The Effect of Temperature on Structural and optical properties of Manganese Oxide Nanoparticles

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Abstract. Manganese Oxide nanoparticles from different phase have been prepared by simple chemical method with different temperature. The cubic MnO nanoparticles synthesis from 600°C and transformation to tetragonal MnO2 nanoparticles and transformation at 800°C to cubic Mn2O3 nanoparticles. X-ray diffraction and FTIR and UV-Visible have been investigated and crystallite size was calculated using Debye-Scherers equation and it is found to be around (23.4-25.66)nm

Introduction
Manganese Oxide with different crystal morphologies are attention because of have a high specific surface area and a high fraction of surface atoms and non-toxic, the physical and chemical characterization and wide applications have been studied including in catalytic [1], antibacterial [2], water treatment [3], malachite green dye [4], electrochemical capacitors [5]. Today, different technique consist of sol-gel method, wet chemical method, template-assisted method and hydrothermal method have been developed to fabrication MnO nanoparticles [6]. Manganese oxide nanoparticles are a transition and have many oxidation numbers (+2, +3, +4) and can give different structural such as MnO, MnO2, Mn2O3 and Mn3O4 nanostructures. Therefore, manganese oxide has attracted many research efforts [7], [8]. MnO nanoparticle is the one of the very attention metal oxide result to its unique characterization. They have a low band gap and high optical constant [9]. Co-chemical method progress making like, simple, easy control of the size and composition can be made in this method and, there are different condition to convert the particle surface state and total identity. The simple chemical method of different salt (Manganese nitrates, Manganese sulphates, Manganese chlorides) with a good control of pH by using NaOH solutions result to corresponding spinel oxide nanoparticles [10]. This work presents the fabrication of MnO nanoparticles using the simple chemical method. The sample was characterized by XRD. The energy gap was calculated via UV-spectroscopy. The functional groups of the samples were detected by FTIR.

Experimental Part
Manganese oxide (MnO, MnO2 and Mn2O3) nanoparticles were prepared by chemical method at 0.2M MnSO4, H2O and 4M of sodium hydroxide NaOH and Urea CO(NH2)2 both of them dissolved in 50ml double distilled water and mixed under magnetic stirring for 20min. The precipitate was
washing and calcinations at 600, 700, and 800°C for 4hr. X-ray Pattern (XRD-Philips) using (cukα) radiation (λ= 1.5406A), a complete 2Ө scan was made between 20° to 70°. From XRD data the average grain size of particles was calculated by Scherrer equation. The optical absorption of the colloidal MnO nanostructures was measured using spectrophotometer (CARY, 100 CONC plus, UV-Vis-NIR, Splitbeam Optics, Dual detectors) in the range of (200-900) nm.

Results and Discussion

Fig.1. Shows the digital photograph freshly of Manganese oxide powder and colloidal nanoparticles NPs prepared by quick chemical precipitation method at different temperature. The first temperature at 600°C prepared MnO nanoparticles have black color in Fig. 1(a) and second temperature at 700°C transformation of phase from MnO to MnO₂ nanoparticles have dark green color in Fig. 1(b) and third temperature at 800°C transformation of phase from MnO₂ to Mn₂O₃ Nanoparticles have dark red color in Fig. 1(c). The relationships between the energies of the different confinement states are treated by energy absorption. If photons of a special wavelength are absorbed by Nanopowder, then when we observe light reflected from or transmitted through that Nanopowder. MnO Nano crystals are optical attractive way to show quantum effects in physical [11].

Figure 1. Image of Manganese Oxide Nanoparticles and colloidal( a) MnO Nanoparticles, (b) MnO₂ Nanoparticles, and (c) Mn₂O₃ nanoparticles
The XRD pattern spectrum for MnO, MnO2, and Mn2O3 prepared by different temperature at 600°C, 700°C, and 800°C respectively are shown in Fig. 2. In the XRD spectrum in Fig. 2(a), the strong peak of MnO nanoparticles along the 34.702° correspond to the planes (111) having cubic structure with lattice parameter $a= 4.46\text{Å}$ which is well agree with JCPDS Card number (07–0230). In the Fig. 2(b), the structural transformation was observed from cubic MnO to tetragonal MnO2, the strong peak of MnO2 nanoparticles along the 35.12° correspond to the planes (301) having tetragonal structure which is well agree with JCPDS Card number (39–0375) and in the Fig. 2(c) the strong peak of Mn2O3 nanoparticles along the 32.27° correspond to the planes (222) having cubic structure $a= 9.43\text{Å}$ which is well agree with JCPDS Card number (24–0508) are agree with [12]. Crystallite size of Manganese Oxide nanoparticles calculated by the Debye-Scherer equation [13], [14].

$$G.S = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where, G.S= represent the crystallite size of nanoparticles, β= the FWHM, θ= is the angle, and $\lambda=1.54\text{Å}$. The strain value and dislocation density can be calculated by using equation [15-17] and listen in the Table (1).

$$\delta = \frac{1}{G.S^2}$$  \hspace{1cm} (2)

$$\eta = \frac{\beta \cos \theta}{4}$$  \hspace{1cm} (3)

| Sample | Temperature (°C) | 2θ (degree) | (hkl) | FWHM (deg) | G.S (nm) | $\eta*(10^{-4}\text{ lines}^2\cdot\text{m}^{-1})$ | $\delta*(10^{14}\text{ lines}^2\cdot\text{m}^{-2})$ |
|--------|------------------|-------------|-------|------------|----------|--------------------------------|--------------------------------|
| MnO    | 600              | 34.70       | (111) | 0.317      | 25.66    | 15.18                          | 13.5                            |
| MnO$_2$| 700              | 35.12       | (301) | 0.386      | 24.5     | 16.65                          | 14.75                           |
| Mn$_2$O| 800              | 32.27       | (222) | 0.68       | 23.49    | 18.1                           | 29.5                            |
FTIR analysis of MnO, MnO2, and Mn2O3 nanoparticles at 600°C, 700°C and 800°C respectively was carried out between 400 cm\(^{-1}\) and 4000 cm\(^{-1}\) as shown in Fig.3. The transmission peak 630.74 cm\(^{-1}\) represent the stretching vibration of Mn-O bonds indication the formation of MnO and MnO2 nanoparticle, and peak 459 cm\(^{-1}\) represent the stretching vibration of Mn-O and indication the formation of Mn2O3 nanoparticles. And a weak asymmetric band at 1423-1440 cm\(^{-1}\) support the presence of (-OH) result to the absorption of water by nanoparticles during the powder fabrication [8].
The optical band gap of MnO and MnO2 nanoparticles is shown in Fig. 4. It is due to a direct allowed transition, the value of the band gap has been determined from the intercept of the straight line at $\alpha = 0$. That is found for MnO nanoparticles to be 3.7eV and 2.5eV. The optical band gap 3.7eV is due to direct transition while 2.5eV attributed due to the indirect transition and it is found for MnO2 nanoparticles to be 3.6eV and 2.4eV. The optical band gap 3.6eV is due to direct transition while 2.4eV attributed due to the indirect transition [18,19].

Conclusions
In this work, we investigated MnO, MnO2 and Mn2O3 nanoparticles synthesis by simple chemical method and calcination under different temperature 600oC, 700oC and 800oC. X-ray diffraction and FTIR and UV-Visible have been investigated and crystallite size was calculated using Debye-Scherers equation and it is found to be around (23.4-25.66 nm).

References
[1] L. Feng, Z. Xuan, H. Zhao, Y. Bai, J. GuO, C.wei Su and X. chen, "MnO2 prepared by hydrothermal method and electrochemical performance as anode for lithium-ion battery," Nanoscale Research Letters, 9:290, 2014.

[2] M. Jayandran, M. Muhamed and V. Balasubramanian, "Green synthesis and characterization of Manganese nanoparticles using natural plant extracts and its evaluation of antimicrobial activity," Journal of Applied Pharmaceutical Science Vol. 5 (12), pp. 105-110, 2015.
[3] J. Fei, Y. Cu, X. Yan, W. Qi, Y. Yang, K. Wang, Q. He, and J. Li, "Controlled preparation of MnO2 hierarchical hollow nanostructures and their application in water treatment," Adv Mater, 20:452–456, 2008.

[4] B.M. Pradeep Kumar, K.H. Shivanprasad, R.S. Raveendra, R. Hari Krishna, S. Karikkat, and B.M. Nagabhushana, "Preparation of MnO2 nanoparticles for the adsorption of environmentally hazardous malachite green dye," International Journal of Application or Innovation in Engineering & Management (IJIAIEM), Volume 3, Issue 12, 2014.

[5] G. Zhang, L. Zheng, M. Zhang, S. Guo, Z.-Huai Liu, Z. Yang and Z. Wang, "Preparation of Ag-Nanoparticle-Loaded MnO2 Nanosheets and Their Capacitance Behavior," Advance in Nano, Biomechanics, Robotics, and Energy Research, 25-28, 2013.

[6] Z. Wang, F. Wang, Y. Li, J. Hu, Y. Lu and M. Xe, "Interlinked multiphase Fe-doped MnO2 nanostructures: a novel design for enhanced pseudocapacitive performance," Electronic Supplementary Material (ESI) for Nanoscale, 2016.

[7] M. Sharrouf, R. Awad, M. Roumié and S. Marhiba, "Structural, Optical and Room Temperature Magnetic Study of Mn2O3 Nanoparticles," Materials Sciences and Applications, 6, 850-859, 2015.

[8] M. Suriyavathana, K. Ramalingam, "Nanoparticles Synthesis and Antibacterial Study on Anisomeles Malabarica using Manganese Oxide (MnO)," International Journal of Chem. Tech Research, Vol.8, No.11 pp 466-473, 2015.

[9] S. Ganeshan, P. Ramasundari, A. Elangovan, G. Arivazhagan and R. Vijayalakshmi, "Synthesis and Characterization of MnO2 Nanoparticles: Study of Structural and Optical Properties," International Journal of scientific Research in Physics and Applied Sciences", Vol. 5, Issue 6, pp. 5-8, 2017.

[10] K.S. Shaker, A.H. AbdAlSalm, "Synthesis and Characterization Nano Structure of MnO2 via Chemical Method," Engineering and Technology Journal, Vol. 36, Part A, No. 9, 2018.

[11] X. Duan, J. Yang, H. Gao, J. Ma, L. Jiao and W. Zheng, "Controllable Hydrothermal Synthesis of Manganese Dioxide Nanostructures: Shape Evolution Growth Mechanism and Electrochemical Properties," Electronic Supplementary Material (ESI) for Cryst. Eng. Comm, 2012.

[12] W. Tang, X. Shan, S. Li, H. Liu, X. Wu and Y. Chen, "Sol–gel process for the synthesis of ultrafine MnO2 nanowires and nanorods," Materials Letters, 132, 317–321, 2014.

[13] S. Akbari, M. Mehdi and M. Foroughi, "Solvent-free Synthesis and Characterization of MnO2 Nanostructures and Investigation of Optical Properties," J. of Nanomedecine & Nanotechnology, 9:3, 2018.

[14] M A Aseel, F H Itab and F M Ahmed, "Producing High Purity of Metal Oxide Nano Structural Using Simple Chemical Method," IOP Conf. Series: Journal of Physics: Conf. Series 1032, 012036, 2018.

[15] S. Karpagavalli, S. John, S. Perumal, S. Perumal, D. Priscilla Koilpillai and A. Suganthis, "A Comparative Study of Optical and Magnetic Properties of Undoped and Cobalt Doped Manganese Oxide Nano Particles," Journal of Applied Physics, PP 34-42, 2017.

[16] Khodair, Z.T., Al-Jubbori, M.A., Hassan, A.M. et al. Journal of Elec Materi (2019) 48: 669.

[17] R K Mohammad, R A Madlol, N M Umran and F I Sharrad Structure and electronic properties of substitutionally doped cycloheptane molecule using DFT, Results Phys. 6 (2016 ) 1036.

[18] M A Aseel, "Preparation and characterization of titanium oxide nanoparticles using sol-gel method," Elixir Nanotechnology, 91, 38435-38439, 2016.
[19] B. K. Pandey, A. K. Shahi and R. Gopal, "Optical and Electrical Transport Properties of MnO Nanoparticles," Materials Focus, vol. 2, pp. 1–6, 2013.