Synthesis and Catalase Mimic Activity of MnO_2 Nano Powder Prepared by Hydrothermal Process

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Abstract

Manganese dioxide (MnO_2) nanopowder has been synthesized by hydrothermal method. MnO_2 was annealed at different temperatures (250, 400, 550, 700˚C). The crystal structure and surface morphology of these nanostructures were characterized by X-ray diffraction (XRD), Atomic Force Microscope (AFM) and Scanning Electron Microscopy (SEM). The catalase mimic activity (catalytic activity) of MnO_2 against hydrogen peroxide (H_2O_2) was studied by using new method and found that 400˚C is the best annealing temperature.

1. Introduction

For many years, manganese dioxide with diverse crystal morphologies are attracting a lot of attention, because of their outstanding structural flexibility combined with novel physical and chemical properties, which are of interest for the following applications, for example, molecular sieves, supercapacitors, catalysts and biosensors [1]. It is n-type semiconductor material [2]. Manganese dioxide exists in various polymorphic forms including α-, β-, γ- and δ-MnO_2 which are different in the arrangement of basic octahedral [MnO_6] units [3]. The hydrothermal method is a powerful synthesis approach for synthesizing various forms of manganese oxides because of the choice of precursors that can be used and control of reaction time, pH, and temperature and it is a simple and inexpensive technique [4].

The catalytic (catalase) activity can be measured by determining the decrease of H_2O_2 absorption (at 240 nm) [5,6]. The difficulties associated to this method, due to using high levels of substrate approximately (5-50 mM) to get acceptable absorbance [7]. Moreover, the high levels of H_2O_2 lead to formation of bubbles in the test cell which cause mistake measurements [8]. Catalase (catalytic) activity can be determined in other methods such as by titrimetric determination of H_2O_2 concentration, determination of oxygen production from decomposition of H_2O_2 by oxygen electrode [9,10]. There are simple colorimetric methods such as by Goth [11] for catalase, by measuring of hydrogen peroxide (unreacted) spectrophotometrically by a complex reaction with ammonium molybdate. Sinha and Hadwan [12,13] use another simple method, in which the decomposition of hydrogen peroxide determined spectrophotometrically by a complex reaction with dichromate/acetic acid reagent. Another method for catalase activity measurement is the titration method, which is used when high (UV) absorption pigmentation or precipitation of the sample does not allow the use of the spectrophotometric method [8].

Our work is new modified method which use spectrophotometric assay to determination of H_2O_2 by potassium permanganate in acidic solution.

2. Theoretical Part

In the present work, we have prepared MnO_2 nanopowder using $KMnO_4$ and HCl as a precursor. The crystalline size for that peak alone calculated, using the Debye- Scherer formula [14]:

$$D = k\lambda / \beta\cos\theta \quad \ldots\ldots\ldots (1)$$

Where k is the constant (0.9), λ is the wave length of X-ray (1.54 nm), β is the full width half maximum (FWHM) of the peak and θ is the reflection angle.

3. Materials used

All reagents were of analytical grade purity and no further purification was done before use. Potassium permanganate ($KMnO_4$), purity 99.9%; and hydrochloric acid (HCl), purity 99.9%, sulphuric acid (H_2SO_4), purity 95% from British Drug House (BDH) company. Hydrogen peroxide (H_2O_2), purity 50 %; Merck company.

3.1 Synthesis of MnO_2 Nano powder

The hydrothermal reaction was done in a 100 mL Teflon-lined stainless steel (autoclave) under autogenous pressure. In this synthesis, 4.115 g (47.298 mmol) of $KMnO_4$ was added into 70 mL of deionized water with vigorous stirring, and stirred for about 10 min. at room temperature. The solution filtered, then 3.405 ml concentrated HCl were added to the filtrated solution under stirring to form the precursor solution. Then the solution poured into a 80 Teflon-lined stainless steel autoclave. The autoclave was sealed and placed in an oven at 200 °C for 6 h. and hydrothermally treated at 200 °C for 12 h. After that, the autoclave was allowed to cool to room temperature naturally. The brown black precipitate ($Mn(OH)_4$) was washed with distilled water (4-5 times), and collected by centrifugation, washed with ethanol (2 times) and lastly the washed precipitates were dried at 90˚C for 2 hours in air.

The reaction took place between potassium permanganate and hydrochloric acid as following steps:

1. $2KMnO_4 + 6HCl + H_2O \xrightarrow[\text{Heat (90˚C)}]{\text{Autoclave}} 2Mn(OH)_4 + 2Cl_2 + 2KCl + 1/2O_2$ ….(1)
2. $2Mn(OH)_4 \longrightarrow 2MnO_2 + 4H_2O$ …..(2)

The overall reaction can be described by equation:

3. $2KMnO_4 + 6HCl + H_2O \xrightarrow[\text{2. Heat (90˚C)}]{\text{1. Autoclave}} 2MnO_2 + 2\,Cl_2 + 2KCl + 1/2H_2O$ ….. (3)

The brown-black precipitate (MnO_2) annealed at different temperatures (250, 400, 550 and 700°C) for 120 min.

3.2 Catalase mimic activity (catalytic activity)

The concentration of $KMnO_4$ was determined by titration with known concentration of sodium oxalate solution, then the concentration of H_2O_2 was determined by titration with known concentration of $KMnO_4$. Standard curve consisted of (0, 1, 2, 3, 4 and 5) $x10^{-5}$ M of $KMnO_4$ was prepared to find the concentration of color absorbed from $KMnO_4$ (as shown in Fig. 1).

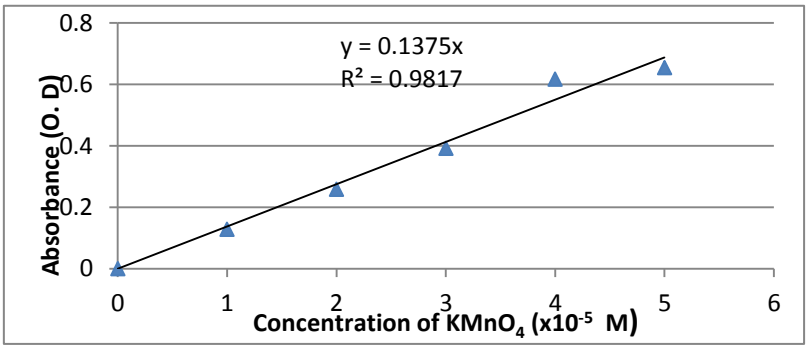


Figure 1: Standard curve of $KMnO_4$ solution at 525 nm.

Catalase mimic activity was determined by using the reaction with final concentration of manganese dioxide (MnO_2) solution (2 mM), and hydrogen peroxide (750 µM), (as the following reaction) [13]:

$$2H_2O_2 \xrightarrow{MnO2} O_2 + 2H_2O \quad \text{…..(4)}$$

After five minutes that acidic solution consist from potassium permanganate ($KMnO_4$) solution (300 µM as final concentration), acidity with some drops of sulphoric acid (H_2SO_4). The permanganate solution (purple color) will reacting with the excess of hydrogen peroxide (H_2O_2) (which no reacted with MnO_2), and reduced to manganese sulfate (color less), as product reaction as following equation:

$$3H_2SO_4 + 2KMnO_4 + 5H_2O_2 \longrightarrow 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O \quad \text{…..(5)}$$

Hydrogen peroxide concentration which used is directly proportional to the concentration of potassium permanganate that used in the reaction. The decreasing in permanganate concentration (color) is measured calorimetrically at 525 nm by using standard curve concentration. The procedure of Catalase mimic activity was done according following steps in describing in table 1.

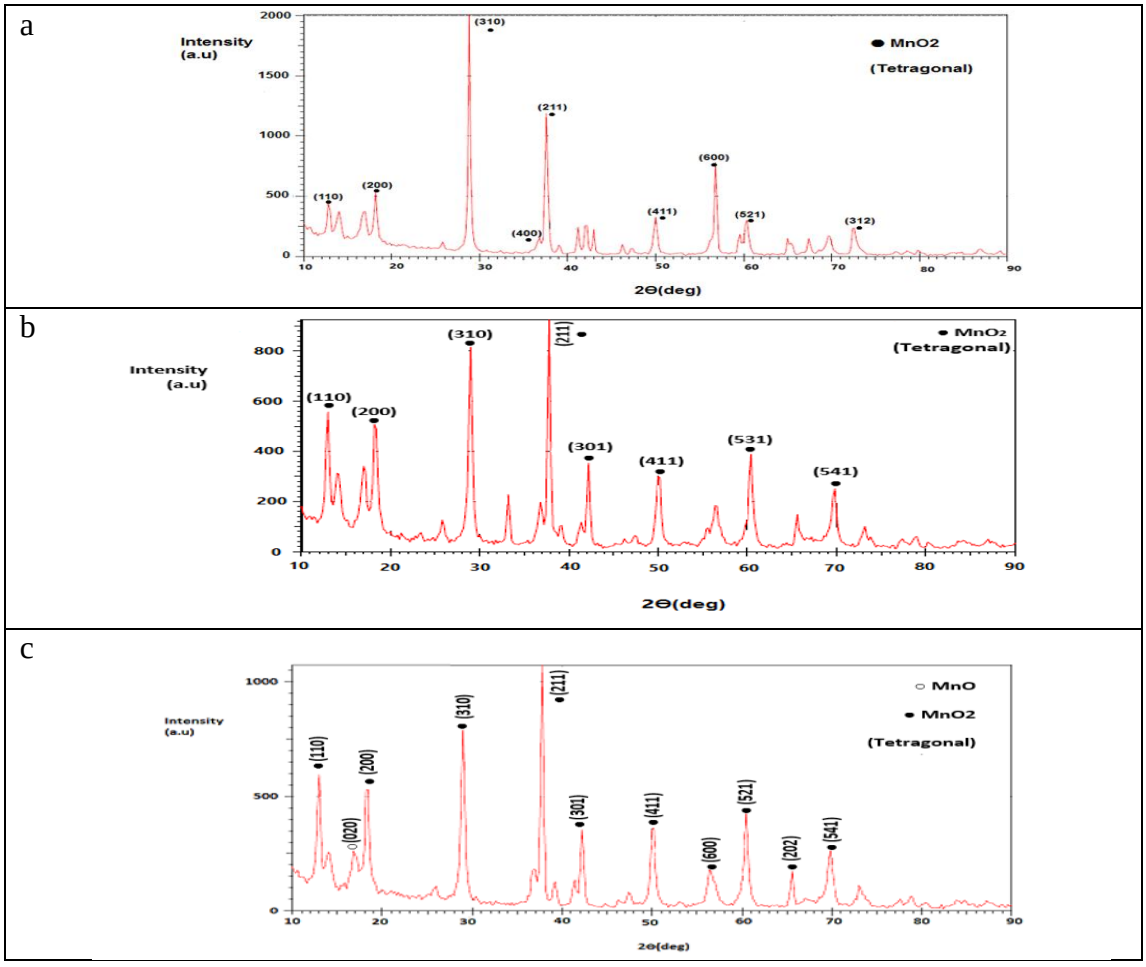
Table 1. Shows the procedure that used for measurement of catalase activity.

Reagents	Test	Control
Metal oxide solution	500 µl	-
Distilled water	1000 µl	2500 µl
Hydrogen peroxide	1000 µl	1000 µl
Mix with vortex and for 5 min, after that, add:		
Acidic solution of potassium permanganate	500 µl	500 µl
Total volume	3000 µl	3000 µl

4. Results and Discussion

The XRD pattern of MnO_2 nanostructure is illustrated in Fig.1 All the diffraction peaks are well indexed to the pure polycrystalline tetragonal α-MnO_2 phase which in a good agreement with (JCPDS Card No.44-0141) with lattice constants of (a = b = 9.78475 Å, c = 2.86302 Å) and (α=β=γ=90˚). Fig. 1-a shows the diffraction patterns of MnO_2 at annealing temperature 250˚C, the diffraction peaks for (211), (310), (200) planes at 2θ=37.57˚, 2θ=28.8˚ and 2θ=218.15˚refer to the tetragonal structure belonged to alpha phase. The new phase at 700˚C was identified as cubic Mn_2O_3 (JCPDS Card No.41 -1442) Fig.1-d.

Table -1 shows the X-ray diffraction patterns of prepared product ($Mn(OH)_2$) at different annealing temperatures (250, 400, 550 and 700˚C) for 120 min. The increase of annealing temperature from 250 to 550˚C increased the intensity of diffraction and increase the lattice constant is in agreement with the reference [15]. At annealing 700˚C the lattice constant is decrease because formation another new phase called Mn_2O_3 [16].



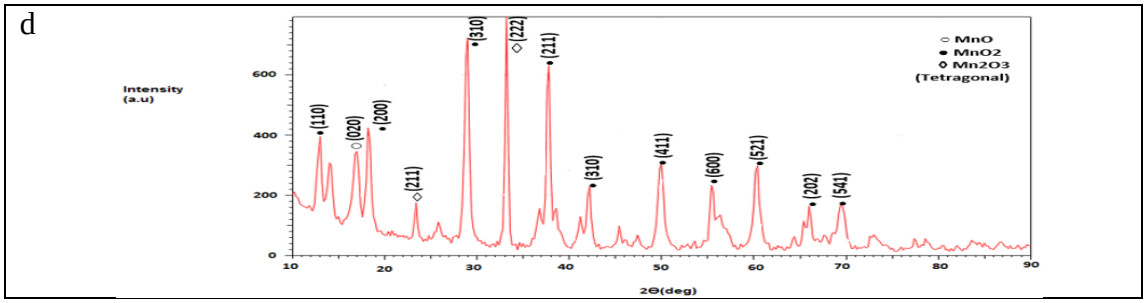
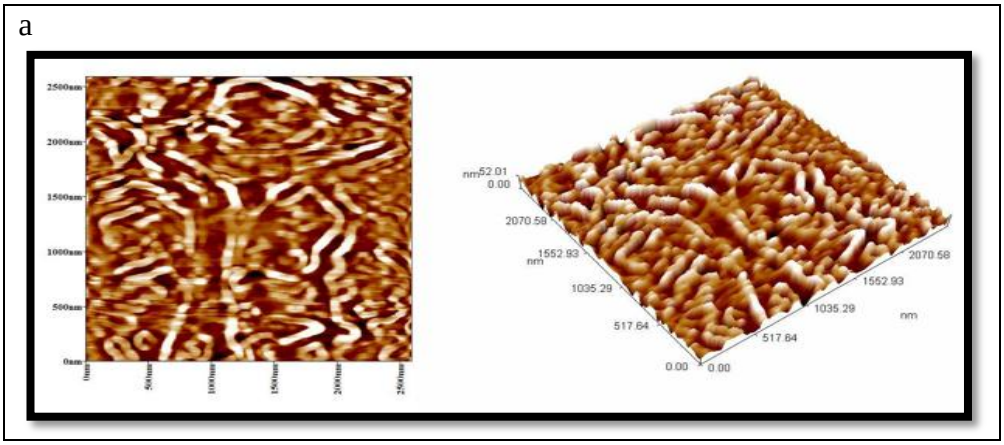


Figure 2- XRD patterns for MnO_2 with annealing temperatures at: (a) 250˚C, (b) 400˚C, (C) 550˚C and (d) 700˚C for 120 min.

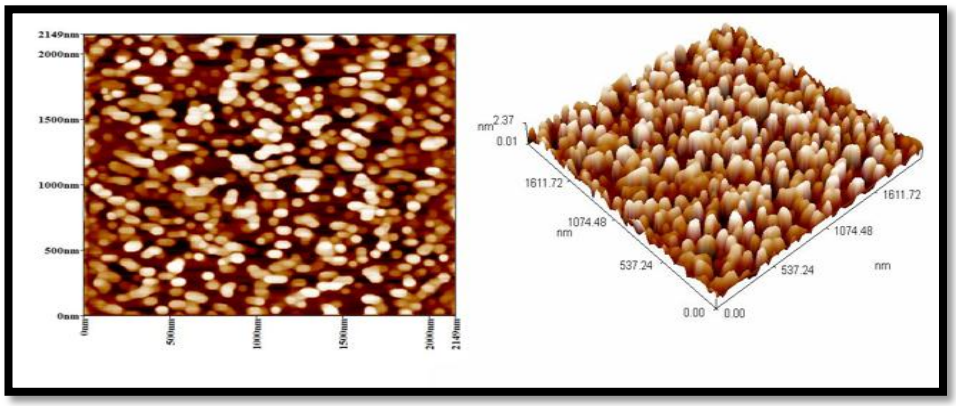
Table 1- The obtained result of the XRD for MnO_2 at different annealing temperatures (250, 400, 550 and 700˚C) for 120 min.

MnO_2 annealing Temperature for 120 min	2θ (deg)	hkl	FWHM (deg)	Grain size (nm)	d XRD (Å)	Lattice parameter	
						a XRD (Å)	c XRD (Å)
MnO_2 250˚C	37.572	211	0.552	15.1928	2.391	9.7930	2.8555
	28.805	310	0.506	16.2018	3.096		
	18.155	200	0.597	13.4781	4.882		
MnO_2 400˚C	37.788	211	0.545	15.3894	2.378	9.7316	2.8406
	28.991	310	0.636	12.8982	3.077		
	18.356	200	0.724	11.1086	4.829		
MnO_2 550˚C	37.794	211	0.541	15.5119	2.378	9.7284	2.8404
	29.001	310	0.645	12.7226	3.076		
	18.346	200	0.694	11.5879	4.831		
MnO_2 700˚C	37.715	211	0.621	13.5230	2.383	9.7673	2.8438
	28.883	310	0.699	11.7420	3.088		
	18.245	200	0.672	11.9633	4.858		

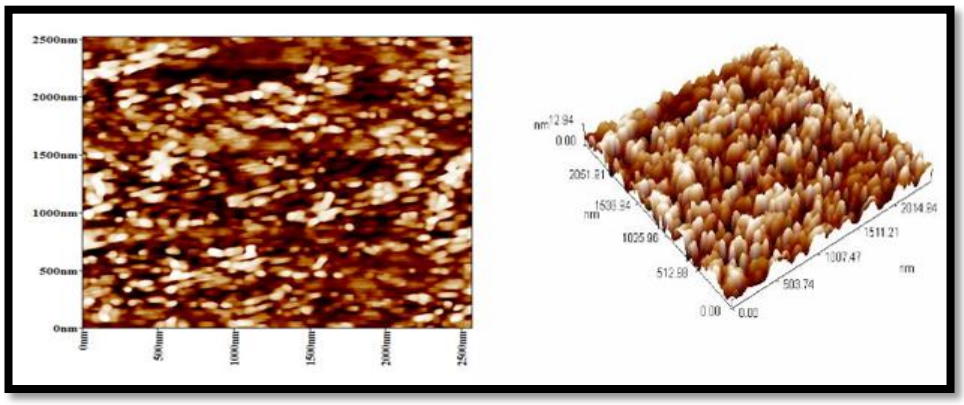
Fig. (3- a to d) show the AFM images and the granularity accumulation distribution chart of MnO_2 powders with annealing at (a-250, b-400, c-550, and d-700)˚C. The average grain size found to be (66.27 – 81.65 nm). AFM results show that the grain size increase by increasing temperature this is due to improving the crystalline of the powders.



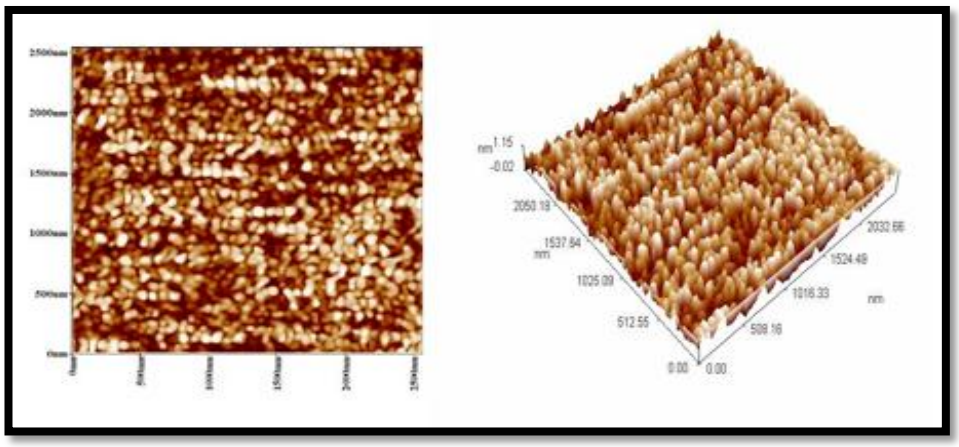
b



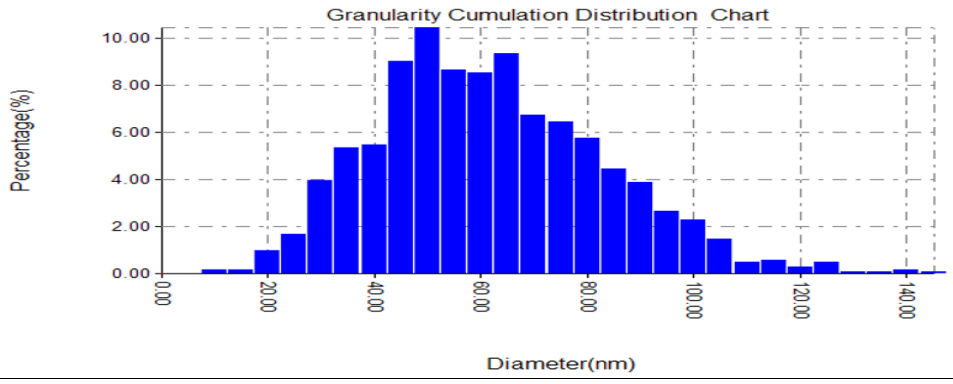
c



d



a


Granularity Cumulation Distribution Chart
Percentage(%)
10.00
8.00
6.00
4.00
2.00
0.00
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
Diameter(nm)

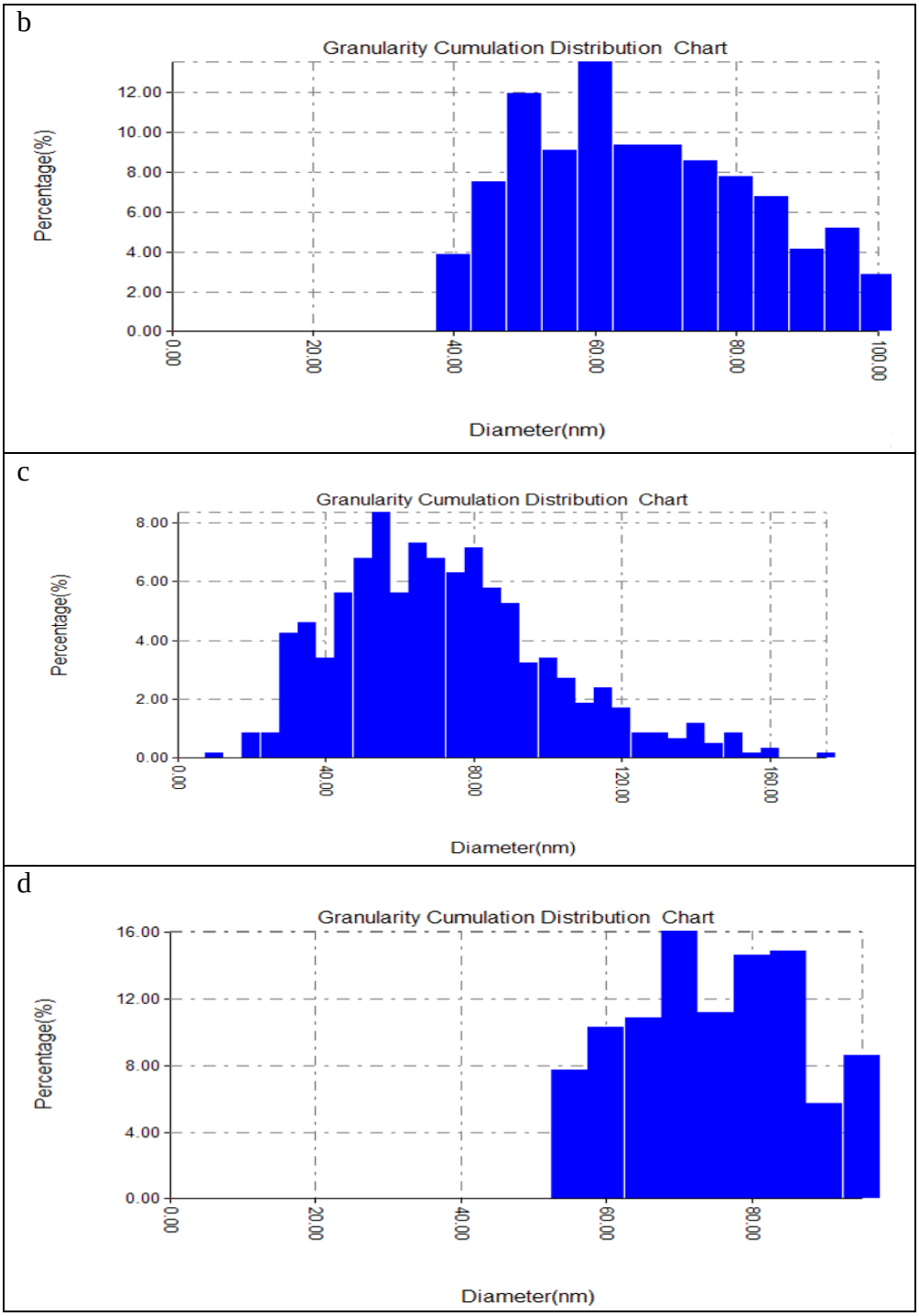
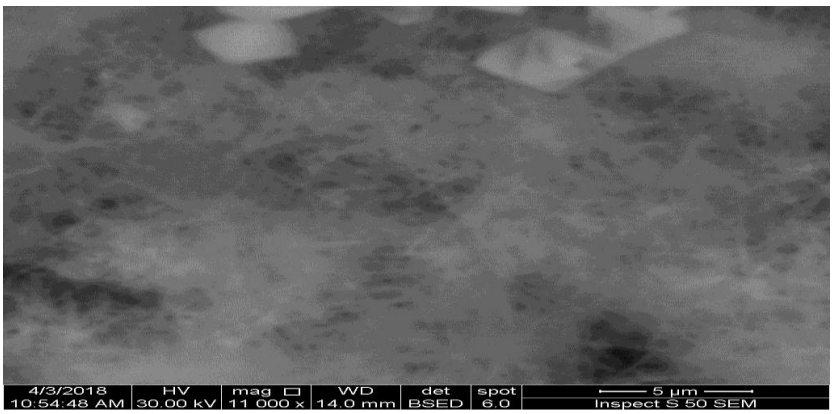


Figure 3: Two and three dimensional AFM images and the morphology o for MnO_2 with annealing temperatures at: (a) 250˚C, (b) 400˚C, (C) 550˚C and (d) 700˚C for 120 min.

For magnifications 5µm (Fig. 4- a to d) , the morphology of the MnO_2 that prepared by hydrothermal method at different temperature (250-700)˚C was primarily investigated by SEM, according to the morphology of MnO_2 there are smooth and high-quality nanowires with diameter of 17.33 to 42.89 nm and several micrometers in length for average. These nanowires aggregate into spherical shape with diameter of about 4.069 to 6.955 µm.

a


4/3/2018
10:54:48 AM
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30.00 kV
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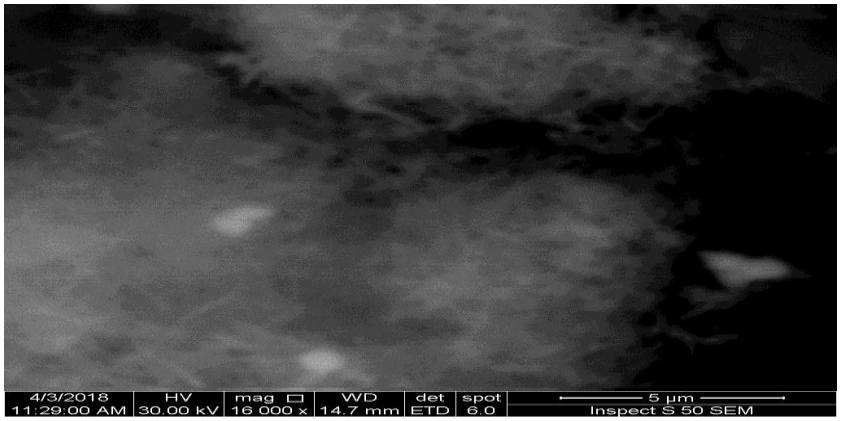
b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c

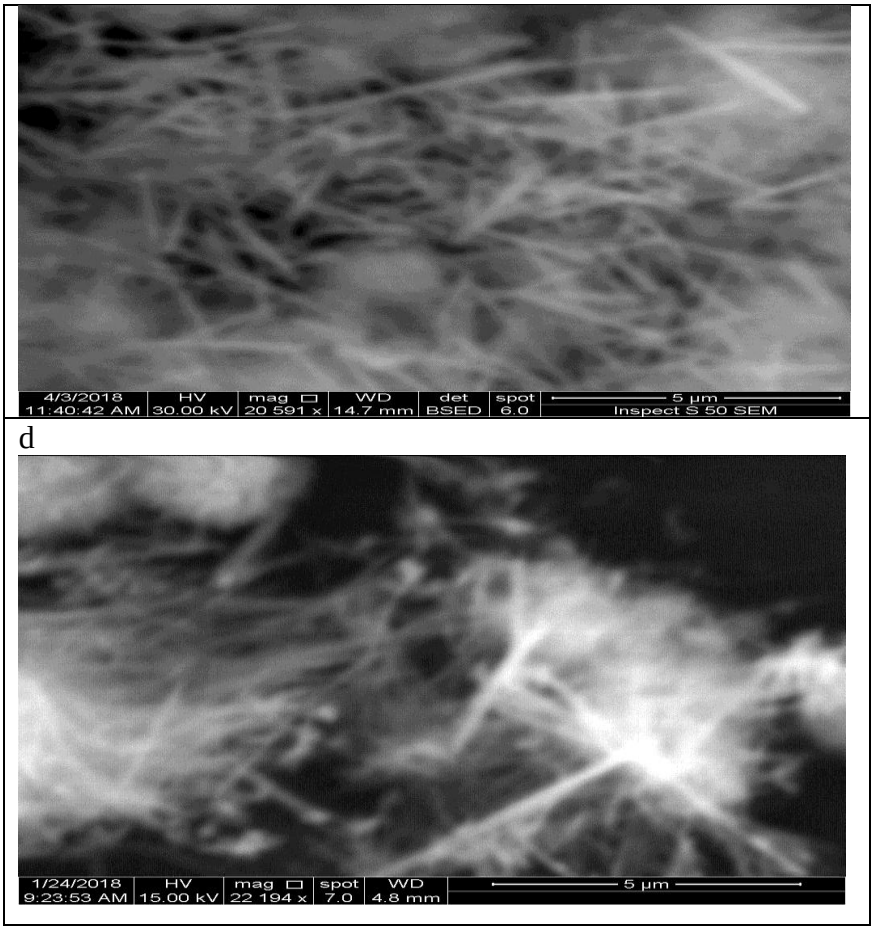

Figure 4: SEM image for MnO_2 at (a) 250˚C, (b) 400˚C, (C) 550˚C and (d) 700˚C for 120 min.

The following equation was used to calculate the rate reaction of catalase mimic activity of MnO_2 annealing at (As-prepared -700 ^oC) for 2 h:

Rate of catalase activity (sec.$^{-1}$) = (2.303/t) x (log (C_o/C)) …..(6)

Where: t = time of reaction (seconds); C_o and C are total concentration of hydrogen peroxide in cell reaction before and after reaction respectively. Our results show that the 400 ^oC is the best rate reaction of catalase mimic activity (2.59 x10^{-2} S^{-1}), these results are show in Fig. 6 and table 2.

Figure 6- The rate of reaction as catalase mimic activity (S^{-1}) of MnO_2 annealing at (as-prepared - 700 ^oC for 2 h.

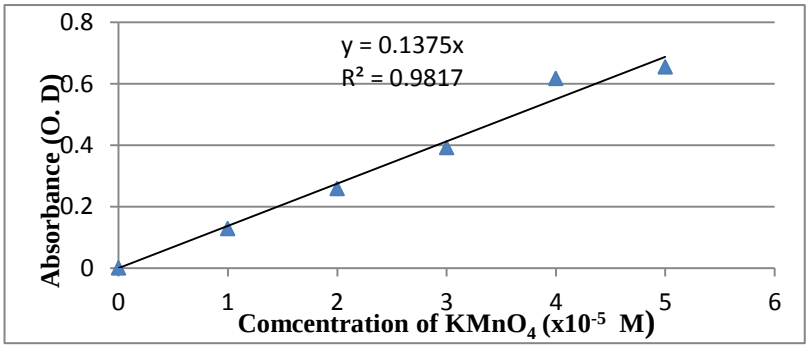

Table 2: The rate of reaction as catalase mimic activity (S^{-1}) of MnO_2 annealing at (as-prepared - 700 ^oC for 2 h.

Annealing Temperature (^oC)	K x10^{-2} S^{-1}. Rate of reaction as catalase mimic activity (S^{-1})
	MnO_2
As-prepared	1.69
250	2.10
400	2.59
550	1.97
700	1.49

5. Conclusions

1. MnO_2 nanostructures were prepared by hydrothermal method and annealing at different temperatures (250, 400, 550 and 700 ^oC) for 2 h.
2. Calculate its rate of reaction (K) as catalase mimic activity against low concentration of hydrogen peroxide (2 mM).
3. The result found annealing at 400 ^oC were the highest activity (2.59 x10^{-2} Sec.) among different annealing temperatures.

CONFLICT OF INTERESTS

There are no conflicts of interest

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تحضير ودراسة الفعالية التحفيزية لثنائي اوكسيد المنغنيز النانوي المحضر بطريقة الضغط الحراري

الخلاصة

حضرثنائي اوكسيد المنغنيز النانوي بطريقة الضغط الحراري (الاوتوكليف). وتم تلدين ثنائي اوكسيد المنغنيز عند درجات حرارية مختلفة (250،400،٥٥٠ و700م°). اخذت القياسات للمساحيق النانوية ولمتغيرات متعددة ومن ثم شخصت البنية التركيبية وطوغرافية الاسطح بوساطة فحص حيود الاشعة السينيه (XRD), مجهر القوه الذريه (AFM) و المجهر الاكتروني الماسح (SEM). درست فعالية ثنائي اوكسيد المنغنيز كعامل مقلد لانزيم الكتليز (الفعالية التحفيزية) ضد بيروكسيد الهيدروجين وباستخدام طريقة جديدة ووجد ان التلدين بدرجة حرارة 400°م هي الافضل.

الكلمات الدالة: مسحوق ثنائي اوكسيد المنغنيزالنانوي، الحرارة المائية، مقلد انزيم الكتليز.