

## Title Page (with Author Details)

# Property Analysis of $\beta$ -Tetragonal Bismite Thin Films: Varied Concentrations and Enhanced Photocatalytic Efficiency

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## Acknowledgements

The authors would like to thank the Algerian Directorate General for Scientific Research and Technological Development-DGRSDT for financial assistance.

Authors wish to thank Mr. Saâd Rahmane and Mr. Brahim Gasmi for his assistance in XRD data acquisition from (LPCMA), University of Biskra, Algeria and Pr. Tibarmacine from the University of Biskra, Algeria.

## Manuscript (Without Author Details)

# Property Analysis of $\beta$ -Tetragonal Bismite Thin Films: Varied Concentrations and Enhanced Photocatalytic Efficiency

### Abstract

In this study, we thoroughly examine  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> thin films as potential photocatalysts. We produced these films using an environmentally friendly Sol Gel method that is also cost-effective. Our research focuses on how different precursor concentrations, ranging from 0.1 M to 0.4 M, affect the photocatalytic performance of these films. We conducted a comprehensive set of tests to analyze various aspects of the films, including their structure, morphology, topography, optical properties, wettability, and photocatalytic capabilities. These tests provided us with a well-rounded understanding of the films' characteristics. To assess their photocatalytic efficiency, we used Methylene Blue (MB) as a contaminant and found that the films, particularly those with a 0.1 M concentration, achieved an impressive 99.9% degradation of MB within four hours. The 0.1 M film had a crystalline size of 39.7 nm, an indirect band gap of 2.99 eV, and a contact angle of 51.37°. Our findings suggest that  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> films, especially the 0.1 M variant, have promising potential for treating effluents from complex industrial dye processes. This research marks a significant step in utilizing sustainable materials to address pollution and environmental remediation challenges.

**Keywords:** Bismuth oxide; Dip coating; photocatalysis; Thin Films; Wettability.

## 1. Introduction

Organic dyes pose a considerable threat to environmental contamination [1–3]. They exhibit high levels of toxicity and can be hazardous when released into the environment, posing risks to aquatic organisms, humans, plants, and animals [4]. Therefore, it is crucial to implement effective treatment of these textile effluents before their discharge into the environment [5]. Out of the numerous techniques at hand, photocatalytic technology emerges as one of the foremost and highly effective methods for the elimination of organic dyes [6,7].

In this procedure, the degradation of pollutants in water is achieved by utilizing a catalyst composed of semiconductor nanoparticles and a radiation source. Typically, ultraviolet radiation is employed, although certain studies explore the utilization of solar radiation [8], which is the reagent of choice for the process of photocatalysis due to its abundance, low cost, and environmentally friendly nature [9]. Many semiconductors such as face centered ZnO [10], CdS, MoS<sub>2</sub>, ZrO<sub>2</sub> [11], and TiO<sub>2</sub>, were used for photocatalysis [12]. Among them, Bi<sub>2</sub>O<sub>3</sub> nano-structured thin films have been proven to be valuable photo-catalyst [13]. Bismuth oxide has many advantages, including a large energy bandgap ranging from (2 to 3.96 eV) [14], also has a high refractive index and dielectric permittivity [15]. Bi<sub>2</sub>O<sub>3</sub> generally exhibits six crystallographic phases viz  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> (monoclinic),  $\beta$ - Bi<sub>2</sub>O<sub>3</sub> (tetragonal),  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> (body-centered cubic),  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> (face-centered cubic),  $\epsilon$ -Bi<sub>2</sub>O<sub>3</sub> (orthorhombic), and  $\omega$ -Bi<sub>2</sub>O<sub>3</sub> (triclinic) [16].

Moreover, heat of the stable low-temperature polymorph  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> results in the formation of the  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> phase at about 730 °C, which, melts at roughly 825 °C. However, two transitions can occur during cooling:  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> to  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> at 650 °C or  $\delta$ -

۲۵ Bi<sub>2</sub>O<sub>3</sub> to  $\gamma$ - Bi<sub>2</sub>O<sub>3</sub> at 640 °C [17]. A variety of deposition methods are used to produce  
۲۶ Bi<sub>2</sub>O<sub>3</sub> thin films, including reactive pulsed laser deposition[18], reactive pulsed laser  
۲۷ deposition [19], dip coating [20], chemical vapor deposition [21], and hydrothermal  
۲۸ synthesis [22]. The dip coating method is one of the low-cost and simple processing  
۲۹ methods. It has attractive advantages including a nonhazardous and well suitable for  
۳۰ deposition at low temperatures [20].

۳۱ Methylene blue finds extensive usage in various applications, such as chemical  
۳۲ indicators, pigments, biological staining, and more, primarily because of its  
۳۳ affordability, solubility in water, and strong coloration [23]. This compound possesses  
۳۴ an aromatic ring structure that is notably resistant to natural decomposition in water  
۳۵ samples [24]. It is crucial to emphasize that the introduction of methylene blue (MB)  
۳۶ into the human body can lead to severe nervous system damage [25], resulting in health  
۳۷ concerns like eye irritation, breathing difficulties, mental disorientation, vomiting, and  
۳۸ excessive perspiration [26].

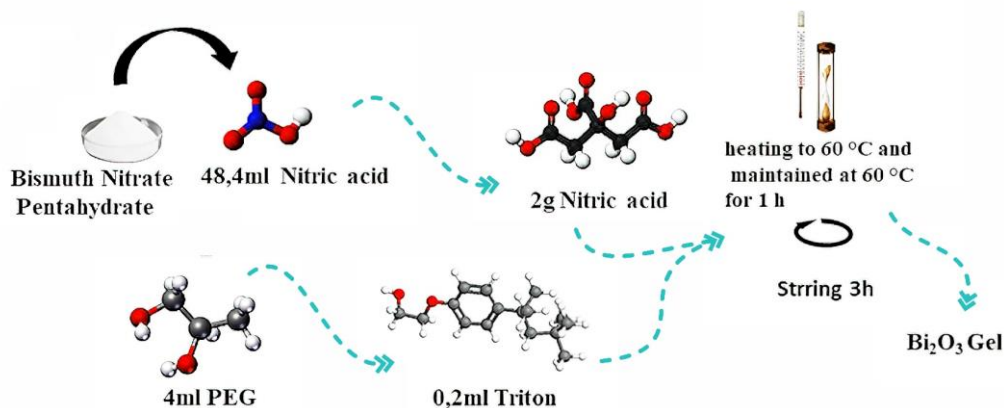
۳۹ To promote the photocatalytic activity of Bi<sub>2</sub>O<sub>3</sub>, Wu Xiaohong et al. demonstrated  
۴۰ that Bi<sub>2</sub>O<sub>3</sub> thin films obtained through a Sol-gel synthesis route and deposited via dip-  
۴۱ coating method showed photocatalytic activity in the degradation of Rhodamine B,  
۴۲ being this property related to the different temperatures applied during thermal  
۴۳ treatment under UV visible irradiation [14]. H. Baqiah et al. studied the Effects of  
۴۴ precursor concentration on the microstructural, optical and photoelectrochemical  
۴۵ properties of Bi<sub>2</sub>O<sub>3</sub> films synthesized by sol-gel method [27]. These studies have not  
۴۶ investigated the influence of the precursor concentration of Bi<sub>2</sub>O<sub>3</sub> on the photocatalytic  
۴۷ performance of MB using the sol-gel with dip-coating method.

48 Within the confines of this manuscript, we have meticulously employed the Sol-gel  
49 dip-coating technique to fabricate Bi<sub>2</sub>O<sub>3</sub> thin films atop transparent glass substrates.  
50 The prime objective of this scholarly endeavor is to delve into the intricate interplay of  
51 precursor concentrations (0.1, 0.2, 0.3, and 0.4 M) and their consequential impact on  
52 the photonic prowess of the generated samples. This research embarks on an  
53 exploration of paramount significance: the measurement of the photocatalytic prowess  
54 of these films. Under the radiant of sunlight, their efficacy in the degradation of  
55 methylene blue is discerningly examined. To fully grasp the multifaceted attributes of  
56 these thin films, analytical tools are meticulously orchestrated. X-ray diffraction  
57 (XRD), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM),  
58 UV-VIS spectroscopy, profilometry, and contact angle measurement collectively  
59 contribute to unraveling the nuanced characteristics of these films.

## 60 **2. Materials and methods**

### 61 *2.1. Preparation of Bi<sub>2</sub>O<sub>3</sub> Thin Films*

62 The following technique was used to elaborate nanostructured Bi<sub>2</sub>O<sub>3</sub> films: Bi-  
63 (NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O was dissolved in a 48.4 mL nitric acid solution (67.5% purity) with  
64 volume ratio [1:8 HNO<sub>3</sub>: H<sub>2</sub>O]. Then, 4 mL of polyethylene glycol  
65 (HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>200</sub>H) was added to the solution, followed by 2 g of citric acid; the  
66 solution was stirred for 15 min before each addition, and then 0.2 mL of Triton X-100  
67 (t-Oct-C<sub>6</sub>H<sub>4</sub>-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>x</sub>. OH, x=9-10) as a surfactant was added drop by drop. After  
68 that, the solution was well stirred for 3h to obtain Sol solution. The sol was heated to  
69 60 °C for 90 min to form a gel. A schematic diagram of the sol-gel synthesis was given  
70 in **Fig. 1**.



**Fig .1.** Schematic diagram of  $\text{Bi}_2\text{O}_3$  preparation by sol-gel synthesis.

The solutions have been deposited on glass substrates (*MICROSCOPE SLIDES*, No. 7101), with dimensions of  $(7.5 \times 2.5 \times 0.1 \text{ cm}^3)$ . Glass slides were cleaned by ultrasonic cleaning in acetone ( $\text{C}_3\text{H}_6\text{O}$ ) and deionized water for 10 min each, then dried in open air to get well-adhered and smooth films. The weight of glass substrates was measured before and after deposition solutions to measure the thickness of samples using a sensitive balance with four digits (an analytical balance). Following that, the glass substrates were immersed in the solution for 3 min before being withdrawn at 5 cm/min and dried at 110 °C for 10 min to allow organic components to be removed. This process was repeated 10 times. The films were annealed with a heating rate of 5 °C/min for 2 h at 550 °C because the crystallization of bismuth oxides annealed at 550 °C is better than that of bismuth oxides annealed at lower temperatures due to the crystallization of the T (tetragonal) phase of bismuth oxide [28].

## 2.2. Film characterization:

$\text{Bi}_2\text{O}_3$  thin films were characterized by using different physical techniques.  $\text{Bi}_2\text{O}_3$  crystalline structure of the samples was characterized using grazing-incidence X-ray diffractometry (*D8 Advance*) using  $\text{Cu K}\alpha$  irradiation of wavelength 0.15405 nm in the

1.09 2θ range of 20–80°. The crystallite size micro strain and dislocation density of the  
1.10 samples determined XRD from spectrum peak broadening.

1.11 The 3D surface topography and surface roughness were assessed using a Tencor P-  
1.12 7 mechanical profilometer, which was operated under standard environmental  
1.13 conditions at room temperature. This evaluation utilized the 2-bar method with a  
1.14 customized filter adjustment, specifically employing a Gaussian filter with a cut-off  
1.15 value of 0.800 μm, while addressing edge effects as well.

1.16 The surface morphology and elemental composition were obtained by field emission  
1.17 scanning electron microscopy (*JEOL JSM 5800*) combined with energy dispersive X-  
1.18 ray (EDX) analysis. The surface roughness of the samples was measured by  
1.19 profilometer (*Tencor P-7*).

1.20 Thickness measurement was carried out with the gravimetric weight difference  
1.21 method. The transmittance and absorbance spectra were recorded in UV–VIS  
1.22 spectrophotometer (*Jasco V-770*) over the 300–900 nm wavelength range. And contact  
1.23 angle measurements are performed via the sessile drop method with IC software.

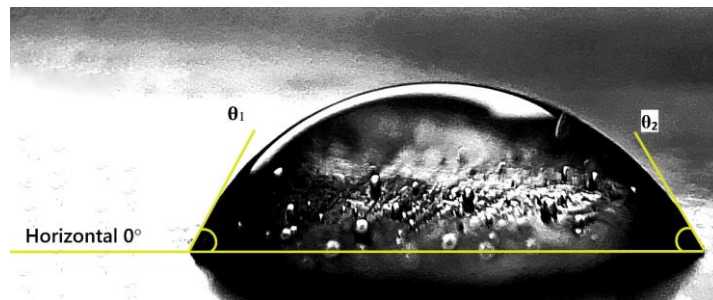
### 1.24 2.3. Contact angle measurement

1.25 The contact angle measurement reflects the ability of a liquid to spread over a surface  
1.26 by wettability. The contact angles of water drop for various bismuth thin films were  
1.27 measured at room temperature in ambient atmosphere by homemade method.  
1.28 Micropipette (*SCIOLOGEX-iso 9001/13485*) was used to meticulously measure the  
1.29 volume of each drop (10 μl), and the distance between micropipette needle and the  
1.30 sample was fixed at 7 mm. All contact angles were averaged from five measurements  
1.31 with a standard deviation of approximately 5%. The average value of each drop contact

112 angle was determined using IC software. **Fig. 2** describes how the average water droplet  
113 contact angle was measured using the following equation:

$$114 \quad \theta_{average} = (\theta_1 + \theta_2)/2 \quad (1)$$

115 Where  $\theta_{average}$  is the average angles of  $\theta_1$  and  $\theta_2$  ( $^\circ$ ),  $\theta_1$  is the angle on the left of a  
116 water drop ( $^\circ$ ),  $\theta_2$  is the angle on the right ( $^\circ$ ) [3,29,30].



117

118 **Fig. 2.** The form denotes how the average value drop's contact angle was calculated.

#### 119 2.4. Preparation of the photocatalytic process for MB

120 The photocatalytic activities of  $\text{Bi}_2\text{O}_3$  photocatalysts were evaluated by the  
121 photodegradation of MB dye under sunlight irradiation at  $\sim 37$   $^\circ\text{C}$ . Each film with  
122 dimensions of  $(4.1*2.5*0.1 \text{ cm}^3)$  was immersed in 100 ml of MB solution (2 mg/L) for  
123 1h in the dark to reach the adsorption-desorption equilibrium between  $\text{Bi}_2\text{O}_3$  particles  
124 and MB, then exposed to sunlight with stirring for 4 hours. After that, a 5 ml sample  
125 was extracted from each suspension at regular intervals (1h) using syringe filter during  
126 the irradiation. After collecting the samples, we recorded UV-vis transmittance of the  
127 samples from 300 to 800 nm to measure the degradation of methylene blue [31].

### 128 3. Results and discussion

129 **Table 1.** Data analysis summary

	Unit	Thin films with different precursor concentrations
--	------	--



		0.1M	0.2M	0.3M	0.4M
<i>Crystallographic dominant Phase</i>		$\beta$ -Bi <sub>2</sub> O <sub>3</sub>	$\beta$ -Bi <sub>2</sub> O <sub>3</sub>	$\beta$ -Bi <sub>2</sub> O <sub>3</sub>	$\beta$ -Bi <sub>2</sub> O <sub>3</sub>
<i>Crystal Size</i>	nm	28.6	48.6	41.3	31.8
<i>Surface Roughness (Rq)</i>	nm	18.3	18.4	12.4	8.73
<i>Film Thickness</i>	nm	~40	~73	~83	~115
<i>Transmission in Visible range</i>	%	78	68	68	63
<i>Optical direct Band Gap</i>	eV	3.34	3.41	3.53	3.33
<i>Optical Indirect Band Gap</i>	eV	2.99	3.1	3.24	2.97
<i>Bi Content</i>	wt.%	18.41	22.33	23.27	31.04
<i>O Content</i>	wt.%	34.73	29.88	30.53	27.48
<i>Si Content</i>	wt.%	46.87	47.80	46.20	40.29
<i>Average contact angle</i>	°	51.37±2.1 3	45.57±2.68	67.14±3.6 6	61.61±3.21
<i>MB degradation</i>	%	~99	~96	~95	~93
<i>Constant rate</i>		1.00	0.81	0.76	0.71

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### ۱۳۱ 3. ۱. X-ray Diffraction

۱۳۲ XRD technique was used to analyze the structure property of the films. The recorded  
 ۱۳۳ XRD patterns of the deposited thin films are shown in **Fig. 3(a)**. Moreover, XRD  
 ۱۳۴ patterns showed that the common structure is corresponding to Tetragonal (T) phase.  
 ۱۳۵ The films (0.1, 0.2, and 0.3 M) mainly consist of monoclinic and tetragonal phases,  
 ۱۳۶ which are labeled M and T, respectively. At 0.4 M film, a new peak appeared  
 ۱۳۷ corresponding to cubic phase, which has been reported by Wu Xiaohong et al. [14]. The  
 ۱۳۸ average crystallite size of the Bi<sub>2</sub>O<sub>3</sub> thin films was estimated using the full width at half  
 ۱۳۹ maximum (FWHM) from the line broadening of the tetragonal orientation. The average  
 ۱۴۰ crystallite sizes were calculated using the Scherrer formula.

$$۱۴۱ \quad D = k \lambda / \beta \cos\theta \quad (2)$$

۱۴۲ where D is the crystal diameter, k is the Scherer constant and is taken equal to 1,  $\lambda$  is  
 ۱۴۳ the wavelength of the X-rays, and  $\beta$  is the full width at half maximum (FWHM) of X-  
 ۱۴۴ ray diffraction peaks in radians [32]. The average crystallite size of the Bi<sub>2</sub>O<sub>3</sub> films

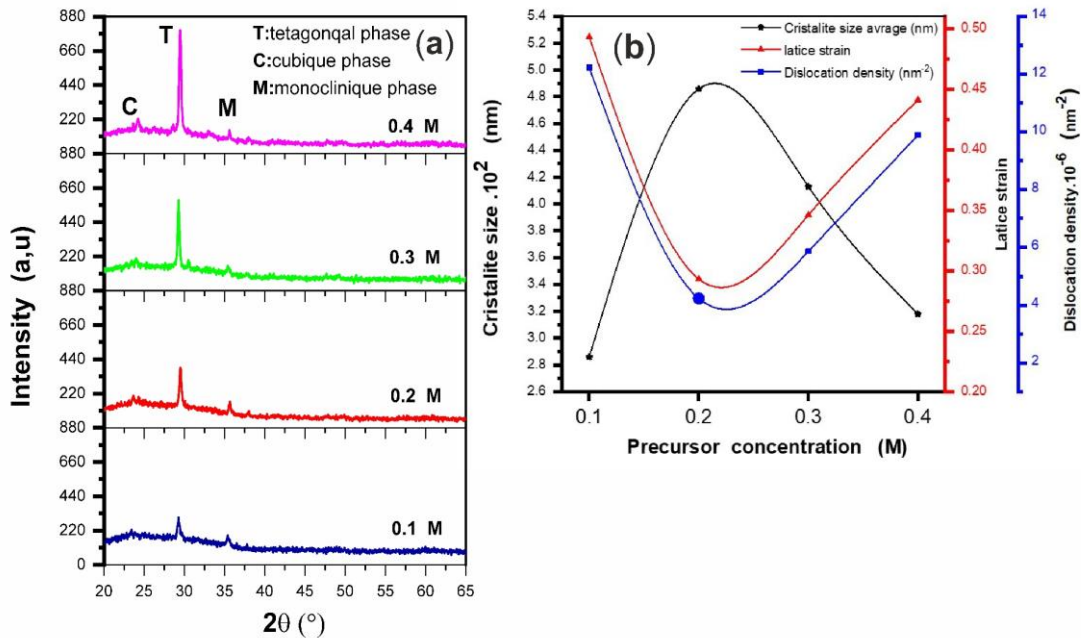
140 prepared by molar precursors of 0.1, 0.2, 0.3, and 0.4 M was found to be 506, 480, 407,  
 146 and 360 nm, respectively.

147 
$$(\epsilon) = \beta \cos \theta / 4. \pi \quad (3)$$

148 The dislocation density ( $\delta$ ), which represents the defects amount in the sample, is  
 149 defined as the length of dislocation lines per unit volume of the crystal [33], and is  
 150 calculated using the following relation [34]:

151 
$$(\delta) = 1/D^2 \quad (4)$$

152 The structural parameters such as crystallite size, strain ( $\epsilon_{\text{average}}$ ), and dislocation  
 153 density ( $\delta_{\text{average}}$ ) are listed in **Table 2**. The variation of these parameters was function  
 154 of the molar precursor, as shown in **Fig. 3(b)**.



155  
 156 **Fig. 3. (a)** XRD spectra of bismuth oxide films prepared by different precursor  
 157 concentrations. **(b)** The variation of crystallite size, lattice strain, and dislocation  
 158 density as a function of molar concentration of precursor.

169 It was noticed that the crystallite size varies (from 286 to 486 nm) has inverse relation  
 170 with the full width at half maximum FWHM. The small value of ( $\delta$ ) obtained in the  
 171 present study confirmed the good crystallinity of the  $\text{Bi}_2\text{O}_3$  thin films [35]. There is a  
 172 direct correlation between dislocation density (from  $9.88 \cdot 10^{-6}$  to  $1.22 \cdot 10^{-5}$ ) FWHM as  
 173 well as strain, since the more strain creates more dislocations in the structure of the  
 174 crystal. This result is in agreement with the previously reported [36].

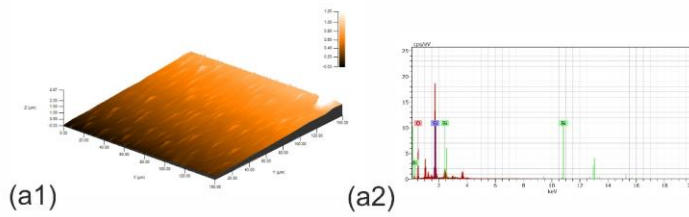
175 **Tables 2.** The structural parameters of various concentration precursor  $\text{Bi}_2\text{O}_3$  thin films.

<i>Precursor concentration</i>	<i>Position <math>2\theta(\text{deg})</math></i>	<i>d spacing</i>	<i>FWHM <math>B_T(\text{deg})</math></i>	<i>D(nm)</i>	<i><math>\delta</math> dislocation density (<math>\text{nm}^{-2}</math>)</i>	<i><math>\varepsilon</math> lattice strain</i>
<i>0.1M</i>	29.28	3.05	0.29	286	$1.22 \cdot 10^{-5}$	0,49
<i>0.2M</i>	29.51	3.06	0.17	486	$4.23 \cdot 10^{-6}$	0,29
<i>0.3M</i>	29.27	3.05	0.20	413	$5.86 \cdot 10^{-6}$	0,34
<i>0.3M</i>	29.43	3.03	0.26	318	$9.88 \cdot 10^{-6}$	0,44

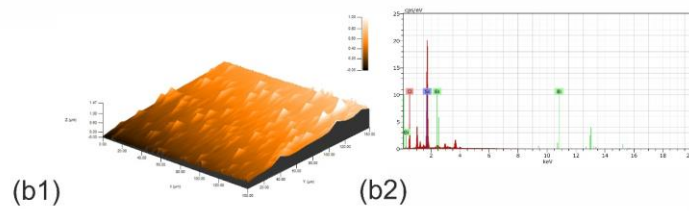
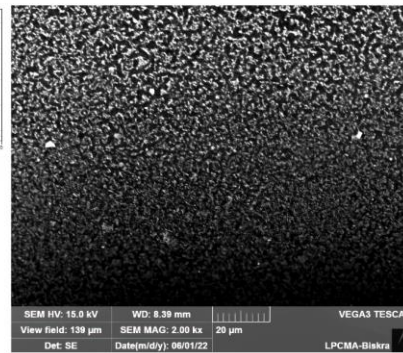
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### 177 3.2. $\text{Bi}_2\text{O}_3$ thin films morphological and 3D surface topography

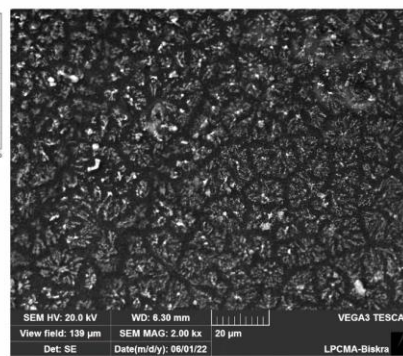
178 The surface morphology of  $\text{Bi}_2\text{O}_3$  films (from 0.1 to 0.4 M) was carried out using  
 179 Scanning Electron Microscope (SEM), as shown in **Fig. 4(a-d)**, respectively. All the  
 180 films have irregular island morphology with good overall coverage. **Fig. 4a** shows  
 181 isolated islands that are not clustered with each other. When the precursor concentration  
 182 is increased, the island grains size increase, this is due to agglomeration in thicker film  
 183 resulting grains growth as shown in **Fig. 4(b)** and slightly decreases until the film surface  
 184 appears as big grains that are more compact and denser, as shown in **Fig. 4(d)**.



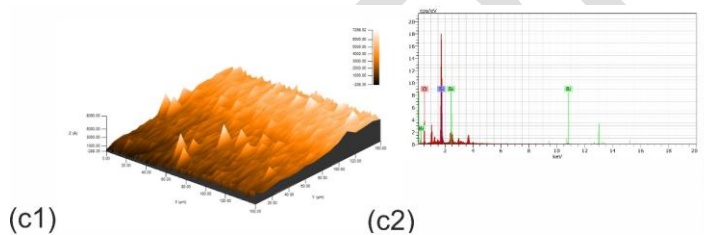
El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Si	14	K-series	20.26	50.14	39.78	0.89
O	8	K-series	17.25	42.69	59.45	2.28
Bi	83	L-series	2.90	7.17	0.76	0.21
Total:			40.41	100.00	100.00	



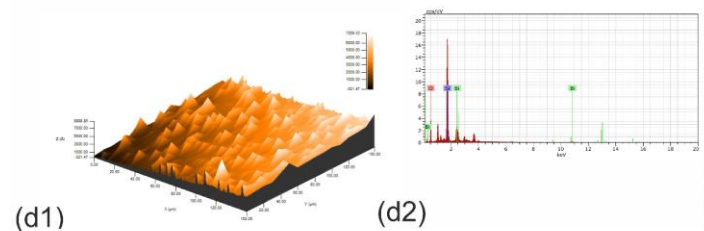
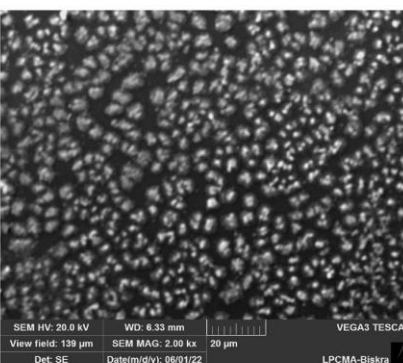
El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Si	14	K-series	22.30	44.44	37.41	0.98
O	8	K-series	20.71	41.27	60.98	2.71
Bi	83	L-series	7.17	14.28	1.62	0.36
Total:			50.18	100.00	100.00	



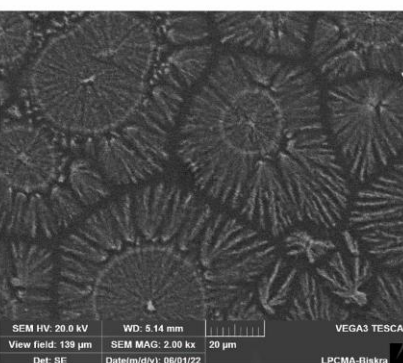
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El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Si	14	K-series	24.38	42.36	43.49	1.07
O	8	K-series	16.79	29.17	52.58	2.33
Bi	83	L-series	16.39	28.48	3.93	0.69
Total:			57.55	100.00	100.00	



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Si	14	K-series	23.72	40.18	43.36	1.04
Bi	83	L-series	19.13	32.40	4.70	0.78
O	8	K-series	16.18	27.42	51.94	2.26
Total:			59.03	100.00	100.00	



۱۷۶

177 **Fig. 4.** SEM images and EDS spectrums of Bi<sub>2</sub>O<sub>3</sub> films synthesized by the different  
 178 precursor concentrations: (a2) 0.1, (b2) 0.2, (c2) 0.3, and (d2) 0.4 M.

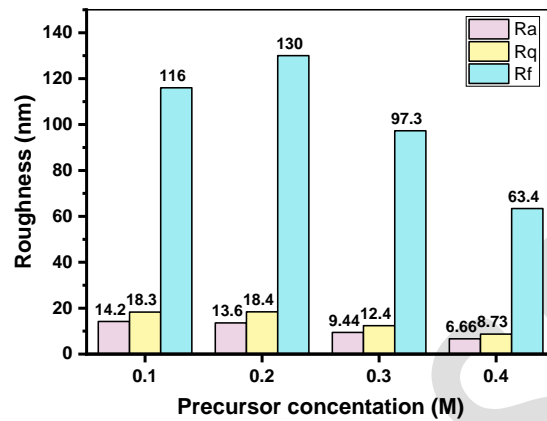
179 The result of cross-sectional SEM images supports the XRD patterns that increasing  
 180 the intensity of all diffraction peaks are influenced by the thickness of film. Which is  
 181 good agreement with reported [37]. A quantitative analysis of the surface topography  
 182 was performed from the data obtained by stylus profilometry. The investigated  
 183 parameters include the average roughness, Ra, which is the arithmetic average height  
 184 from a mean line over some evaluation length L; the second parameter is the root-mean-  
 185 square roughness, Rq, indicating the geometric average height measured from a mean  
 186 line within sampling length L; Rt denotes the third parameter and corresponds to the  
 187 distance between the highest peak and deepest valley of the profile within the evaluation  
 188 length L) [38]. The roughness parameters Ra, Rq, and Rt of different precursor  
 189 concentrations are shown in **Table 3.** **Figs. 4** and **5** indicates that Rq values ranged from  
 190 8.73 to 18.3 nm, which are slightly higher than Ra (6.66 to 14.2 nm) values, indicating  
 191 that the average amplitude from the mean line is higher than the average of peaks and  
 192 valleys in the height direction.

193 **Table 3.** 3D surface topography roughness analysis and shape parameters for Bi<sub>2</sub>O<sub>3</sub>  
 194 thin films.

<i>Roughness profile (nm)</i>	<i>Precursor concentration (M)</i>			
<i>Parameters</i>	0.1	0.2	0.3	0.4
<i>Rt (nm)</i>	116	130	97.3	63.4
<i>Rq (nm)</i>	18.3	18.4	12.4	8.73
<i>Ra (nm)</i>	14.2	13.6	9.44	6.66

195 The highest roughness values (18.4 and 18.3 nm) correspond to the compounds  
 196 deposited with 0.2 and 0.1M films, which increase the photocatalytic efficiency. The

197 lower roughness values were 9.44 nm and 6.66 nm, corresponding to 0.3 and 0.4 M  
198 films. Larger surface grains of prepared films engendered a rougher surface feature.  
199 Similarly, a substantially increased surface grain size, as reported in the ZnO film [39].



200

201 **Fig. 5.** The roughness parameters Ra, Rq, and Rf of Bi<sub>2</sub>O<sub>3</sub> films prepared at various  
202 molar concentrations.

### 203 3.3. Bi<sub>2</sub>O<sub>3</sub> thin films EDS analysis patterns

204 The EDS compositional analysis of bismuth thin films at different precursor  
205 concentrations is shown in **Fig. 4(a-d)**, respectively. This spectrum confirms the  
206 presence of Bi and O elements in the films. The results also indicate the presence of Si,  
207 which is attributed to the substrate glass used [40]. The Bi content increases (from 18.48  
208 to 27.48 wt. %) as the molar concentration increases from 0.1 to 0.4 M, which is  
209 attributed to rise in its atomic percentage. Whereas the decrease in oxygen content  
210 (from 34.73 to 27.48 wt.%) could be due to the chemisorbed oxygen from the  
211 atmospheric air [41].

### 212 3.4. Spectral analysis UV-visible

۲۱۳ The optical properties of Bi<sub>2</sub>O<sub>3</sub> thin films prepared by using various precursor  
 ۲۱۴ concentrations were studied by UV–visible spectrophotometer in the range of 300–900  
 ۲۱۵ nm at room temperature, is depicted in **Fig. 7(a)**. As noticed, the transmittance increases  
 ۲۱۶ with increasing wavelength, and its average value in the visible region of the spectrum  
 ۲۱۷ is (78, 67.66%, 67.68%, and 63%); in the ultraviolet region, it is (51, 32, 34%, and  
 ۲۱۸ 18%), with rising precursor concentrations (from 0.1 to 0.4 M), respectively. The  
 ۲۱۹ transmittance can be associated with the values of grain size, RMS, porosity, and  
 ۲۲۰ thickness of the films. It is generally expected that increased thickness and surface  
 ۲۲۱ roughness lead to reduced transmittance, while decreasing porosity and grain size  
 ۲۲۲ decrease transmittance [42]. The gravimetric weight differential method (weight  
 ۲۲۳ increase method) was used to determine the thickness of the Bi<sub>2</sub>O<sub>3</sub> films.

$$۲۲۴ \quad D = \Delta m / A \cdot \rho \quad (4)$$

۲۲۵ Where  $\Delta m$  is the mass difference in grams,  $A$  is the area of deposited films in cm<sup>2</sup>, and  
 ۲۲۶  $\rho$  is the density of the deposited material (Bi<sub>2</sub>O<sub>3</sub>= 9.17 g/cm<sup>3</sup>) [43]. **Fig. 7(d)** shows the  
 ۲۲۷ average thickness variation as a function of concentration precursor values. The film  
 ۲۲۸ thickness increased (from 40 to 115 nm) as the precursor concentration increased (from  
 ۲۲۹ 0.1 to 0.4 M); this is due to the high viscosity of the solution. The absorption coefficient  
 ۲۳۰  $\alpha$  of the mentioned films was obtained via the following equation:

$$۲۳۱ \quad \alpha = \ln I_0 / I \cdot 1 / d \quad (5)$$

۲۳۲ Where,  $d$  is film thickness, and  $I_0/I$  is the ratio of incident beam intensity to emergent  
 ۲۳۳ beam [17][30]. Band gap values are calculated from absorption spectra, and the method  
 ۲۳۴ was described in previous literature [45]. The data were analyzed using the following  
 ۲۳۵ classical relationship for optical transitions:

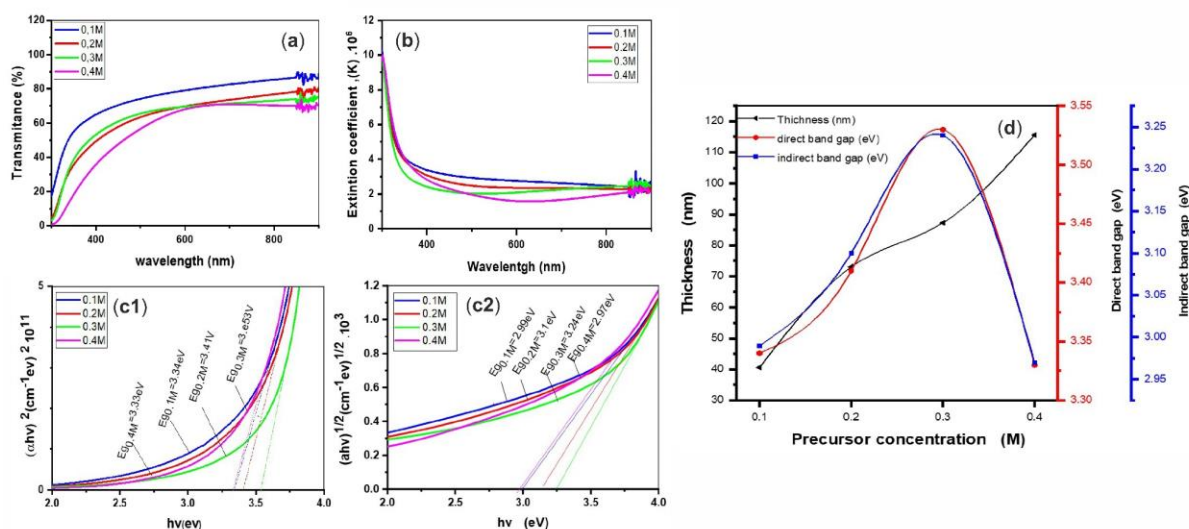
۲۳۶  $(\alpha h\nu)^2 = A(h\nu - E_g)^n$  (6)

۲۳۷ Where  $\alpha$ ,  $h$ ,  $\nu$ ,  $E_g$ , and  $A$  are the absorption coefficient, Planck constant, light  
۲۳۸ frequency, band gap energy, and  $a$  is constant, respectively [46,47]. There are two types  
۲۳۹ of band gaps: direct band gaps and indirect band gaps; an electron can emit a photon  
۲۴۰ directly in a direct band gap but not in an indirect band gap because the electron must  
۲۴۱ pass through an intermediate state to transfer momentum to the crystal lattice [46]. The  
۲۴۲ estimated direct and indirect transition band-gap values are demonstrated in **Fig. 7(c1,**  
۲۴۳ **c2)**, which show the variation of direct and indirect band-gap values with different  
۲۴۴ precursor concentrations. Both the direct and indirect band gap energies increased as  
۲۴۵ the precursor concentration increased from 0.1 to 0.3 M, and then they decreased at  
۲۴۶ 0.4M, these results were related to the transmittance of the films. The direct and indirect  
۲۴۷ band gaps of the  $\text{Bi}_2\text{O}_3$  films with precursor concentrations of 0.1 and 0.4 M were the  
۲۴۸ lowest; on the other hand, 0.2 and 0.3M are the highest. The extinction coefficient ( $k$ )  
۲۴۹ can be obtained from the relation [48] :

۲۵۰  $K = \alpha\lambda / 4.\pi$  (7)

۲۵۱ The variation of extinction coefficient with wavelength was shown in **Fig. 7(b)**. The  
۲۵۲ extinction coefficient was high in the 300–400 nm range and low in the 400–900 nm  
۲۵۳ range. The rise in the extinction coefficient is directly related to absorption of light.



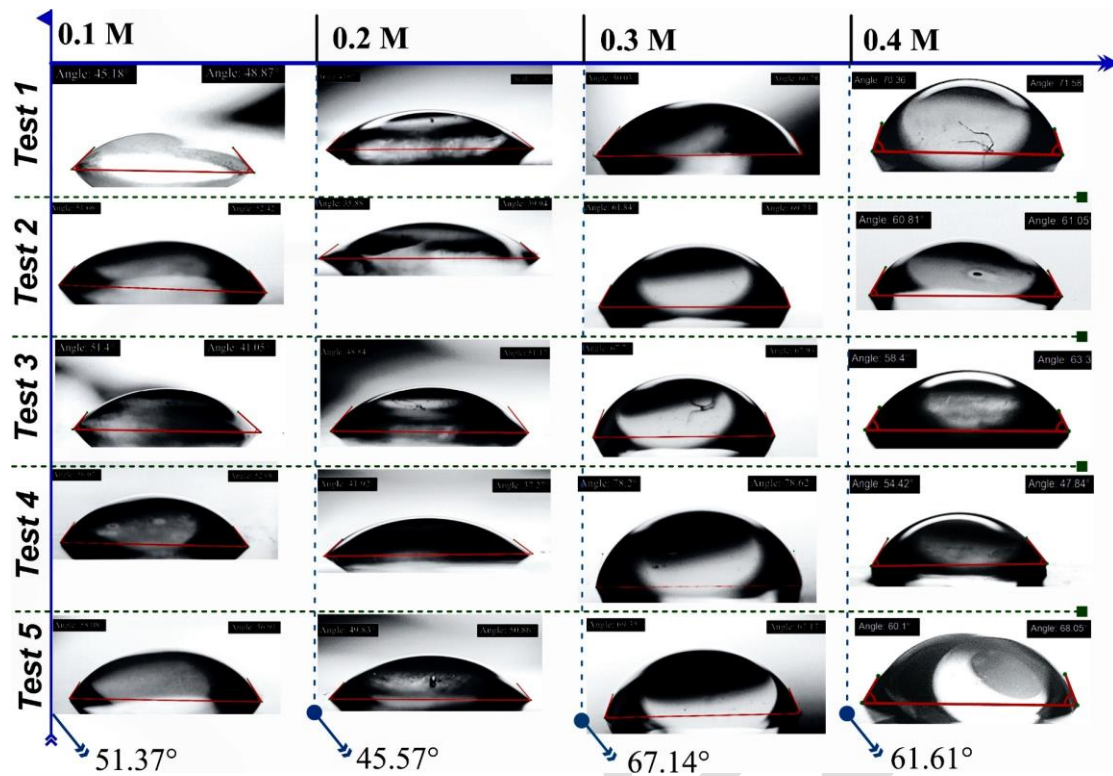


۲۵۴

۲۵۵ **Fig. 7.** (a) Optical transmittance spectrum of  $\text{Bi}_2\text{O}_3$  synthesized by the different  
 ۲۵۶ precursor concentrations. (b) Variation of extinction coefficient ( $k$ ) versus wavelength  
 ۲۵۷ with various molar concentrations. (c1) Direct and (c2) indirect band gap of the  $\text{Bi}_2\text{O}_3$   
 ۲۵۸ films. (d) Variation of thickness and band gap with different precursor concentrations.

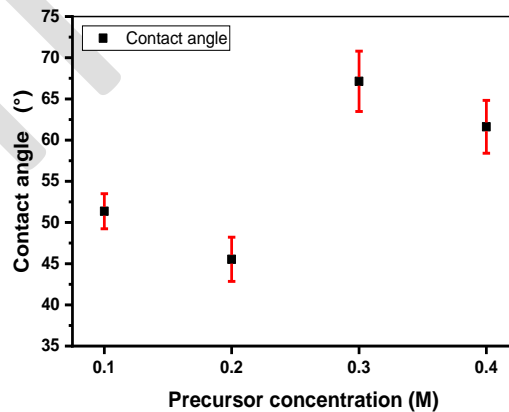
### ۲۵۹ 3.5. Wettability analysis

۲۶۰ The wetting behavior of a solid surface in contact with water is determined by the  
 ۲۶۱ interfacial tension between the surrounding medium (usually air) and water. When a  
 ۲۶۲ surface exhibits high wettability, it tends to have a low contact angle, indicating that it  
 ۲۶۳ is hydrophilic in nature and readily interacts with water. Conversely, when the  
 ۲۶۴ wettability is low, the contact angle is high, suggesting that the surface is hydrophobic  
 ۲۶۵ and repels water [43,49]. In the case of  $\text{Bi}_2\text{O}_3$  films, as depicted in **Fig. 8**, water contact  
 ۲۶۶ angle measurements were conducted.



۲۷۱ **Fig. 8.** Contact angles measurements images of  $\text{Bi}_2\text{O}_3$  thin films.

۲۶۹ The average contact angles for the samples with concentrations of 0.1 M, 0.2 M, 0.3  
 ۲۷۰ M, and 0.4 M were found to be 51.37°, 45.57°, 67.14°, and 61.61°, respectively, as  
 ۲۷۱ illustrated in **Fig. 9**.



۲۷۲ **Fig. 9.** Average contact angles of distilled water ( $\text{H}_2\text{O}$ ) on the  $\text{Bi}_2\text{O}_3$  substrates.

۲۷۳ These results indicate that all the films exhibit a hydrophilic nature, implying that  
 ۲۷۴ they have a strong affinity for water. This hydrophilic property facilitates the interaction  
 ۲۷۵

of the photocatalysts with contaminants in water, leading to improved degradation performance [50].

### 3.6. The photocatalytic efficiency

The photocatalytic efficiency of  $\text{Bi}_2\text{O}_3$  thin films synthesized with variable precursor concentrations was evaluated by MB (2 ppm) photobleaching in an aqueous solution.

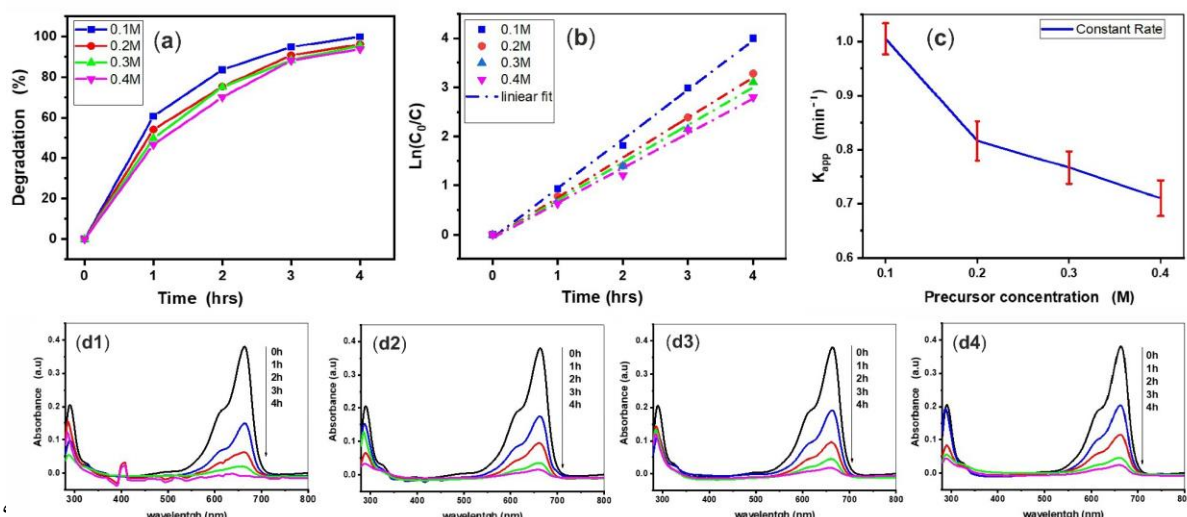
**Table. 4** shows the variation of temperature, wind, and humidity for each hour. **Fig.**

**10(a)** shows the time-dependent visible light photocatalysis of thin films (0.1, 0.2, 0.3, 0.4 M) which decomposes the MB dye with a total exposure time of 4 h.

**Table 4.** Change in temperature, wind, humidity, and the amount of solar radiation per hour in the BM degradation test (Biskra, Algeria) on 20 April 2021.

<i>Time (h)</i>	0	1	2	3	4
<i>Day temp (C<sup>0</sup>)</i>	25	26	27	27	28
<i>Wind speed (km/h)</i>	12	11	10	9	9
<i>Humidity (%)</i>	41	40	38	37	35
<i>Radiation amount</i>	moderate				

The absorbance edge of MB dye at 664 nm was decreased with increasing sunlight irradiation time.



۲۸۷

۲۹۰ **Fig. 10.** (a) The degradation rate of MB dye by Bi<sub>2</sub>O<sub>3</sub> thin films. (b) Photocatalytic  
 ۲۹۱ kinetics for the all Bi<sub>2</sub>O<sub>3</sub> thin films. (c) Effects of varying precursor concentrations of  
 ۲۹۲ Bi<sub>2</sub>O<sub>3</sub> thin films on MB removal under irradiation time. Absorbance spectra of the  
 ۲۹۳ MB solutions by Bi<sub>2</sub>O<sub>3</sub> thin films prepared with different precursor concentrations:  
 ۲۹۴ (d1) 0.1, (d2) 0.2, (d3) 0.3, and (d4) 0.4 M.

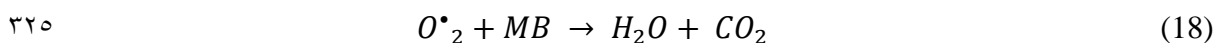
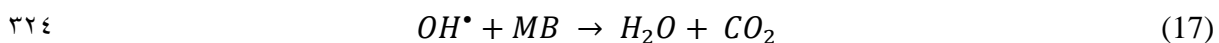
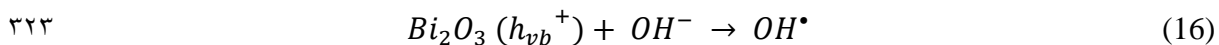
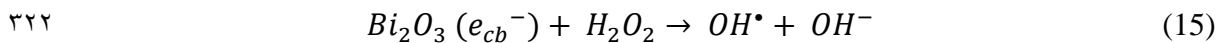
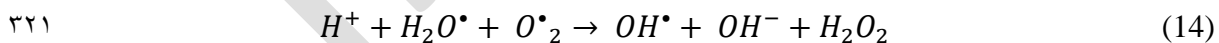
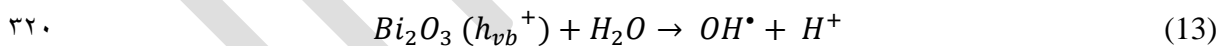
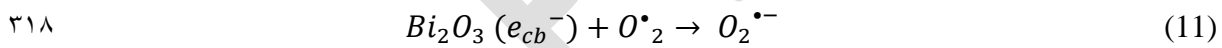
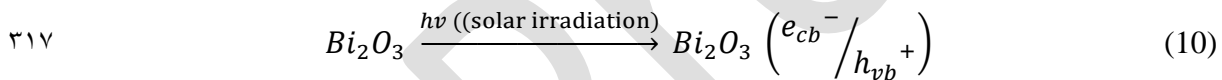
۲۹۵ The degradation rate of MB dye is revealed in the presence of thin films as a catalyst.  
 ۲۹۶ The following equation was used to calculate the photo degradation rate: [51]

$$D = A_0 - A_t/A_0 * 100 \% \quad (8)$$

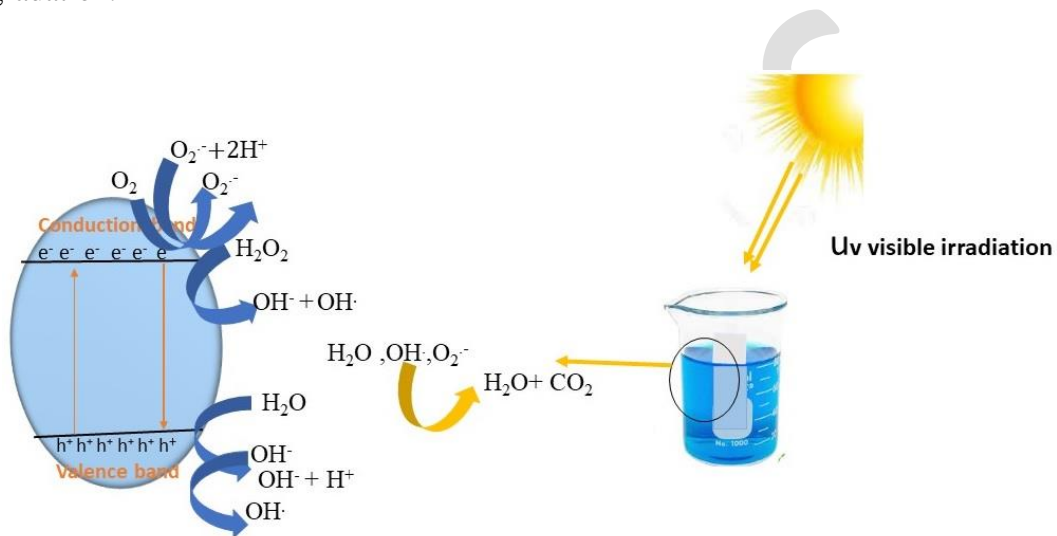
۲۹۸ Where A<sub>0</sub> is the initial absorbance at time t = 0 h, A<sub>t</sub> is the absorbance after time t. The  
 ۲۹۹ absorbance of MB dye over the Bi<sub>2</sub>O<sub>3</sub> thin films under sun irradiation for 4 h is shown  
 ۳۰۰ in **Fig. 10(d(1, 2, 3, and 4))**. It was observed that after 2h the relative amounts of MB  
 ۳۰۱ decomposed by photocatalysis were 47.09, 49.47, 53.97, and 83.60 % when Bi<sub>2</sub>O<sub>3</sub>  
 ۳۰۲ synthesized at 0.1, 0.3, 0.4, and 0.5 M was used as photocatalyst, respectively. Bi<sub>2</sub>O<sub>3</sub>  
 ۳۰۳ thin films prepared at 0.1M have the highest photocatalytic efficiency among all  
 ۳۰۴ samples, with 99.9 % at 4 h irradiation time. The kinetics of the photocatalytic  
 ۳۰۵ degradation process can be generally explained by the L-H kinetic mode. [52]

$$3.6 \quad \ln(C_0/C_t) = kt \quad (9)$$

3.7 Where  $C_0$  is the concentration at time  $t_0$ ,  $C_t$  is the concentration at particular irradiation  
 3.8 time, and  $k$  is the apparent pseudo-first-order rate constant ( $\text{min}^{-1}$ ). The apparent rate  
 3.9 constant ( $k$ ) was successfully calculated from the slopes of the straight line obtained  
 3.10 from the plot of natural logarithm by plotting the  $\ln(C_0/C_t)$  vs irradiation time [31]. The  
 3.11 plot of  $-\ln(C/C_0)$  as a function of irradiation time for films  $\text{Bi}_2\text{O}_3$  prepared by different  
 3.12 precursor molarities is presented in **Fig. 10(b)**. **Fig. 10(c)** shows kinetic rate of  
 3.13 degradation of the dye solutions with increasing amounts of bismuth precursor. As  
 3.14 observed, the highest kinetic rate decreases with increasing molar precursors, so the  
 3.15 highest rate 99.9% is exhibited by 0.1 M. The following equations outline the  
 3.16 photocatalytic attributes of  $\text{Bi}_2\text{O}_3$  films within an MB solution under sunlight [53–55]:



۳۲۶ When bismuth oxide is activated with visible light ( $\lambda \geq 420$  nm), electrons are promoted  
 ۳۲۷ from the valence band to the conduction band, generating an electron/hole pair (e-/h+).  
 ۳۲۸ (Eq. (10)) which are strong oxidizing and reducing agents, as shown in **Fig. 11** [56].  
 ۳۲۹ **Table 5** presents a thorough comparative examination between the current study and  
 ۳۳۰ various other research papers that have incorporated thin films and powders as a pivotal  
 ۳۳۱ element in their investigations assessing the efficacy of photocatalysts in organic dye  
 ۳۳۲ degradation.



۳۳۳  
 ۳۳۴ **Fig. 11.** Illustrates the photocatalytic mechanisms of Bi<sub>2</sub>O<sub>3</sub> films for MB degradation  
 ۳۳۵ under sunlight irradiation.

۳۳۶ The photo-induced holes are powerful oxidizers because of their attraction for  
 ۳۳۷ electrons. They oxidize the adsorbed water molecule or hydroxide ion to produce  
 ۳۳۸ hydroxyl radicals (**Eq. 13**). On the other hand, the electron from the photoexcitation  
 ۳۳۹ attacks the oxygen (**Eq. 11**), it can be reduced to the different oxygen activated species  
 ۳۴۰ (**Eq. 11**), Then all these highly oxidizing species (•OH, •OH, H<sub>2</sub>O<sub>2</sub>, etc.) are capable  
 ۳۴۱ of oxidizing organic molecules, such as MB into simpler molecules such as CO<sub>2</sub>, H<sub>2</sub>O  
 ۳۴۲ [57,58].

۳۴۳ **Table 5.** Illustrates a comparison between the photocatalytic efficiency of organic dye  
 ۳۴۴ degradation observed in this investigation and findings from other studies.

<i>materials</i>	<i>Dye type and concentration</i>	<i>Technique type</i>	<i>Degradation (%)</i>	<i>Time (min)</i>	<i>Irradiation Source</i>	<i>Reference</i>
$\beta$ -Bi <sub>2</sub> O <sub>3</sub> (0.1M), Thin film	Methylene blue, 0.002 g/l	Dip-coating (glass Substrate)	~99	240	Visible light	Current study
$\beta$ -Bi <sub>2</sub> O <sub>3</sub> , Thin film	Methylene blue, 10 <sup>-6</sup> mol/l	Spin-coating Deposition (Pt-coated silicon substrates)	~100	1440	Solar lamp (Ultra-Vitalux 300 W, Osram)	[59]
$\beta$ -Bi <sub>2</sub> O <sub>3</sub> , Powder	RhB, 5 mg/L	Situ chemical transformation method	~7	25	Xe lamp (350 W)	[60]
BiOBr, Powder	RhB, 5 mg/L	Situ chemical transformation method	~30	25	Xe lamp (350 W)	[60]
Co <sub>3</sub> O <sub>4</sub> (Co-3), Thin film	Methylene orange, 0.01 g/l	Nebulizer spray (glass and FTO Substrate)	~57	180	Tungsten Halogen lamp of 300 W (1 > 400 nm)	[61]
Co <sub>3</sub> O <sub>4</sub> (withdrawn speed of 5 mm/s), Thin film	Methylene blue, 0.002 g/l	Dip-coating (glass Substrate)	~77	240	Visible light	[62]
CuO/ZnO (simple A), Thin film	Methylene blue, 0.005 g/l	Spin-coating with Glass Substrate	~44	120	Xe lamp of 150 W	[63]
ZnO, Thin film	Methylene blue, 0.003 g/l	Spraying (glass Substrate)	~80	360	Visible light	[64]
CoTiO <sub>3</sub> /Co <sub>3</sub> O <sub>4</sub> , Thin film	Indo Light Blue, 0.01 g/l	Doctor blade and spin coating (glass Substrate)	~29	60	Hg lamp of 250 W	[65]
Cu:Co (30:70), Thin film	Methylene blue, 0.003 g/l	Dip-coating (glass Substrate)	~49	240	Visible light	[7]

۳۴۵

## ۳۴۶ **4. Conclusion**

۳۴۷ In this study, Bi<sub>2</sub>O<sub>3</sub> films are deposited by sol-gel technique. The structural,  
۳۴۸ morphological, optical, and photocatalytic properties of Bi<sub>2</sub>O<sub>3</sub> thin films were  
۳۴۹ investigated as a function of precursor concentrations. The films are polycrystalline  
۳۵۰ with tetragonal structure peak as a preferred orientation. The crystallite size of Bi<sub>2</sub>O<sub>3</sub>  
۳۵۱ films was not gradually affected by the change in precursor concentration or film  
۳۵۲ thickness. The morphology of the Bi<sub>2</sub>O<sub>3</sub> surface indicates irregular and good overall  
۳۵۳ coverage, which increase with increasing molar precursor concentration, which is  
۳۵۴ supported by Rq area roughness of the sample. The optical spectrum shows that the  
۳۵۵ transmission increases with decreasing precursor concentration, and the maximum  
۳۵۶ average value of about 78 % in the visible region is observed for film prepared with 0.1  
۳۵۷ M. The direct band-gap values varied between 3.33 and 3.53 eV, and the direct band  
۳۵۸ gap varied between 2.97 - 3.24 eV when the precursor concentration was from 0.1 to  
۳۵۹ 0.4 M. The average contact angles. Measurements proved the hydrophilic nature of the  
۳۶۰ films as contact angle between 51.37° and 61.61°. The degradation of MB decreases  
۳۶۱ with the increase in precursor concentration, and the kinetic rate of degradation and  
۳۶۲ degradation rate also have the highest values among all the thin films. Thus, the Bi<sub>2</sub>O<sub>3</sub>  
۳۶۳ thin film of 0.1M shows the fastest apparent photocatalytic reaction rate MB, at 99.9%,  
۳۶۴ corresponding to 39.7 nm crystal size, 2.01 eV band gap energy, 55 nm surface  
۳۶۵ roughness, and 51.37° contact angle. From the above results, it can be concluded that  
۳۶۶ this Bismuth oxide film is a good photocatalyst for water purification.

## ۳۶۷ **Declarations**

## ۳۶۸ **Competing interests**



۳۶۹ The authors report that there are no interests of a financial or personal nature in this  
۳۷۰ work.

#### ۳۷۱ **Ethical approval**

۳۷۲ Not applicable.

#### ۳۷۳ **Informed consent**

۳۷۴ Not applicable.

#### ۳۷۵ **Authors' contributions**

۳۷۶ All of the authors have studied this work.

#### ۳۷۷ **Funding**

۳۷۸ The authors have reported that they did not receive any funding.

#### ۳۷۹ **Availability of data and materials**

۳۸۰ The statement regarding the datasets used in this work can be accessed through the  
۳۸۱ corresponding author.

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