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Synthesis and Characterization Nano Structure of MnO_2 via Chemical Method

Abstract-*In the current research, Magnesium oxide II (MnO_2) nanostructures were prepared by chemical route from hydro manganese chloride salt using Potassium hydroxide as reducing agent. X-Ray diffraction (XRD), SEM and Fourier transformation infrared (FTIR) used to characterize both particle size and structure of MnO_2 nanoparticles. XRD results confirmed impurity of synthesized powder with α-MnO_2 as predominant phase. The average particle size of manganese dioxide was in the range 25- 30 nm. Photographs of scanning electron microscope (SEM) showed two hierarchical structures, cluster agglomeration and chain appearance.*

Keywords- *MnO_2 Nanostructure, Characterization and precipitation method*

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1. Introduction

Manganese is a transitional element existing in three various valence states and its oxides considered highly complex [1]. Manganese oxide II is a complex, an inorganic, blackish or brown color compound exists in nature as ore of manganese called pyrolusite [2]. Manganese oxides, including MnO, MnO_2, and Mn_3O_4, are interesting composites used in wide range of applications in treatment of wastewater, catalyst, biosensors, supercapacitors, and batteries due to their distinctive physical and chemical properties and [3–7]. Figure 1 shows diagram of MnO_2 structure forms at which, each structure form preferred specific properties than the others [8].So far, multiple efforts dedicated to prepare MnO_2 using various strategies including thermal decomposition, co-precipitation, sol-gel, simple reduction, solid-phase process, hydrothermal method and microwave process …etc [9-14]. Most of researches attracted to use hydrothermal and sol gel processes because the shape of materials that can be easily controlled, while others preferred precipitation method since it offers simplicity, low cost, quick preparative method, finally easily controlled of both particle size and composition [15]. Singh et al. synthesized firstly manganese oxyhydroxide γ-MnOOH nanowires via hydrothermal route and transferred into β-MnO_2 by calcination at 300℃ [16]. Figure 2 indicate to manganese oxides transformations under different conditions [17]. Feng et al. used hydrothermal route to produce two forms of α-MnO_2 crystals urchin-like under acidic circumstances and is caddice-clew-like under neutral [18]. Zadeh et al. prepared successfully MnO_2 by hydrothermal and sol–gel routs. Results indicated that each of α-MnO_2, β-MnO_2, and δ-MnO_2 nanorods synthesized by hydrothermal route while γ-MnO_2 by sol–gel route [8]. Kumar et al. and Balamurugan synthesized nano crystalline with tetragonal structure manganese oxide nanoparticles by co precipitation using two different anions salts (i.e. sulphate monohydrate and Oxalate) [15,19]. Wu et al. studied concluded that different forms of MnO_2 nanostructures can be synthesized via hydrothermal such as *alpha*-MnO_2 with different shapes like nanorods, nanotubes, nanocubes, nanowires and *beta*-MnO_2 cylinder/spindle-like nanosticks by changing the weight ratio of Mn precursor solution respect to HCl, $Mn(Ac)_2{\cdot}4H_2O$ or $C_6H_{12}O_6{\cdot}H_2O$, types of surfactants, finally temperature and time of reaction [20]. Finally, Adelkhani succeeded in synthesis novel electro active nano structure manganese dioxide via pulse laser deposition [1]. In the present work, nanostructure MnO_2 synthesized by precipitation method has been reported using single manganese anion salt. Structural and crystallographic characteristics of samples have been compared with other researches.

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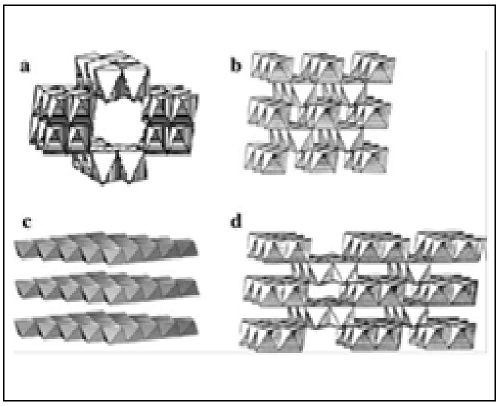

Figure 1: Sketch diagram of a α-MnO_2 (Hollandite), b β-MnO_2 (Pyrolusite), c δ -MnO_2 (Birnessite), d γ -MnO_2 (Nsutite) [8]

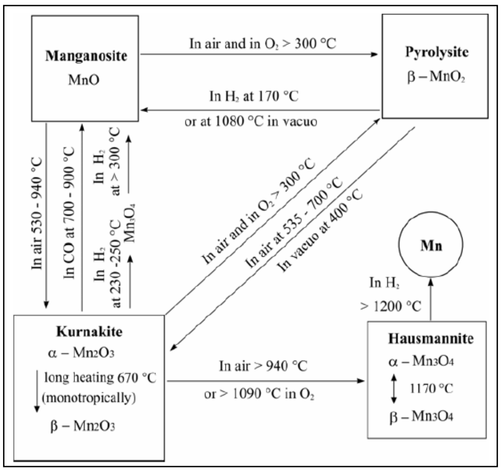

Figure2: Schematic illustration of the transformations of manganese oxides under different conditions [17].

2-Experimaintal Part

I .Material

Manganese chloride ($MnCl_2$. 6(H_2O)), Potassium hydroxide (KOH), toluene (C_7H_8) were purchased from Sigma Aldrich, distilled water from Lab.

II. Characterizations Techniques

The optical transmittance properties of MnO_2 by Fourier Transform-Infrared Spectroscopy (FT-IR) from (SHIMADZO IRAFFINITY) probes. The morphology of MnO_2 were investigated with scanning electron microscope (SEM, the VEGA Easy Probe). Phase composition of MnO_2 was observed by X-ray diffraction (Philips PW 1050 X-ray diffract meter of 1.5^{o}A from Cu-Kα. Additionally).

Crystallite size calculated by Debye-Scherer equation

$$D = 0.9\, \lambda / B_{1/2} \cos(2\theta) \quad (1)$$

Whereas:

λ is the wave length of the used radiation.B1/2 is the broadness of peak with maximum intensity in half height.

III. Synthesis of MnO_2Nanostructure

MnO_2Nps have been prepared by using 20 ml of toluene as solvent to dissolve 2 g of KOH pellets with vigorous stirring for 10 hrs at room temperature. Then, 3 g of $MnCl_2 \cdot 6H_2O$ added into this solution, refluxing process takes 3 hrs followed by filtration for separation, then MnO_2 precipitate washed with distilled water. The compound was dried for 6 hrs at 100 ℃ in an oven, finally calcinations process at 500 ℃.

3. Results

I. XRD results

For studying the crystallinity and crystal, phases of the prepared powder X-ray diffraction used. It is well known that MnO_2 has various polymorphs (i.e. exist in various crystal structure) α-, β-, γ-, δ-, ε- and λ-types and so forth, each form differs from the other in the arrangement of the basic structural unit of ([MnO_6] octahedron).According to these links of octahedron, MnO_2 may exist as tunnel structure similar to chain such as α-, β-, and γ-types, layered or sheet structure like δ-MnO_2, and as 3D structure like λ-type [21].α-MnO_2, β- MnO_2 and γ- MnO_2 phases have one-dimensional (1D) tunnels with X*X octahedral cross section (X= 5 1, 2, 3, or 4) in their crystal structure, the phase δ- MnO_2 is 2D-layered compound, while γ- MnO_2 has 3D spinel structure [21]. Figure 3 shows XRD pattern of the prepared powder. It shows the presence of 28.5˚ which is the highest peak belong to α-MnO_2 phase according to the standard (JCPDS: 44 - 0141) making it the predominant phase [20]. Moreover, the other detected peaks indicating impurity of the synthesized powder with presence of mixture of Mn_3O_4 and Mn_2O_3 as shown in Fig.3, at which compared with the powder prepared from reaction of water-free glycerol added to $Mn(NO_3)_2$ and calcinated around 500^{o}C [22].Also, the sharp diffraction peaks reveal that the products are well crystalline e in nature. Table (2) shows all characteristics of XRD of prepared powder. Manganese dioxide crystallite size calculated by Debye-Scherer was 17.3 nm.

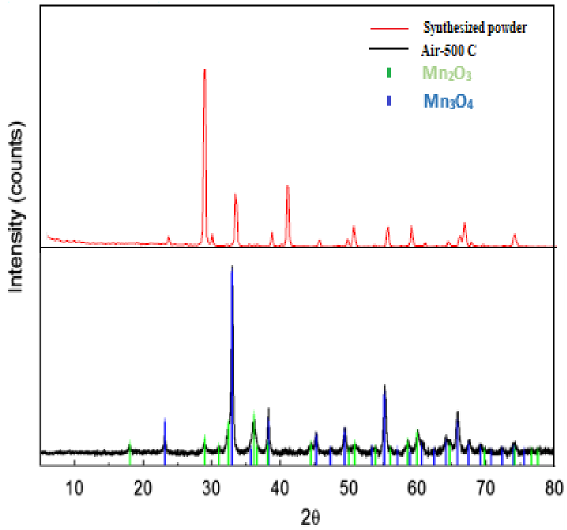

Figure 3: X-ray diffraction pattern of the prepared powder.

Table 1: Characteristics of XRD of prepared powder

No.	2 theta (deg)	d (A)	I/I1	FWHM	Intensity
1	23.2813	3.81766	4	0.4537	72
2	28.5263	3.12653	100	0.4951	1843
7	45.3232	1.99929	3	0.488	57
8	49.4968	1.84003	4	0.489	74
9	50.3713	1.81012	10	0.4827	192
10	55.3101	1.6596	11	0.5005	196
11	58.8252	1.56853	11	0.4803	207
12	65.8225	1.41771	6	0.3302	104
13	66.5698	1.4036	13	0.5319	243
14	73.9157	1.28121	7	0.5568	129

II. FTIR results

Fourier transformation infrared (FTIR) spectroscopy has high sensitivity for detection both organic and inorganic species with low content. Spectrum of FTIR for synthesized nanomaterial presented in Figure 4. usually bands in the range of (400-800) cm^{-1}assigned to Mn-O vibrations [23], still for more specification the two absorption bands at (661.58 and 474.49) cm^{-1} belong to the stretching collision of O–Mn–O, which denotes to the presence of MnO_2. The broad bands of absorptions in the range between 4000 and 3000 cm^{-1} are assigned to both H–O–H stretching collision and hydroxylgroups, while the at 1649cm^{-1} it was characterized to bending collision of adsorbed water H_2O molecule.

III. SEM results

Manganese dioxide (MnO_2) has various crystal structures because the wide variety of corners and/or edges sharing arrangements of building block units [l]. Figure 5 shows SEM photographs at different magnifications. It is clear that the synthesized powder has two different shapes like – chains give porous form Figure (5a) and clusters Figure (5 b and c) which have a great tendency for agglomeration due to their surface energy leading to the formation of large surface area, this irregular agglomerated form similar with Abdul Hakeem [24] at which cubic MgO nanoparticles were synthesized by non aquous-sol gel and so big particle takes place due to Ostwald ripening process with a limited porosity and crystalinity.

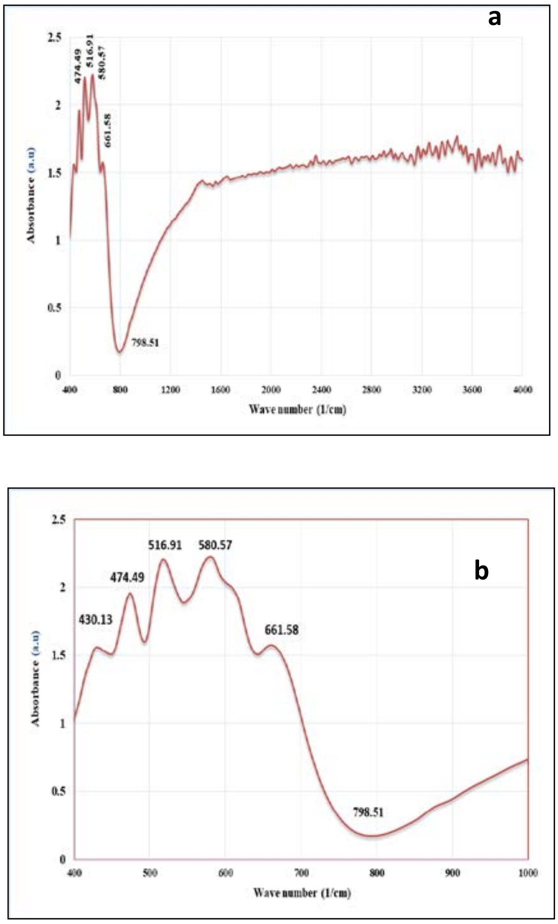

Figure 4: FTIR spectrum of MnO_2 nanostructure at range (a) 400-4000cm^{-1} (b) 400-1000 cm^{-1}

4. Conclusion

MnO_2 nanoparticles a have large number of potential applications in the field of sensors, catalysis, pharmaceutical industries, piezoelectric crystals and electrodes of fuel cells.In current work, MnO_2 nanoparticles synthesized by precipitation method using inorganic precursor and toluene as solvent. Calcination temperature was 500°C in order to obtain MnO_2 nanoparticles, since it plays a vital role in the formation of the final product as well as nanoparticles morphology. XRD result indicate to the presence of predominant α-MnO_2 phase and mixture of Mn_3O_4 and Mn_2O_3.Different shapes chain with porous appearance regular chips have a great tendency for agglomeration due to their surface energy leading to the formation clusters.

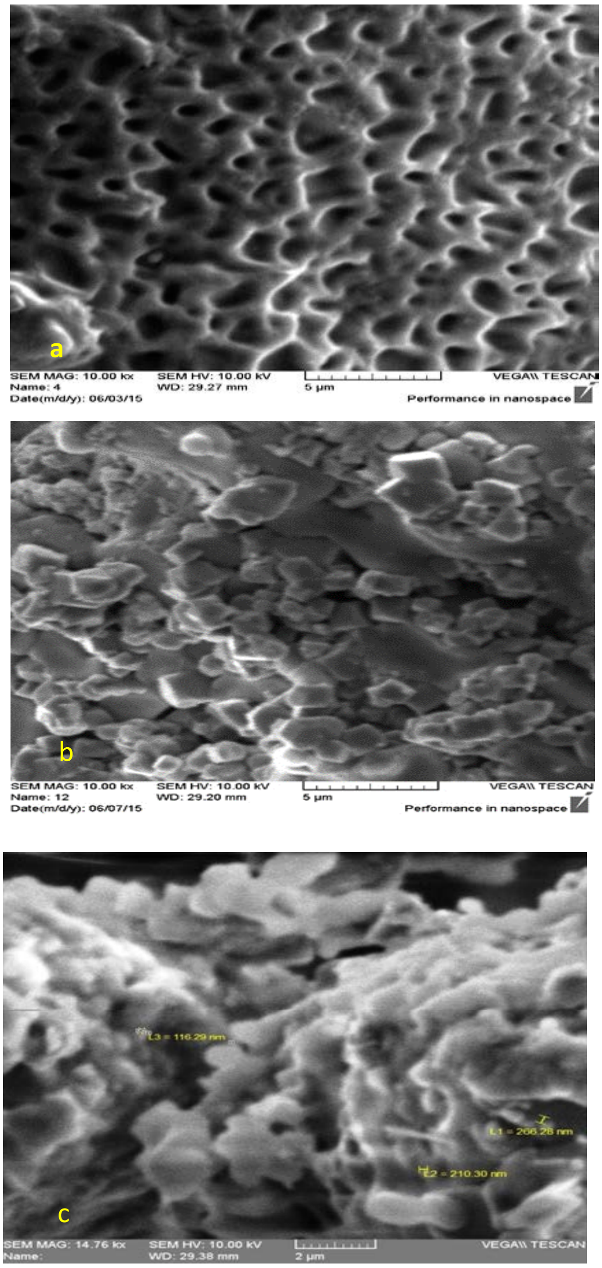

Figure 5: SEM photographs of MnO_2 nanostructure

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