

Preparation, Characterization And Nanozymes Activity Of Zno And Sno₂ Nanoparticles

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Abstract

Different nanoparticles zinc oxide (ZnO), and tin dioxide (SnO₂) were prepared by different methods (autoclave and sol-gel). The nanoparticles were annealed at different temperatures (90°C and 400°C). The structures and surface morphology were characterized by Uv/Visible and FT-IR measurements, x-ray diffraction (XRD), Atomic Force Microscope (AFM), and Scanning Electron Microscopy (SEM). The nanozymes (enzyme mimetic) activity as Catalase (CAT), and Peroxidase (Pxase) were measured. The results of nanozymes activity showed there is a maximum activity as CAT for ZnO (90°C) while there is a maximum activity as Pxase for SnO₂ (90°C), and there are decreasing in the activity for both nanoparticles when annealed at 400°C.

Keywords: Zinc oxide, tin dioxide, catalase, peroxidase, nanozyme

1. Introduction

Scientists are interested in nanomaterials and nanocomposites because of their unique magnetic, chemical, optical, and electrical characteristics, which make them useful for a variety of applications, such as catalysts [1],chemical sensors [2], gas sensors [3],antibacterialactivity [4], and colorimetric sensors [5].Nanoparticles in the size range of 100 nm have become a focus of research and concern in recent years. Because of their safety and stability, inorganic metal oxides (TiO₂, MgO, CaO, and ZnO) are studied as antibacterial agents. The minimum antibacterial activity of ceramic powders has been investigated using methods such as indirect conductometric tests[6].ZnO is a material having a direct bandgap (3.37eV)[7] at room temperature, a high exciton binding energy (60 meV), and good chemical stability. It has a hexagonal structure with a = b = 3.250 and c = 5.206 lattice constants[8]. Because of their characteristics and uses, SnO₂ nanostructures have become one of the most significant oxide

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nanostructures[9]. Tin oxide (SnO_2) is one of the most promising n-type wide bandgap semiconducting materials among metal oxides (3.6 eV)[10].Different methods can be used to make zinc oxide nanoparticles whichinclude the sol-gel method [11]. chemical vapor deposition, thermal decomposition, and thermal evaporation process[12], and preparation methods of SnO₂ nanoparticles are similar toZnO nanoparticles chemical vapor deposition, the sol-gel method, and thermal evaporation of oxide powders[13]. The applications that have been used for nano-oxides are imitating enzyme action such as vanadium oxide, cerium oxide, and manganese oxide[14]. At ambient temperatures, nanozymes are a subgroup of nanoparticle-based catalysts that catalyze enzyme-like processes. Nanozymes are appealing not just because of their great stability and inexpensive cost, but also because they may be used to explore basic processes at nanoscale surfaces. Many nanoparticles have oxidase, peroxidase, and/or catalase-like activities, such as gold, graphene oxide, and other metal oxides. It's worth noting that while numerous peroxidase nanozymes have been described (those that use H_2O_2 as a substrate), only a handful exhibit oxidase activity [15]. Catalase (CAT) is a metalloprotein that is present in all oxygenconsuming organisms [16]. Catalase activity in blood is nearly exclusively attributed to erythrocytes since this enzyme is soluble in erythrocytes and human erythrocytes are generally rich in catalase[17-19]. peroxidase is a heme-containing enzyme that oxidizes a wide range of organic and inorganic substances using hydrogen peroxide[11].

In this work, we prepared nanopartcles (ZnOand SnO₂) in different methods and measured the enzymatic activity (Catalase and peroxidase).

2. Experimental

2.1 Materials

Ammonium hydroxide (NH₄OH), Zincacetate Zn(OAC)₂ and Tin chloride (SnCl₂.2H₂O) were purchased fromSigma (Sigma–Aldrich, Taufkirchen, Germany). Urea (NH₂CONH₂)was purchased from (Merck, Germany),Cetyltrimethyl ammonium bromide(CTAP) was purchased from (BDH)and hydrogen peroxide (H₂O₂) was purchased from (Chem-lab).

2.2 Methods

2.3 Preparation of zinc oxide nanoparticles (ZnO NPs)

The hydrothermal method (autoclave) was used to prepare zinc oxide nanoparticles, with minor modifications [12,20]. Zinc acetate (Zn(CH₃COO)₂), urea (NH₂CONH₂), and cetyltrimethylammonium bromide (CTAB) are used in the following processes, dissolve 3 g zinc acetate, 1.25 g urea, and 0.5 g CTAB in 50 ml distilled water, stirring continually until completely dissolved. Then place it in an autoclave and

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heat it at 200° C for 6 hours. When the reaction is finished, the precipitate should be washed three times to remove any impurities, then dried at 90° C for 60 minutes and annealed at 400°C for 120 minutes, as shown in the equations.

 $NH_4CONH_4+3H_2O \rightarrow 2NH_4OH+CO_2.....(1)$

 $Zn (CH_3COO)_2 + 2NH_4OH \rightarrow Zn(OH)_2 + NH_2CH_3COO \dots(2)$

 $NH_2CONH_2 + Zn(CH_3COO)_2 + 3H_2O \xrightarrow{CTAB} Zn(OH)_2 + CO_2 + NH_4(CH_3COO) \dots (3)$

 $Zn(OH)2 \xrightarrow{\Delta} ZnO + H_2O \dots$ (4)

2.4 Preparation of tin dioxide nanoparticles (SnO₂ NPs):-

The sol-gel method was used to make tin dioxide nanoparticles, as described in reference [21]. Tinchloride (SnCl₂.2H₂O), cetyltrimethylammonium bromide (CTAB), and ammonium hydroxide (NH₄OH) were employed, with the first step consisting of dissolving (3 gm.) of tin (II) chloride in distilled water (50 ml) and then adding (0.5 gm.) of cetyltrimethylammonium-ammonium bromide (CTAB).Ammonium hydroxide in distilled water at a ratio of (1:10) was titrated with the above solution until the reaction was complete (the solution became alkaline pH \approx 8). Then it was dried for 60 minutes at 90°C before being annealed at 400°C for 120 minutes, the equations were explained as follows:

 $SnCl_2.2H_2O+2NH_4OH \xrightarrow{CTAB} Sn(OH)_2+2NH_4CI+2H_2O \quad \quad (5)$

$$Sn(OH)_2 + [O] \xrightarrow{\Delta} SnO_2 + H_2O \dots$$
 (6)

 $SnCl_2.2H_2O+2NH_4OH \xrightarrow{CTAB/\Delta/[O]} SnO_2 + 2NH_4Cl + 3H_2O$ (7)

3. Enzyme measurements

3.1 Catalase(CAT) mimetic activitymeasurements

Catalase (CAT) mimetic activitymeasurements were used absorbance by the Uv/Visible spectrometer method at a wavelength of 240 nm as the following procedure:three containers (50 mL) labels as (T, C, and B) to every nanoparticle (ZnO and SnO₂).A weight (0.001g) and (0.002 g) of (ZnO and SnO₂) respectively were added to both T and B containers. Twoand one milliliters of buffer phosphate (50 mM, pH = 7) were added toC, B and T containers respectively. One milliliter of hydrogen peroxide (2.8 mM) was added to both T and C containers. All containers were shaking for 5 minutes, on the

shaker.Measuring the absorbance of each container by the Uv/Visible spectrometer at a wavelength of 240 nm.The following equation was used to determine catalase mimic activity based on first-order reaction[22]

Catalase mimic activity (K) = $(2.303 / t)\log (C_{\circ} / C) \dots (8)$

Where (t) is the reaction time inminutes. C_0 and C are the concentrations of H_2O_2 in the cell reaction before and after the reaction, respectively, C is equal to (C1 - T1).

3.2 Peroxidase mimetic activitymeasurements

Peroxidase mimetic activitymeasurements were used by the Uv/Visible spectrometer method at a wavelength of 292 nm for zinc oxide and tin dioxide as the following procedure: three containers (50 mL) labels as (T, C, and B) to every nanoparticle (ZnO and SnO₂). A weight (0.012g) of (ZnO and SnO₂) were added to both T and B containers. 4.95 mL and 5 mL of buffer phosphate (50 mM, pH = 7.2) were added to T, C, and B containers respectively. 0.05 ml of orthophenylenediamine (OPD)was added to C and T containers. Thenone milliliter of hydrogen peroxide (2.8 mM) was added to all containers. All containers were shaking for 5 minutes, on the shaker. Measuring the absorbance of each container by the Uv/Visible spectrometer at a wavelength of 292 nm. The following equation was used to determine peroxidase mimic activity [23].

U/t min = [C-(T-B)] (Vol/Wt)/t min (9)

Where; B = blank, C = control, T = test, Vol. = total volume of solutionreaction, and Wt. = weight of nanoparticles in container. t = the reaction time after 45 minutes

4. Results and discussion

4.1Optical properties of the nanoparticles solutions.

The optical characteristics of nanoparticle solutions (about 1×10^{-5} M) were produced by dissolving the metal oxides in ethanol. Figure (1) shows the optical prosperity (transmittance) ofmetal oxides at various temperatures (90 °C and 400 °C) between region 250 nm to about 550 nm

4.1.1 The spectrum of ZnO nanoparticles

The spectrum of ZnO nanoparticlesas-prepared display a small drop in transmittance edge (blue shift) from 370 nm to 366 nm with increasing annealing temperatures to 400°C, as seen in figure(1), resulting in optical transmittance and attributed to structural homogeneity and particle crystallization. The following equation can be used to calculate the value of the energy gap [24].

Energy gap (eV) = $1240/\lambda max$ (10)

Where 1240 is the factor used to convert nm to eV and λ max is the maximum transmittance in nm.

According to equation (7) and the results of figure (1), the energy gap of ZnO as-prepared is 3.35eV and that of annealing at 400 °C is 3.38eV, this result agrees with the reference

4.1.2 The spectrum of SnO₂ nanoparticles

The optical transmission of SnO₂ (as-prepared) nanoparticles shows a small rise in the transmittance edge (redshift) with increasing annealing temperature from 366 nm to 372 nm, which is related to an increase in orientation and may be attributable to heat treatment that increases the mobility of atoms in rearrangement processes within the lattice. As a result and equation (7), the energy gap of SnO₂ as-prepared is 3.38 eV, while that of SnO₂ annealing at 400 °C is 3.33 eV, this result agrees with the reference [25].

4.2 Fourier Transform infrared (FT-IR) analysis

4.2.1 FTIR Spectra for Zn(OH)₂ and ZnO nanoparticles

FTIR spectra spectrum of Zn (OH)2 nanoparticles, figure (2-a), show two bands at 3305 cm⁻¹ refer to O-H bond vibrations stretching [26]. The peak at 468 cm⁻¹ relates to Zn-O bonding [27]. While the weak vibrations at 1506 cm⁻¹, and 1010 cm⁻¹ corresponds to the stretching C=O, andC-O for acetate [28]. FTIR spectra spectrum of ZnO nanoparticles, figure (2b), show two bands at 3461 cm⁻¹ and 1606 cm⁻¹ are refer to O-H bond vibrations stretching and bending of water respectively. Meanwhile, the peak at 565 cm⁻¹ corresponds to the stretching Zn-O mode, indicating the synthesis of ZnO[29].

4.1.2 FTIR Spectra for Sn(OH)₄ and SnO₂ nanoparticles

FTIR samples of Sn(OH)₄ nanoparticles figure (2-c), show peaks at 3396 cm⁻¹ and 1639 cm⁻¹ attributed to a surface-absorbed hydroxyl group[30, 31]. The stretching and flexing vibrations were given for bands at 2922 cm⁻¹, 2852 cm⁻¹relate tothe organic trace residues of the CTAB surfactant were ascribed to these C-H peaks [32]. The NH deformation of ammonia and the NH vibration of deforming the ammonium hydroxide has been attributed to the peak at about 1470 cm⁻¹, SnO₂ stretching modes Sn-O-Sn and Sn-OH, respectively, were ascribed to bands of 665 and 554 cm⁻¹ figure (2) [33]. FTIR samples of SnO₂ nanoparticles figure (2-d), show peaks at 3421 cm⁻¹ and 1635 cm⁻¹ attributed to a surface-absorbed hydroxyl group. The smallest strips at 578 cm⁻¹and 559 cm⁻¹ ascribed to Sn–O strip are the most significant absorbents identified after thermal bonding [34].

4.3. X-Ray Diffraction (XRD)

X-ray Powder Diffraction (XRD) to determine their crystal structure was performed using an X-ray diffractometer with cu k α radiation (λ = 1.5418 A) in the range (20–80°).

4.3.1. The X-Ray Diffraction for Zn(OH)₂ and ZnO nanoparticles

X-Ray Diffraction patterns of zinc oxide nanoparticles as prepared is similar to X-ray diffraction (XRD) the crystallinity of annealed ZnO nanoparticles. The XRD spectra of ZnO nanoparticles as prepared see Fig. (3-a) (No. JCPDS Card 008, 82-1042 and 5-0664)[35]. The typical X-ray diffraction (XRD) patterns of annealed ZnO nanoparticles are seen in Fig(3-b) All of the observed XRD patterns included well-defined diffraction reflections at 2= 31.5° , 34.4° , 36.1° , 47.6° , 56.5° , 62.9° , 66.3° , 68.1° , 69.3° , which corresponded to the wurtzite hexagonal phase ZnO lattice planes of (100), (002), (101), (102), (110), (103), (200),(112)[29].The lattice constants (a = b = 3.229 Angstrom and c = 5.175 Angstrom, c/a = 1.602) and diffraction peaks corresponding to the planes (100), (002), (101), (102), (110), (103) obtained from X-ray diffraction data are consistent with the JCPDS data of ZnO

4.3.2. The X-Ray Diffraction for Sn(OH)₂ and SnO₂ nanoparticles

The X-ray findings of SnO₂ heated at 90°C are extremely comparable to the 400°C radiation result (JCPDS 77-0452).The obtained lattice constant a=4.759 Å and c=3.201Å indicate the nanocrystal belongs to the tetragonal system. As in figure (3-c).

 $1/d_{hkl}^2 = (h^2 + k^2)/a^2 + l^2/c^2$ ------(12)

The XRD patterns of SnO₂ particles shows polycrystalline phases and is compared with (JCPDS card no. 41–1445), the patterns display four diffraction peaks at (2Θ = 26.58, 33.88, 38.18, 51.90°, 65.42° and 76.610) that correspond to the diffraction planes (110), (101), (200), (211), (301) and (321) respectively[36]. As in figure (3-d) and table (1).

4.4. Surface Morphology by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX).

The surface morphology image SEM with magnification at (100 nm) and its EDX results of the metal oxides (ZnO and SnO₂) nanoparticles produced by hydrothermal technique and annealed to 400 °C for 120 minutes. The SEM images morphology of ZnO nanoparticles, figures (4- a), demonstrate the nanoparticle aggregation is and the samplesynthesized as nanoflakes. The binding energies of O and Zn are displayed as peaks in the ZnO EDX spectrum figure (4-b) at 0.55, 1.0, and 8.6 keV, respectively. And the SEM images of tin dioxide nanoparticles synthesized by sol-gel method figure (4-c). The shape

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seems clustered foam-like, with tiny agglomerations of SnO_2 nanoparticles. While figure (4-d) represents the EDX spectrum of SnO_2 nanoparticles which confirms the produced are composed of Sn and O are displayed as the peak at 3.5, 4.0, 0.5 keV, respectively.

4.5. Surface Morphology

AFM results of nanoparticles (ZnO and SnO₂) in three (3D) dimension images and Granularity accumulation distribution chartswith different temperatures: (a) as-prepared (90 °C), and (b) 400 °C,

4.5.1 AFM of Zinc oxide nanoparticles

Threediminutions and distribution accumulation of zinc oxide nanoparticles convert from the oval shape (figure 5-a) to a small conical shape (figure 5-b). This relates to converting the hydroxides (Zn(OH)₂) to oxides (ZnO) when heating at a high temperature (400 °C). At the same time the average grain size decreases a little from 77.99 nm (as-prepared) to 72.00 nm (annealing), as in table (2) the decrease in the size may be due to converting of hydroxide to oxide form according to the following equation:

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$
 (13)

4.5.2 AFM of Tin dioxide nanoparticles

Three diminutions and distribution and accumulation of tin dioxide nanoparticles convert from balls shape (figure 5-c) to smaller shape (figure 5-d). This relates to converting some of the hydroxides $(Sn(OH)_4)$ to oxides (SnO_2) when heating at a high temperature (400 °C). The average grain size decreases a little from 91.49 nm (as-prepared) to 88.10 nm (annealing), as in table (2), the little decrease in the size may be due to converting of hydroxide to oxide form according to the following equation:

$$Sn(OH)_4 \rightarrow SnO_2 + H_2O$$
 (14)

5. Applications

5.1Catalase Mimetic Activity

The mimic activities of our produced nanoparticles as Catalase in phosphate buffer solution (50Mm, pH=7.0) by employing a concentration of H_2O_2 were measured spectrophotometrically using the extinction coefficient of 40 M⁻¹.Cm⁻¹ at 240 nm [37].The Catalase mimetic activity was determined by the equation(8).

The results demonstrate that the catalase mimetic activities of nanoparticles change depending on the kind of nanoparticle and the degree of heating. The highest catalase mimetic activity of the nanoparticles (as-prepared) relates to ZnOwhile the lowest activity relates to SnO₂. The sequence of

these mimetic activities was fellow by the following arrangement (ZnO> SnO₂). On the other hand, the lowest Catalase mimetic activity of the nanoparticles (annealing) relates to ZnOwhile the higher activity relates to SnO₂. The sequence of these mimetic activities was fellow by the following arrange (SnO₂ >ZnO), as in figure (6) and table (3).

4.2 Peroxidase Mimics Activity

The mimetic activities of our produced nanoparticles as peroxidase in phosphate buffer solution (50 mM, pH= 7.2), utilizing the reference[30], with minor modification by employing spectrophotometric technique at the wavelength (λ = 292 nm), including the use of orthophenylenediamine solution as an indicator, The equation (9)was used to calculate the peroxidase mimetic activity.The mimetic activities of nanoparticles as peroxidase were varying depending on the nanoparticle type and the degree of heating. The nanoparticles with the highest peroxidase-mimicking activity (as prepared) are SnO₂, while the nanoparticles with the lowest activity are ZnO. The simulation activity was organized in the following order:(SnO₂>ZnO).The nanoparticles with the highest peroxidase-mimicking activity (annealing) are ZnO, while the particles with the lowest activity are SnO₂. The simulation activity was arranged in the following order (ZnO> SnO₂) exactly the opposite of the prepared as shown in figure (7) and table (4).

The very high decrease in the mimetic activity of SnO₂ nanoparticles (annealing) from 5.800 U/min⁻¹ to 0.307 U/min⁻¹ despite convergence in average grain size between both samples (91.49 nm and 88.10 nm) respectively, as in table (4), maybe due to higher activity of hydroxide form (Sn(OH)₄) form asprepared compare with oxide form (SnO₂ annealing form).On the other hand, the increased peroxidase mimetic activity of Zn(OH)₂ nanoparticlesis more than ZnO) as in table (3), although the size of the annealing nanoparticles are smaller than that of as-prepared this indicates that there is no relationship to size in this mimetic activity.

Conclusion

Different methods (autoclave and sol-gel) were used to prepare ZnO and SnO₂ nanoparticles respectively. Both nanoparticles were annealed at 400 °C for 2 hours. Then catalase and peroxidase mimetic activities were determined against H_2O_2 and OPD as substrate. The results indicated that the asprepared of both nanoparticles were the highest as peroxide mimetic activity. While ZnO annealing at 400 °C has the highest catalase mimetic activity compared with as-prepared.

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Figure (1) The optical transmittance for nanoparticles as-prepared (blue line) and annealing at 400 $^{\circ}$ C (red line) of A, ZnO NPs and B, SnO₂ NPs.





Figure (2) : FTIR Spectra for (a) $Zn(OH)_2$ at 90 °C for 60 min , (b) ZnO at 400 °C for 120 min. (c) $Sn(OH)_2$ at 90 °C for 60 min ,(d) SnO_2 at 400 °C for 120 min.



Figure (3) XRD of (a)Zn(OH)₂, (b) ZnO, (c) Sn(OH)₂ and SnO₂ heating at 90°C for 60 min (a and c), annealing at 400 °C for 120 min (b and d).



Figure (4) SEM image of (a) ZnO and (b) its EDX spectrum, (c) SEM image of SnO₂ and (d) its EDX spectrum.





Figure (5): AFM images at 3D and Granularity accumulation distribution charts of (a) ZnO, as-prepared, (b) ZnO annealing, (C) SnO₂ as-prepared and (d) SnO₂ annealing at 400 °C for 120 min.



Figure: (6) Catalase mimetic activities of ZnO and SnO_2 at heating 90 C for 60 min and ZnO and SnO_2 at annealing 400 C for 120 min



Figure (7): Peroxidase mimetic activities of ZnO, SnO_2 at heating 90 °C for 60 min and ZnO, SnO_2 at annealing 400 °C for 120 min.

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	20	hkl	FWHM (deg)	d	D	Lattice	Lattice
	(deg)			(A°)	(A°)	constant	constant c
ZnO						a = b (A°)	(A°)
heating at 90 ∘C	36.39	101	0.556	2.466	150.1	3.231	5.219
for 90 min	31.93	100	0.569	2.799	144.9	-	-
	56.76	110	0.518	1.620	174.1	-	-
ZnO	36.34	101	0.576	2.469	145.0	3.238	5.205
annealing at 400	31.87	100	0.545	2.805	151.2	-	-
∘C for 120 min	56.66	110	0.554	1.623	162.7	-	-
SnO2	26.67	110	3.461	3.339	23.573	4.7229	3.180
at heating 90°C	52.03	211	3.716	1.756	23.772	-	-
	33.95	101	3.771	2.638	22.012	-	-
SnO ₂	26.58	110	1.950	3.350	41.85	4.7377	3.184
annealing at 400	33.88	101	1.970	2.643	42.12	-	-
∘C for 120 min							

Table (1): The results of the XRD for ZnO and SnO₂ at temperatures (90 °C, and 400 °C) for 120 min.

Table (2): Average grain size of nanoparticles at (90 °C, and 400 °C) and their ionic potential.

	Average grair	Ionic Potential	
Metal Oxide	heati	(Charge/radii)	
Nanoparticles	90 °C	400 °C	
ZnO	77.99 nm	72.00 nm	0.027
SnO ₂	91.49 nm	88.10 nm	0.057

Table (3): CAT mimetic activity values of nanoparticles at two (90 °C and 400 °C).

Metal Oxide	CAT activity		
Nanoparticles	(K. min⁻¹)		
	As-prepared	Annealing	
ZnO	260.56	62.29	
SnO ₂	13.39	48.65	

Table (4): Peroxidase mimetic activities of metal oxides nanoparticles at heating 90 $^{\circ}$ C for 60 min and annealing at 400 $^{\circ}$ C for 120 min.

Metal Oxide	Peroxidase activity		
Nanoparticles	(U/min ⁻¹)		
	As-prepared	Annealing	
ZnO	2.533	1.755	
SnO ₂	5.800	0.307	