

Synthesis and Catalase Mimic Activity of MnO₂ Nano Powder Prepared by Hydrothermal Process

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Abstract

Manganese dioxide (MnO₂) nanopowder has been synthesized by hydrothermal method. MnO₂ 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 MnO₂ against hydrogen peroxide (H₂O₂) was studied by using a new method and found that 400°C is the best annealing temperature.

Keywords: Manganese Dioxide (MnO₂) Nanopowder, Hydrothermal Method, Catalase Mimics Activity.

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 -MnO₂ which are different in the arrangement of basic octahedral [MnO₆] 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 H₂O₂ 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 H₂O₂ 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 H₂O₂ concentration, determination of oxygen production from decomposition of H₂O₂ 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 H₂O₂ by potassium permanganate in acidic solution.

2. Theoretical Part

In the present work, we have prepared MnO₂ nanopowder using KMnO₄ and HCl as a precursor. The crystalline size for that peak alone calculated, using the Debye- Scherer formula [14]:

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

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.

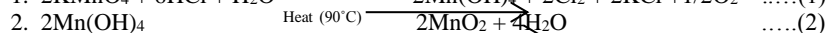
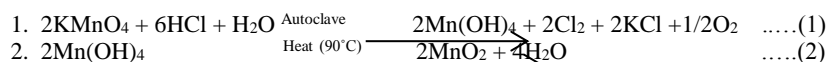
3. Materials used

All reagents were of analytical grade purity and no further purification was done before use. Potassium permanganate (KMnO₄), purity 99.9%; and hydrochloric acid (HCl), purity 99.9%, sulphuric acid (H₂SO₄), purity 95% from British Drug House (BDH) company. Hydrogen peroxide (H₂O₂), purity 50 %; Merck company.

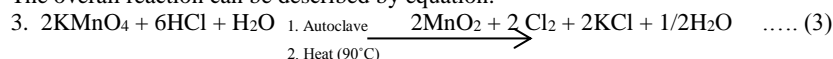
3.1 Synthesis of MnO₂ Nano powder

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 KMnO₄ 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:



The overall reaction can be described by equation:



The brown-black precipitate (MnO₂) annealed at different temperatures (250, 400, 550 and 700 °C) for 120 min.

3.2 Catalase mimic activity (catalytic activity)

The concentration of KMnO₄ was determined by titration with known concentration of sodium oxalate solution, then the concentration of H₂O₂ was determined by titration with known concentration of KMnO₄. Standard curve consisted of (0, 1, 2, 3, 4 and 5) × 10⁻⁵ M of KMnO₄ was prepared to find the concentration of color absorbed from KMnO₄ (as shown in Fig. 1).

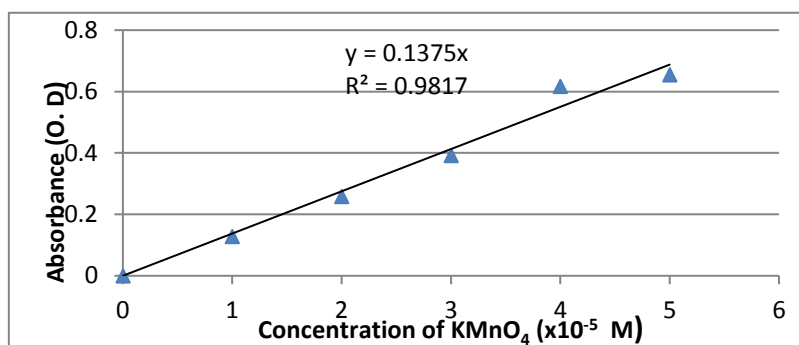
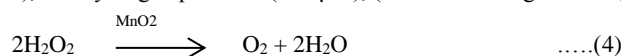


Figure 1: Standard curve of KMnO₄ solution at 525 nm.

Catalase mimic activity was determined by using the reaction with final concentration of manganese dioxide (MnO₂) solution (2 mM), and hydrogen peroxide (750 μM), (as the following reaction) [13]:



After five minutes that acidic solution consist from potassium permanganate (KMnO₄) solution (300 μM as final concentration), acidity with some drops of sulphoric acid (H₂SO₄). The permanganate solution (purple color) will reacting with the excess of hydrogen peroxide (H₂O₂) (which no reacted with MnO₂), and reduced to manganese sulfate (color less), as product reaction as following equation:



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.

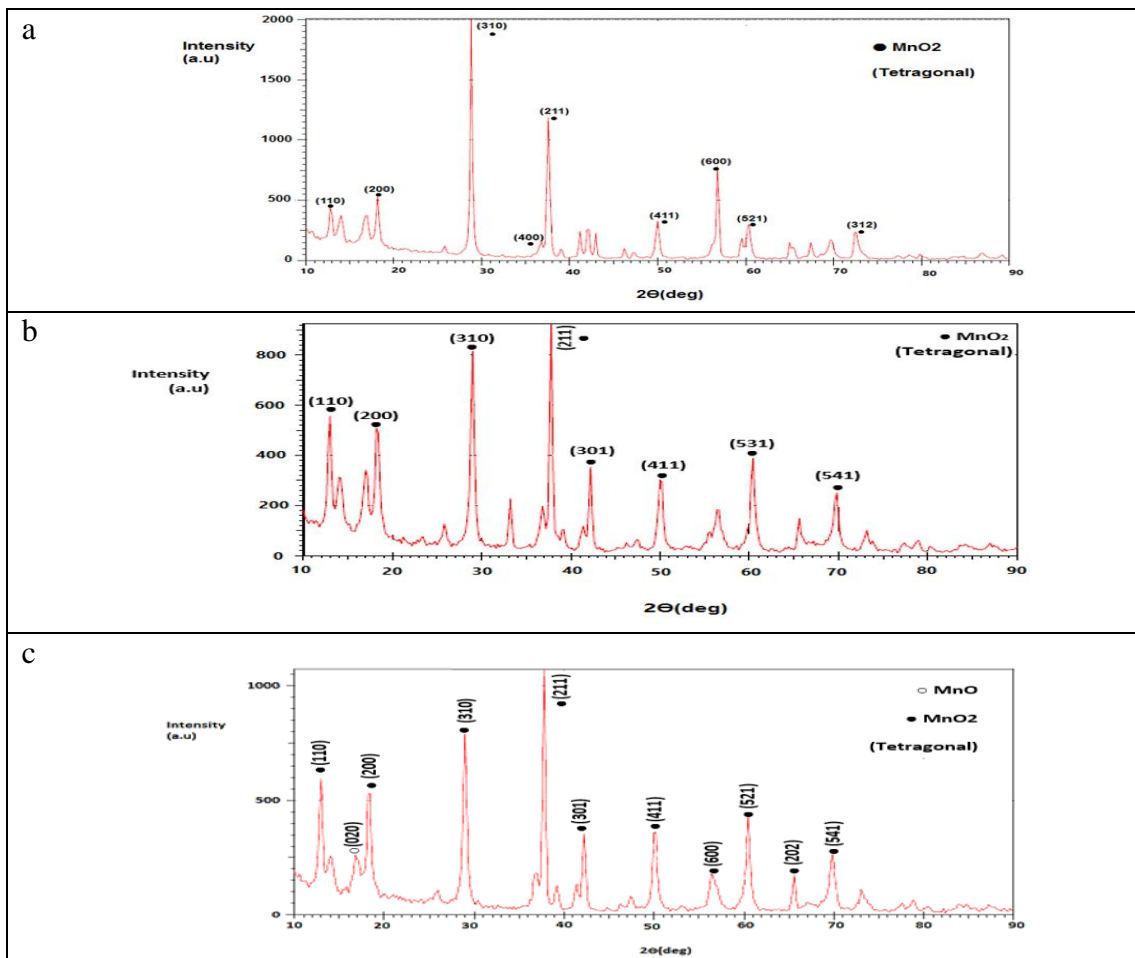
Table 1. Shows the procedure that used for measurement of catalase activity.

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

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 ($a = b = 9.78475 \text{ \AA}$, $c = 2.86302 \text{ \AA}$) and ($\alpha = \beta = \gamma = 90^\circ$). Fig. 1-a shows the diffraction patterns of MnO_2 at annealing temperature 250°C , the diffraction peaks for (211), (310), (200) planes at $2\theta = 37.57^\circ$, $2\theta = 28.8^\circ$ and $2\theta = 218.15^\circ$ 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].



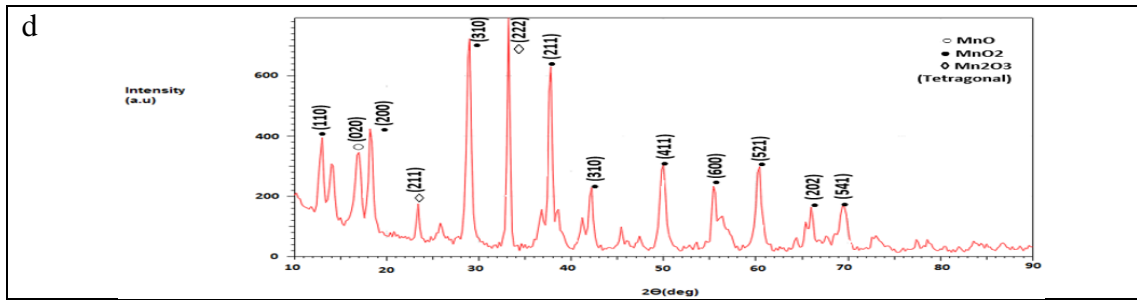
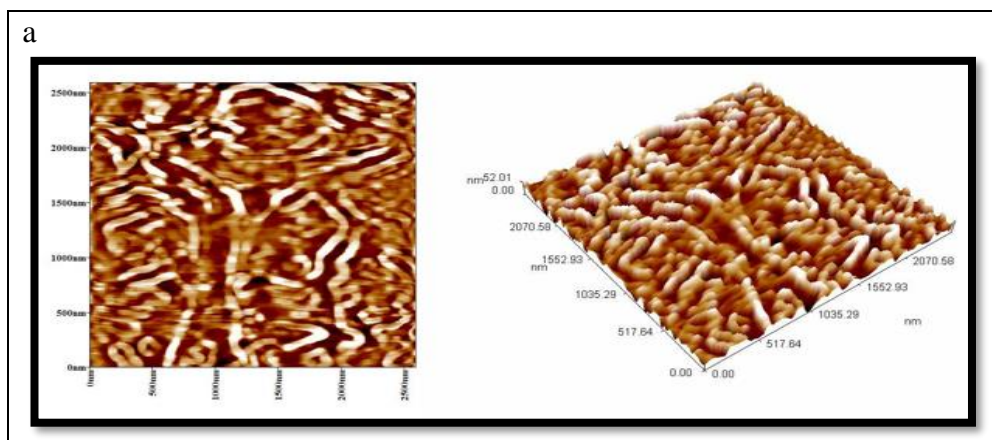


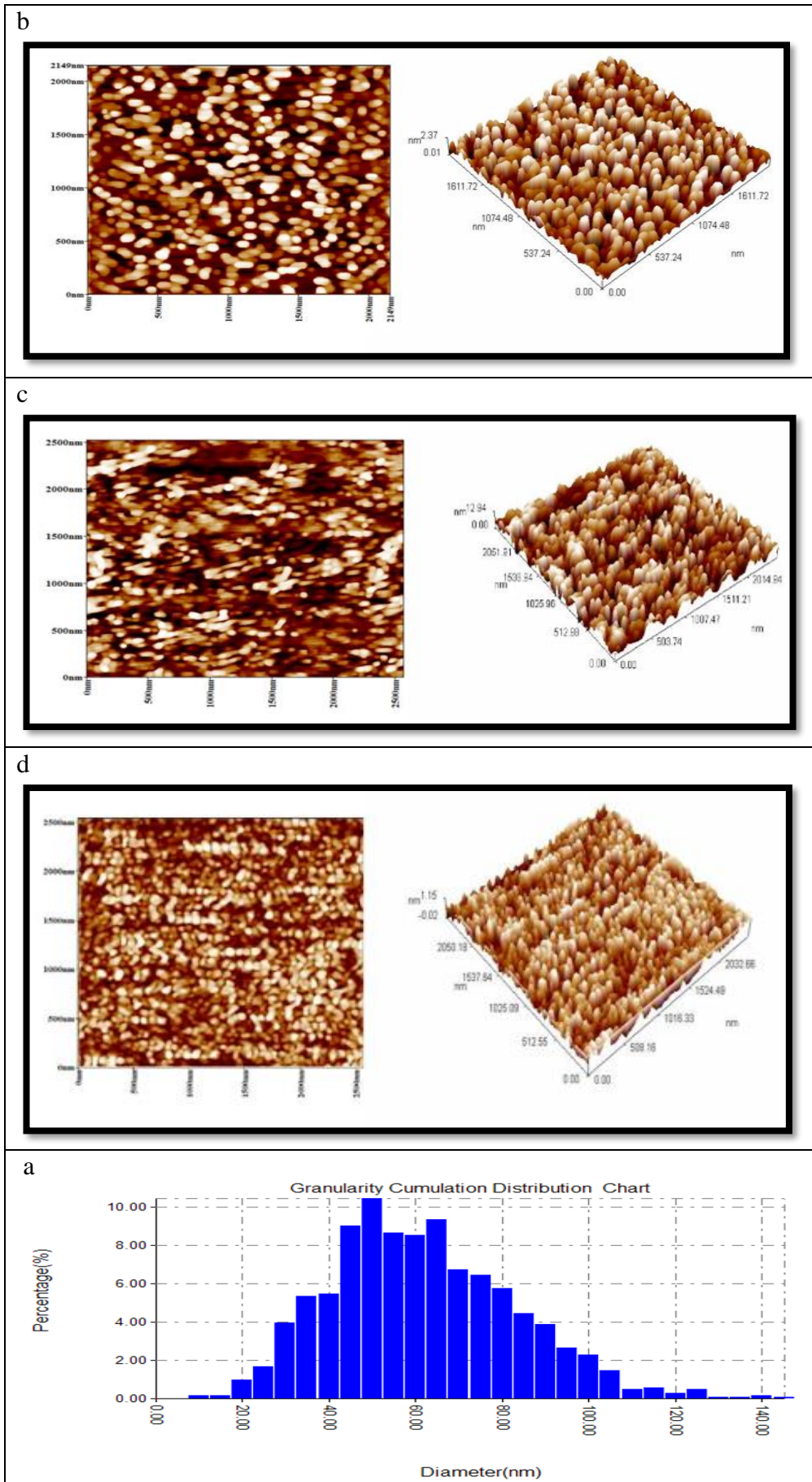
Figure 2- XRD patterns for MnO₂ with annealing temperatures at: (a) 250°C, (b) 400°C, (C) 550°C and (d) 700°C for 120 min.

Table 1- The obtained result of the XRD for MnO₂ 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 MnO₂ 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.





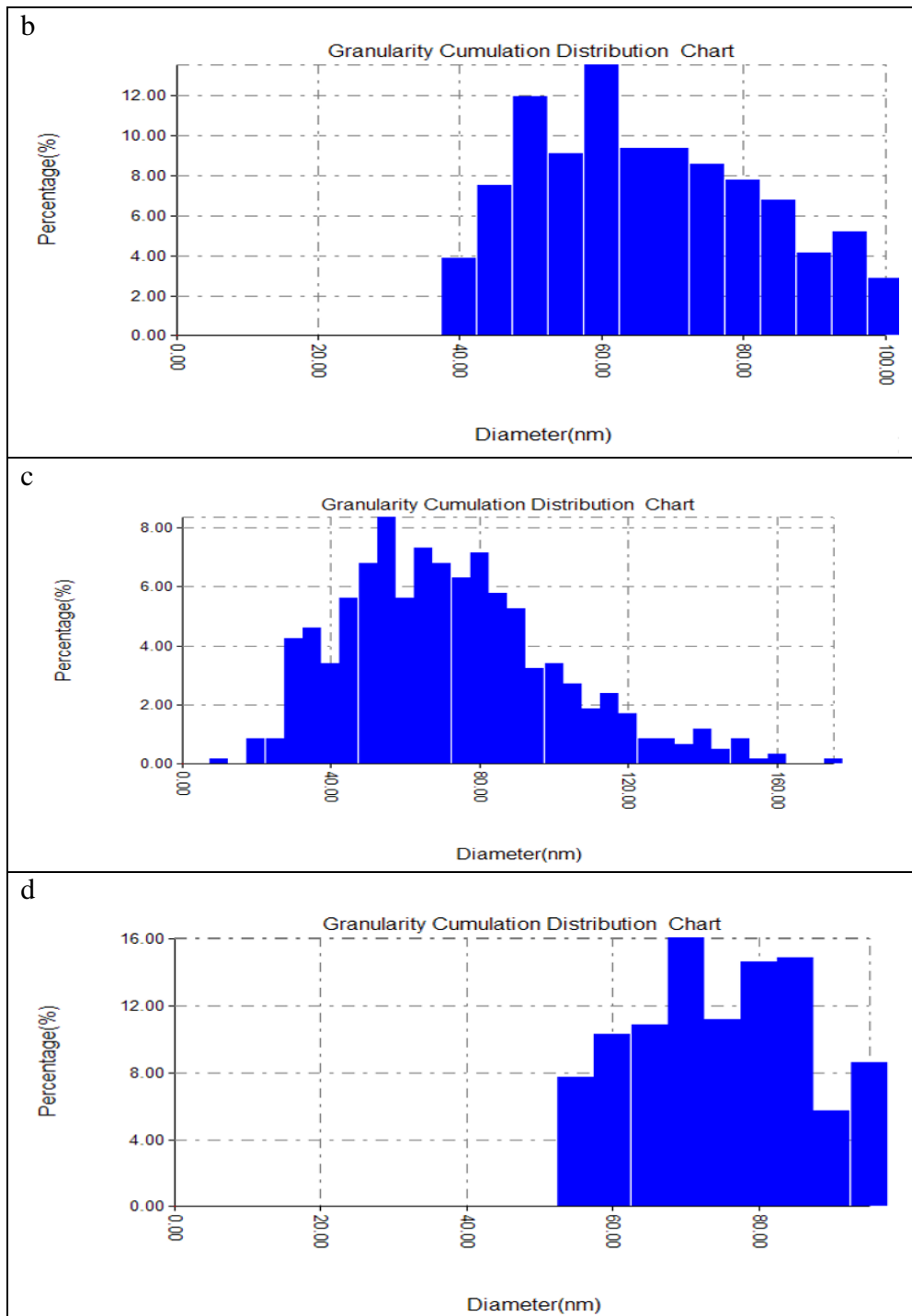
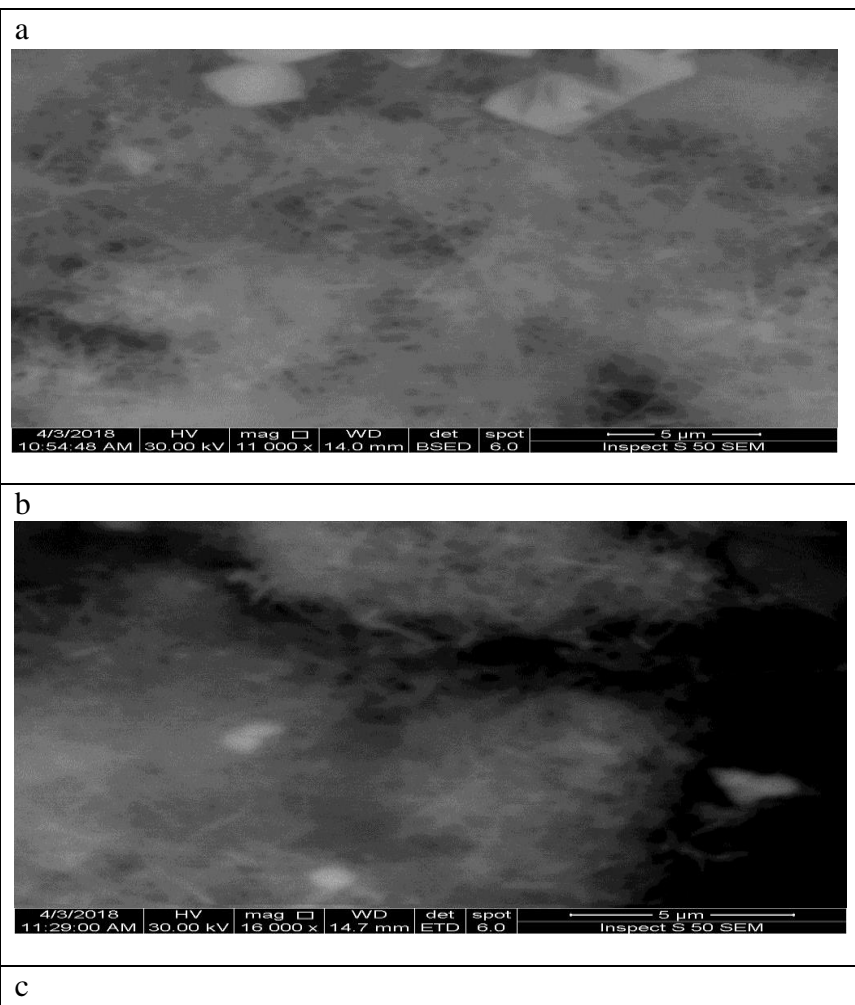


Figure 3: Two and three dimensional AFM images and the morphology o for MnO₂ with annealing temperatures at: (a) 250°C, (b) 400°C, (C) 550°C and (d) 700°C for 120 min.

For magnifications 5 μ m (Fig. 4- a to d), the morphology of the MnO₂ that prepared by hydrothermal method at different temperature (250-700) $^{\circ}$ C was primarily investigated by SEM, according to the morphology of MnO₂ 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 μ m.



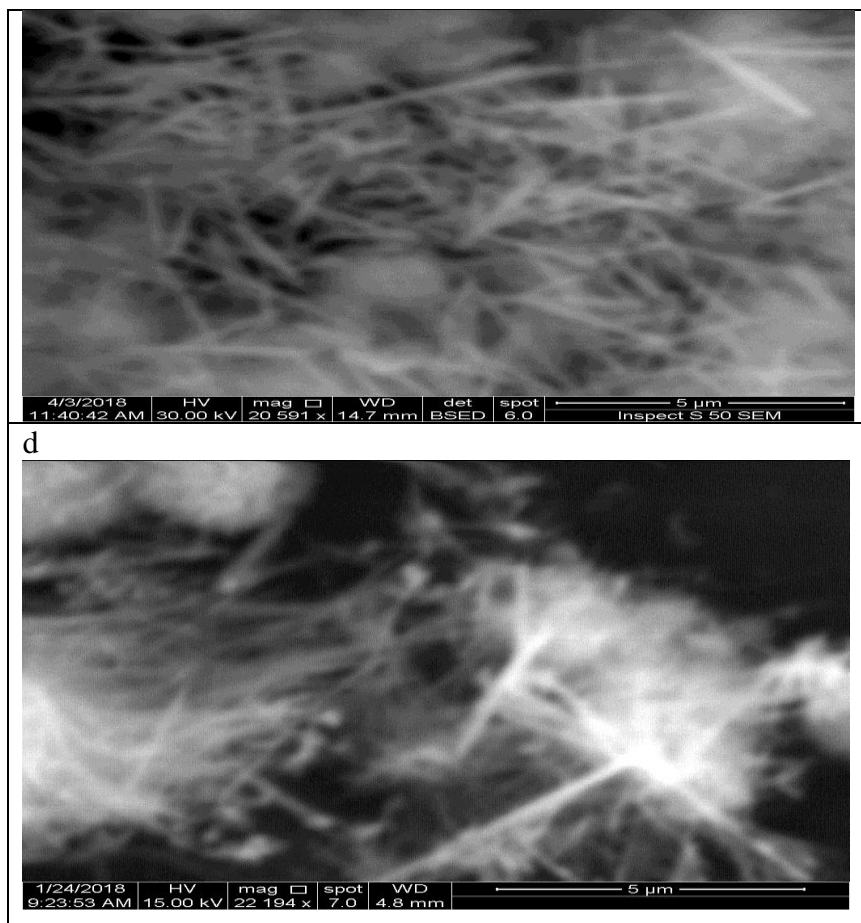


Figure 4: SEM image for MnO₂ at (a) 250°C, (b) 400°C, (C) 550°C and (d) 700°C for 120 min.

The following equation was used to calculate the rate reaction of catalase mimic activity of MnO₂ annealing at (As-prepared -700 °C) for 2 h:

$$\text{Rate of catalase activity (sec}^{-1}\text{)} = (2.303/t) \times (\log (C_0/C)) \quad \dots(6)$$

Where: t = time of reaction (seconds); C₀ and C are total concentration of hydrogen peroxide in cell reaction before and after reaction respectively. Our results show that the 400 °C 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 MnO₂ annealing at (as-prepared - 700 °C for 2 h.

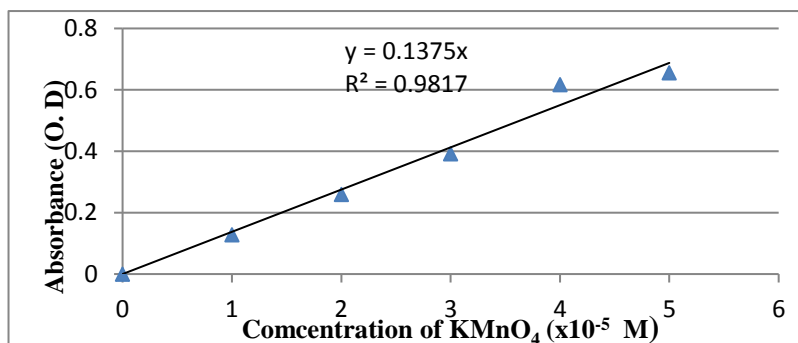


Table 2: The rate of reaction as catalase mimic activity (S^{-1}) of MnO_2 annealing at (as-prepared - 700 °C for 2 h.

Annealing Temperature (°C)	$K \times 10^{-2} S^{-1}$. 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

MnO_2 nanostructures were prepared by hydrothermal method and annealing at different temperatures (250, 400, 550 and 700 °C) for 2 h. The calculation rate of reaction (K) as catalase mimic activity against the low concentration of hydrogen peroxide (2 mM) has been done.

The result found annealing at 400 °C were the highest activity (2.59×10^{-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

حضر ثنائي اوكسيد المنغنيز النانوي بطريقة الضغط الحراري (الايوتوكليف). وتم تلدين ثنائي اوكسيد المنغنيز عند درجات حرارية مختلفة (250، 400، 550، 700°م). اخذت القياسات للمساحيق النانوية ولمتغيرات متعددة ومن ثم شخصت البنية التركيبية وطوغرافية الاسطح بواسطة فحص حيود الاشعة السينيه (XRD)، مجهر القوة الذرية (AFM) و المجهر الالكتروني الماسح (SEM). درست فعالية ثنائي اوكسيد المنغنيز كعامل مقلد لانزيم الكتلينز (الفعالية التحفيزية) ضد بيروكسيد الهيدروجين وباستخدام طريقة جديدة ووجد ان التلدين بدرجة حرارة 400°م هي الافضل. الكلمات الدالة: مسحوق ثنائي اوكسيد المنغنيز النانوي، الحرارة المائية، مقلد انزيم الكتلينز.