared MnO_2NPs, the nitrogen gas absorption-desorption technique was used. Thus, Langmuir isotherm, Brunner-Emmett-Teller (BET) and Barrett-Joyner-Holland (BJH) academic models were applied.

The adsorption-desorption of Langmuir isotherm of the N_2 gas molecules on MnO_2NPs surface was shown in Figure 5. It's worth noting that as the pressure applied at all points rises, so does the adsorption of gas molecules. As a result, the adsorption isotherm is type II, referring to multi-layer adsorption [25]. Also, as the applied pressure is reduced, the volume of gas desorbed decreases at all of the pressure points studied.

Figure 6 shows Brunner-Emmett-Teller (BET) diagram for nitrogen adsorption on the surface of prepared MnO_2NPs, illustrating that the number of nitrogen gas molecules increases as the applied pressure increases, peaking at 0.45 at 0.045 P/P°. This means that MnO_2NPs will adsorb nitrogen gas molecules at any of the pressures examined.

Barrett-Joyner-Holland (BJH) diagram for adsorption of nitrogen gas molecules on the prepared MnO_2NPs surface is shown in Figure 7. The average pore size is 6.95 nm, with pore volumes of 0.2454 cm^3g^{-1} and nanoparticle surface areas of 57.449 m^2g^{-1}. In the explanations between BET and BJH diagram of the studied MnO_2NPs surface is not attributable to BJH model's incompatibility with the micro pores in general [26].

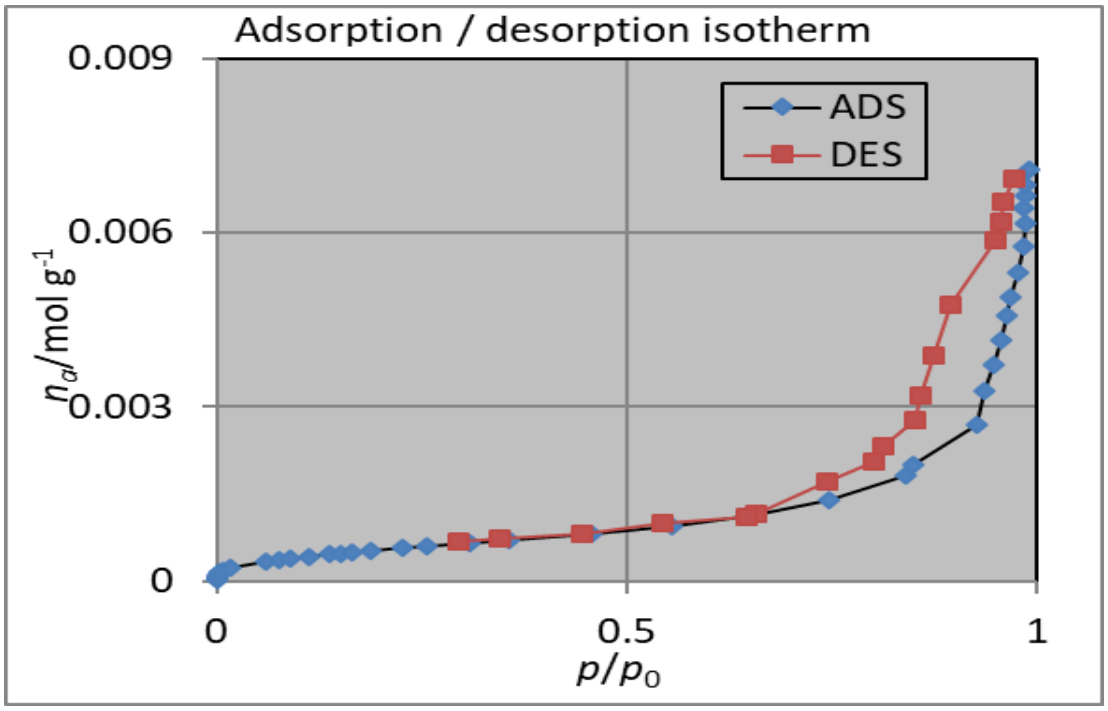

Figure 5: Langmuir diagram of adsorption- desorption of prepared MnO_2NPs.

Annals of R.S.C.B., ISSN:1583-6258, Vol. 25, Issue 5, 2021, Pages. 2962 – 2969
Received 15 April 2021; Accepted 05 May 2021.

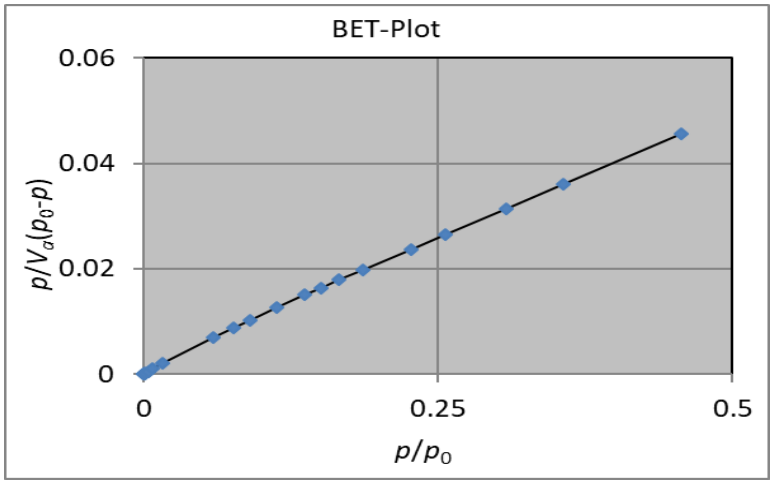

Figure 6: BET diagram of adsorption of prepared MnO_2NPs.

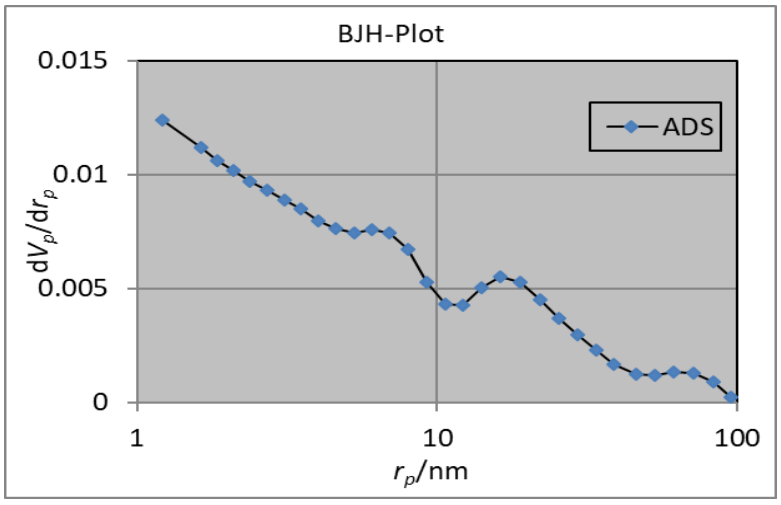

Figure 7: BJH diagram of adsorptionof prepared MnO_2NPs.

Conclusion

Manganese nanoparticles MnO_2NPs were successfully prepared by confined preciptation methodand characterized utilizing Fourier-transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), X-ray dispersion spectroscopy (EDS) and X-ray diffraction spectroscopy (XRD). This method resulted nanoparticles owned a uniform particle size and higher purity.The nanoparticles had a tetragonal crystalline with nanoflowers structure, and the particle size distribution ranges from 30 to 40 nm, according to the average equivalent particle size determined by SEM and verified by XRD and BET data. According to the BET adsorption equation, the sample's specific surface area is 57.449 m^2g^{-1}. The cumulative pore volumes are 0.2454 cm^3g^{-1} and average pore diameter is 6.95 nm, according to the BJH model.

References

1. Abu-Dief, A. M., & Abdel-Fatah, S. M. (2018). Development and functionalization of magnetic nanoparticles as powerful and green catalysts for organic synthesis. Beni-Suef

University Journal of Basic and Applied Sciences, 7(1), 55-67.
2. Astruc, D. (2020). Introduction: nanoparticles in catalysis. Chemical reviews, 120(2), 461-463.
3. Naser, J. A., Ahmed, Z. W., & Fendi, W. J. (2021). Microstructure and Dielectric Properties of Polyaniline Doped with Copper Nanoparticles. Egyptian Journal of Chemistry, 64(1), 487-494.
4. Khan, I., Saeed, K., & Khan, I. (2019). Nanoparticles: Properties, applications and toxicities. Arabian journal of chemistry, 12(7), 908-931.
5. Liu, R., Wu, D., Feng, X., & Müllen, K. (2011). Bottom-up fabrication of photoluminescent graphene quantum dots with uniform morphology. Journal of the American Chemical Society, 133(39), 15221-15223.
6. Nikam, A. V., Prasad, B. L. V., & Kulkarni, A. A. (2018). Wet chemical synthesis of metal oxide nanoparticles: a review. CrystEngComm, 20(35), 5091-5107.
7. Haoran, Y., Lifang, D., Tao, L., & Yong, C. (2014). Hydrothermal synthesis of nanostructured manganese oxide as cathodic catalyst in a microbial fuel cell fed with leachate. The Scientific World Journal, 2014.;
8. Shaker, K. S., & AbdAlsalm, A. H. (2018). Synthesis and characterization nano structure of MnO2 via chemical method. Engineering and Technology Journal, 36(9 Part A).
9. Dawadi, S., Gupta, A., Khatri, M., Budhathoki, B., Lamichhane, G., & Parajuli, N. (2020). Manganese dioxide nanoparticles: synthesis, application and challenges. Bulletin of Materials Science, 43(1), 1-10.
10. Kumar, H., Manisha, S. P., & Sangwan, P. (2013). Synthesis and characterization of MnO2 nanoparticles using co-precipitation technique. Int J Chem Chem Eng, 3(3), 155-160.
11. Hoseinpour, V., & Ghaemi, N. (2018). Green synthesis of manganese nanoparticles: Applications and future perspective–A review. Journal of Photochemistry and Photobiology B: Biology, 189, 234-243.
12. Ociński, D., Jacukowicz-Sobala, I., Mazur, P., Raczyk, J., & Kociołek-Balawejder, E. (2016). Water treatment residuals containing iron and manganese oxides for arsenic removal from water–characterization of physicochemical properties and adsorption studies. Chemical Engineering Journal, 294, 210-221.
13. Liu, X., Chen, C., Zhao, Y., & Jia, B. (2013). A review on the synthesis of manganese oxide nanomaterials and their applications on lithium-ion batteries. Journal of Nanomaterials, 2013.
14. Victor, R. P., Fontes, L. L., Neves, A. A., de Queiroz, M. E., Oliveira, A. F. D., & Miranda, L. D. (2019). Removal of Orange G Dye by Manganese Oxide Nanostructures. Journal of the Brazilian Chemical Society, 30(8), 1769-1778.
15. Wilk, Ł. J., Ciechanowska, A., & Kociołek-Balawejder, E. (2020). Adsorptive-Oxidative Removal of Sulfides from Water by MnO2-Loaded Carboxylic Cation Exchangers. Materials, 13(22), 5124.
16. Dey, S., & Kumar, V. P. (2020). The performance of highly active manganese oxide catalysts for ambient conditions carbon monoxide oxidation. Current Research in Green and Sustainable Chemistry, 100012.

17. Rajab, W. F., Asad, J. S., Shaat, S. K., Musleh, H. S., Shurrab, N. K., Issa, A. A., ... & Al Dahoudi, N. M. (2019, March). Synthesis and Characterization of Manganese oxides Nanoparticles for Supercapacitor-Based Energy-Storage Device. In 2019 IEEE 7th Palestinian International Conference on Electrical and Computer Engineering (PICECE) (pp. 1-6). IEEE.
18. Chen, J., Meng, H., Tian, Y., Yang, R., Du, D., Li, Z., ... & Lin, Y. (2019). Recent advances in functionalized MnO 2 nanosheets for biosensing and biomedicine applications. Nanoscale horizons, 4(2), 321-338.
19. Fouad, H., Hongjie, L., Hosni, D., Wei, J., Abbas, G., Ga'al, H., & Jianchu, M. (2018). Controlling Aedes albopictus and Culex pipiens pallens using silver nanoparticles synthesized from aqueous extract of Cassia fistula fruit pulp and its mode of action. Artificial cells, nanomedicine, and biotechnology, 46(3), 558-567.
20. Cherian, E., Rajan, A., & Baskar, G. (2016). Synthesis of manganese dioxide nanoparticles using co-precipitation method and its antimicrobial activity. International Journal of Modern Science and Technology, 1(01), 17-22.
21. Wan, X., Yang, S., Cai, Z., He, Q., Ye, Y., Xia, Y., ... & Liu, J. (2019). Facile synthesis of MnO2 nanoflowers/N-doped reduced graphene oxide composite and its application for simultaneous determination of dopamine and uric acid. Nanomaterials, 9(6), 847.
22. Wypij, M., Czarnecka, J., Świecimska, M., Dahm, H., Rai, M., & Golinska, P. (2018). Synthesis, characterization and evaluation of antimicrobial and cytotoxic activities of biogenic silver nanoparticles synthesized from Streptomyces xinghaiensis OF1 strain. World Journal of Microbiology and Biotechnology, 34(2), 1-13.
23. He, Q., Liu, J., Liu, X., Li, G., Chen, D., Deng, P., & Liang, J. (2019). A promising sensing platform toward dopamine using MnO2 nanowires/electro-reduced graphene oxide composites. Electrochimica Acta, 296, 683-692.
24. Bokuniaeva, A. O., & Vorokh, A. S. (2019, December). Estimation of particle size using the Debye equation and the Scherrer formula for polyphasic TiO2 powder. In Journal of Physics: Conference Series (Vol. 1410, No. 1, p. 012057). IOP Publishing.
25. Jadoo, S. A., & Naser, J. A. (2020, November). Adsorption Optimization of Congo Red Dye onto Electrospun Nanofibers of Polyacrylonitrile functionalized with Fe3O4 Nanoparticles. In IOP Conference Series: Materials Science and Engineering (Vol. 928, No. 5, p. 052024). IOP Publishing.
26. Jadoo, S. A., & Naser, J. A. (2019). Adsorption Thermodynamic Study of Congo Red Dye on Electrospun Nanofibers Mat of Polyacrylonitrile. Journal of Global Pharma Technology, 11(7), 401-411.