Bio activity testing of SnO_2-TiO_2 nanocomposite synthesis by chemical methods

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In this work, SnO_2:TiO_2 nano composite with silver dopant have been prepared by chemical route method at preparation temperature 100 ℃ , with 6% Ag ratio. Titanium chloride ($TiCl_3$) has been used as the precursors of TiO_2 and tin chloride ($SnCl_2$) were taken as the precursors of SnO_2 in the laboratory. The prepared samples were described by FESEM, X-Ray diffraction and uv-visible spectrophotometer. Results show that compared to pure SnO_2 and pure TiO_2 ,SnO_2:TiO_2 nano composite calcined 400℃ shows a large surface area. The average crystalline size was estimated from XRD analysis by using Debye-Scherrer's formula and the result shows that the crystalline size increases from (27.78) nm to (29.2354)nm after adding Ag. Bio activity application of the prepared composite has been tested after immersion SnO_2:TiO_2 nano composite in the simulated body fluid SBF, the morphology and particle size of the prepared immersed samples have been estimated after 20 days by FESEM images.

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1. Introduction

Metal oxides based on (nano dispersed and nanostructured) are a very important class of materials with Chemical, electronic, and structural characteristics [1]. Nano materials based on metal oxide materials becoming interesting popular materials which can be used in many medicine and ecology applications such as diagnosis, drug delivery, tissue culturing, gene therapy, DNA sequencing and in cancer treatment [2,3]. Adsorption nanomaterials have a high capacity, fast kinetics and high surface area [4, 5]. Moreover, metal oxide nanomaterials have considerable interested because of high advantages compare with bulk materials and, they have excellent prospects for getting new materials. However, nanomaterials oxides also have a significant debit their operation as environmental pollution with nanoparticles, photocatalysts and adsorbents as well as for the manufacture of monitoring device [6]. It is promising to produce nano composites an incredibly intriguing kind of nanostructures material because of their parcels that could surpass the parcels of its several phases. [7]. Also, nano composites due to their structure have occasionally unique, chemical, and physical characteristics, which can be used in many fields, such as product of new accoutrements can used in the fields of drug, ecology and energy [8,9].

TiO_2 and SnO_2 are semiconductors materials with different band gap (3.2) eV for TiO_2 and (3.6) eV for SnO_2 [10]. These materials have comparable ionic radii. (0.69 Å of Sn4+ and 0.605 Å of Ti4+), this similarity provide these materials an electronic intermixed density states [11]. Also, SnO_2 and TiO_2 have same structural (tetragonal structure) and electronic properties and that lead to easily form a composite and doping [12]. Coupling such materials to form nano composite is claimed to be a successful method for achieving quantum efficiency. [13]. These materials are very good for making nano composites. The extensive use of SnO_2 and TiO_2 as composite increases in the last years compared to other materials because of its special chemical and physical characteristics that make it appropriate for many important field such as, biomedical field, optical

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emitters, catalysts, electronic conductors, and amplified detection signals attention [14–16]. When this material irradiated with light, electrons are generated and move from TiO_2 to SnO_2. As the conduction band of TiO_2 is greater than that of SnO_2, holes stayed in the valence band of TiO_2, whereas electrons moved to the conduction band of SnO_2. [17]. Several methods can be used for investigated (SnO_2-TiO_2) nano composite, these include hydrothermal, sol-gel, thermal evaporation, chemical method, electrospinning, chemical vapor deposition (CVD) [18]. Among these methods, chemical method has been widely used as a low-cost route to prepare nanostructures oxide and good control size, shape and morphology of nanostructures [19]

2. Experimental part

SnO_2-TiO_2 nano composite has been synthesized by chemical precipitation method as in the following procedure: Firstly (0.1 M) of $SnCl_2 \cdot 5H_2O$ was added to 100 ml deionized water and ethanol (2:1) ratio in a 100 mL beaker. To obtain a homogeneous solution, a continuous magnetic stirring was used for 30 min. Then 10 mL of HCl was added gradually while stirring constantly for 10 min to get a transparent solution. Later NaOH was added dropwise to the solution leading the pH became 8. After that for preparing TiO_2 solution: (0.1M) $TiCl_4$ was slowly added dropwise into 100 ml of deionized water and 100ml of ethanol for 30 minutes of constant magnetic stirring followed by the dropwise addition of 10 mL of HCl to the mixture. The reaction was performed under a fume hood because of the large amount of Cl2 and HCl gases evolved from this reaction.

SnO_2:TiO_2 nanocomposite was prepared using chemical route method by mixing the two solution $SnO_{2(0.50)}$:$TiO_{2(0.50)}$ and transfer to 500 mL container with magnetic moving for 30 minute after that the beaker was heated at a temperature of 100 ℃ for 4 h. The result solution washed with deionized water remove the chlorine content. The product was drying on a hot plate and then dried powder was heated at 400℃ for 1 hour.

SnO_2:TiO_2 nano composite was doped by Ag with 6% ratio by adding $AgNO_3$ (0.058 wt. %) to the mixture solution with continues stirrer for 15 min. Then, the mixture was heated at 100 ℃ for 4h to achieve a homogeneous material it was left until the second day for dry. Finally, the sample was washed with distilled water and dried. All samples were annealing in electric oven at 400 ℃ for 1h. The optical properties of the samples were investigated using (double beam spectrophotometer UV-210A Shimadzu).The absorbance have been recorded in the wavelength rang (300-900)nm .

Simulated body fluid (SBF) is a solution that has ions that equivalent to those in the solution of human body, Show Table (1). In order to examine the material's bioactivity, all the prepared Samples immersion in this solution for 20 days**.** To prepare SBF solutions, appropriate quantities of these materials were dissolving in 500 mL deionized water one by one to each material was completely dissolved.

Table 1. Componant of SBF solution.

Order	material	Amount (g/l)
1	$NaHCO_3$	0.350 g
2	Nacl	7.996 g
3	$CaCl_2$	0.278 g
4	KCl	0.224 g
5	$MgCl_2$ $6H_2O$	0.305 g
6	K_2HPO_4 3H2O	0.228 g
7	Na_2SO_4	0.071 g
8	1 M-HCl	40.0 ml
9	$(CH_2OH)_3CNH_2$	6.057 g

3. Result and discussion

The X- ray diffraction pattern of SnO_2-TiO_2 nanocomposite pure and doping with silver (6%wt) are showing in figure (1-a,b,c,d). Figure (1-a) shows poly crystalline structure of SnO_2 with diffraction peaks related to 2Θ = 26.61^0 ,33.8^0 , 37.83^0 , 51.8^0 and 54.72^0 corresponding to (110),(101),(200) , (211) and (220) planes All the peaks related to the tetragonal rutile tin dioxide structure JCPDS : (41-1445).While Figure (1-b) shows x- ray diffraction pattern of SnO_2-TiO_2 nanocomposite, another two peaks related to TiO_2 at 2Θ = (25.27^0) and (48.03^0) were identified as matching the hkl (101) and (220) respectively planes. From the sharp peaks it can be indicated the formation of high crystalline TiO_2–SnO_2 nano composite. Figure (1-c) show the XRD pattern of TiO_2 the diffraction data showed good agreement with the JCPDS card (21–1272) and all the peaks can be indexed as anatase phases of TiO_2. [16]. Additionally, diffraction peak changes of silver doped SnO_2-TiO_2 are observed in figure (1-d). Which 2θ = 32.79^0 correspond to the crystallographic planes (111) for Ag_2O and 2θ= 38.05^0 are assigned as (200) (according to (JCPDS) file No. which is because the ions created by doping NPs may have an ionic radius that is lower than Ti+. Notably, characteristic diffraction peaks of Ag_2O or Ag were detected possibly due to the high content of Ag rate of doping [17].The crystallite size can be estimated for the prepared sample from the XRD pattern using Scherrer equation [20].

$$D = \frac{k\lambda}{\beta cos\theta} \tag{1}$$

where λ is the wavelength of the XRD (equal to 1.5405 Å), k is a constant= 0.9, θ is the reflection angle and β is the FWHM in rad. As shown in Table 2.

Table 2. XRD information.

Sample	Material	2θ	Sample (h k l)	FWHM (β)	D (nm)
Sample1	SnO2	33.85^0	(101)	0.289	28.2471
Sample2	($SnO_{2(0.50)}$ - $TiO_{2(0.50)}$)	25.27^0	(101)	0.293	27.7865
Sample 3	TiO_2	25.27^0	(101)	0.293	27.7865
Sample 4	(SnO_2 - TiO_2) + 6% Ag	33.85^0	(101)	0.284	29.2354

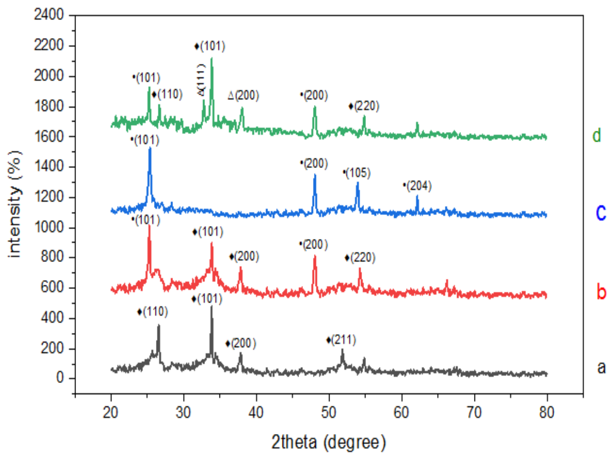

Fig. 1. X-Ray diffraction pattern of (a) pure SnO_2 (b) pure TiO_2 (c) SnO_2-TiO_2 nanocomposite (d) silver doped SnO_2-TiO_2 nanocomposite.

Figure (2 a,b) shows the FE-SEM images of the SnO_2 and TiO_2 samples respectively. The dominate structures obtained from the figure were nanoparticles uniformly distributed with average diameter about (30)nm for SnO_2 and (45)nm for TiO_2 and some pores between them. FE-SEM images of SnO_2-TiO_2 nanocomposite and Ag doped SnO_2-TiO_2 nanocomposite are showing in figure (2) c and d respectively, from figure (2-c) the sample content aggregation of nanoparticles with non-uniform distribution while figure (2-d) showed that the samples contained a composition of nanoparticles with diameter from 70 to 90 nm and a small nanoparticles can be shown on the surface of sample. Also, those particles were agglomerated together which can be because of the heat treatment.

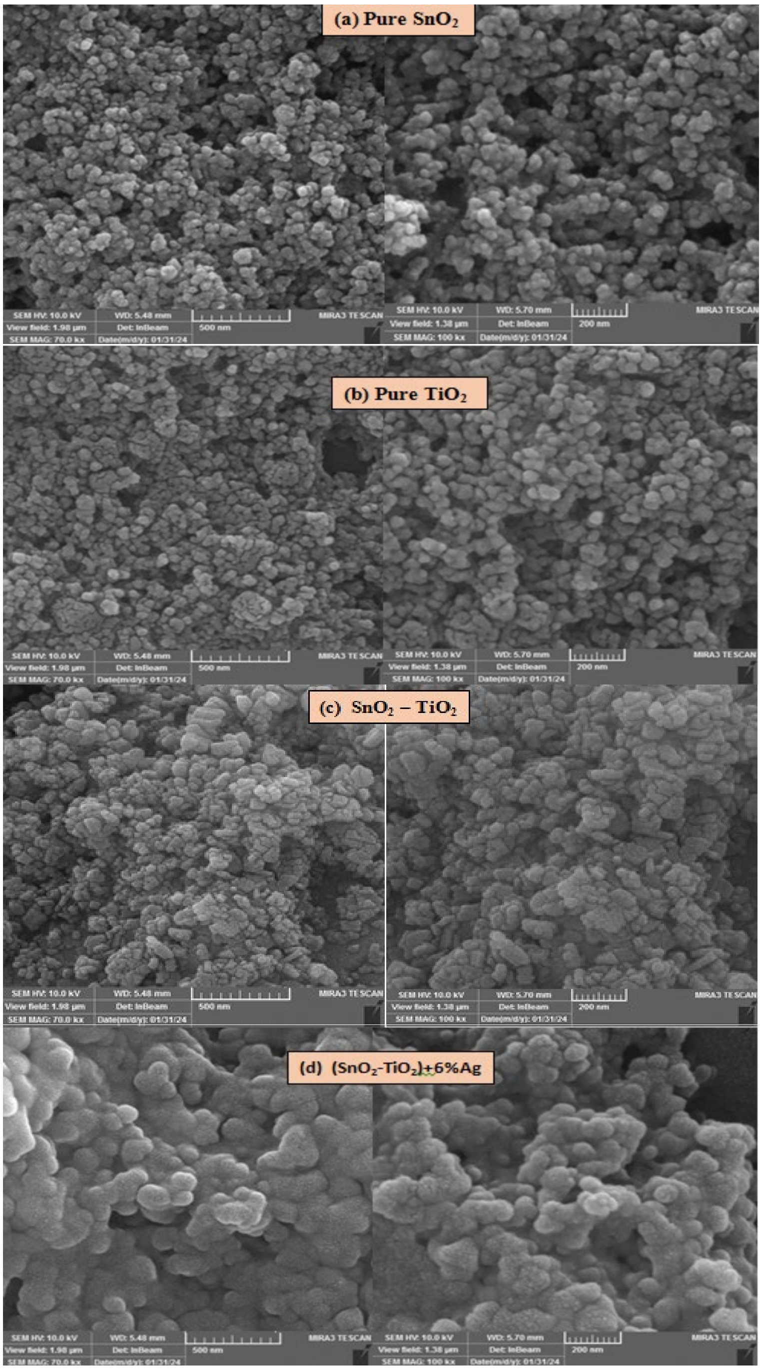

Fig. 2. FE-SEM images of (a) pure SnO_2 (b) pure TiO_2 (c) SnO_2-TiO_2 (d) Silver doped SnO_2-TiO_2.

The relation between the absorbance spectra (A) and wavelength (λ) is shown in figure (3). It can be shown from the figure that the absorbance is low in the visible region, and it decreases sharply between (300 -400)nm region. Also, from the figure the spectra of absorbance were found to increases for SnO_2-TiO_2 nanocomposite comparing with pure SnO_2. While figure (4) shows the absorbance spectra of undoped and Ag doped SnO_2-TiO_2 nanocomposite and it can be notice from the figure that the absorbance spectra increase after doping with Ag and the edge of absorption shifted toward higher wavelength.

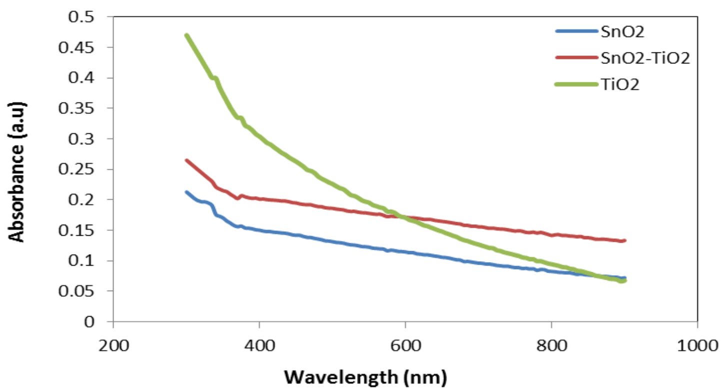

Fig. 3. Absorbance spectra of undoped samples.

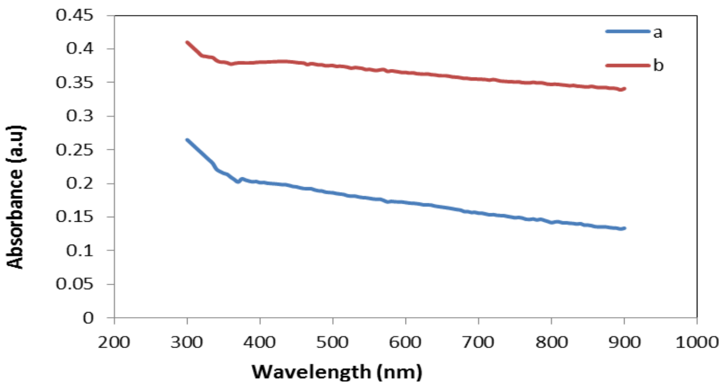

Fig. 4. Absorbance spectra of (a) pure SnO_2-TiO_2 (b) Ag doped SnO_2-TiO_2.

Bioactivity testing of the prepared samples was performed by taking simulated body fluids (SBF) solution. SBF solution was prepared with the chemical investigations matching those of human bodily fluid and the amounts of ions equal to the inorganic constituents of human blood plasma[21]. Figure (5-a,b) shows the FE-SEM image of pure SnO_2 and TiO_2 nanostructures , as seen from the figure agglomeration of Sno_2 and Tio_2 at discrete grains on the surface and unordered crystallites do not adhere to each other. Also, the cavity within the grain increases, that is encouraging for in vitro bioactivity testing.

Figure (5-c) shows the FE-SEM image of SnO_2-TiO_2 nanocomposite after 20 days immersion in the SBF solution. The surface morphology of the SnO_2-TiO_2 nanoparticles is examined by FE-SEM and clearly seen a contact of nanoparticles with each other and the porosity within the grain increases. Compared with the pure SnO_2-TiO_2 nanocomposite, the size of nanoparticles was enlarged and uniform, so it surfaces area was larger. The growth of the fine particles of Ag in regular pattern is observed on the surface of the sample as show in figure (5-d).

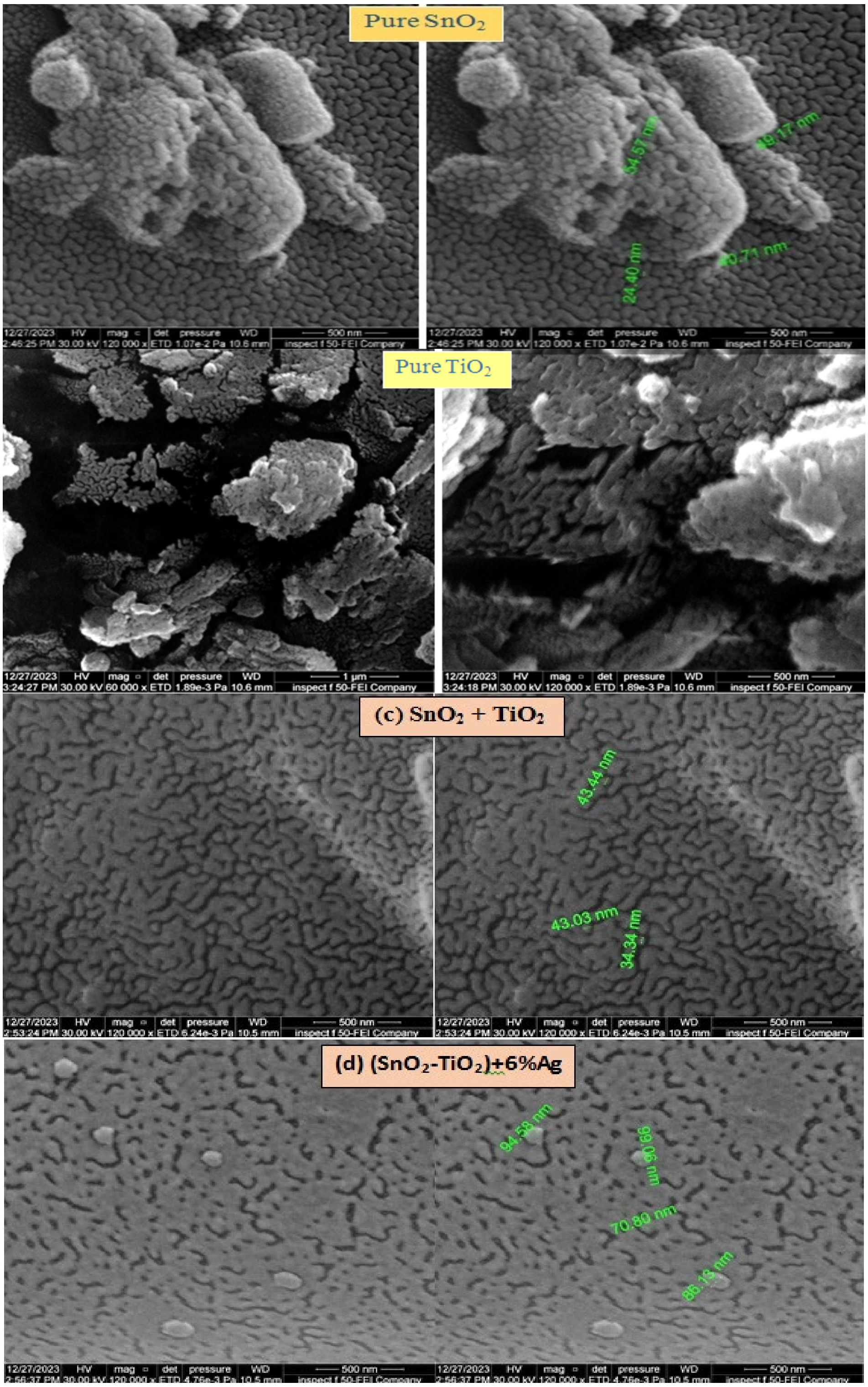

Fig. 5. FE-SEM images after immersion of (a) pure SnO2 (b) pure TiO2 (c) SnO2-TiO2 (d) Silver doped SnO2-TiO2.

4. Conclusion

In summary, pure and Ag doped SnO_2-TiO_2 nanocomposite were effectively produced via chemical route method. The morphological, optical and structural characteristics of the samples were examined. The result of the XRD revealed that the crystallite size of prepared composite increases after doping with Ag. The obtained nanocomposite displayed a polycrystalline structure, Also the interaction of nanocomposite of with (SBF) solution was successfully achieved. Uniform distribution of spherical NPs on the surface of nanocomposite showed good morphologic effects that provided high efficiencies biomaterial.

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